INK MANUFACTURE

INCLUDING

WRITING, COPYING, LITHOGRAPHIC, MARKING, STAMPING AND LAUNDRY INKS

BY

SIGMUND LEHNER

TRANSLATED FROM THE GERMAN OF THE FIFTH EDITION
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WITH THREE ILLUSTRATIONS

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PREFACE.

IN preparing this edition the author has strictly adhered to the practice of including only such novelties as have been proved useful by his own personal experience. This edition can therefore claim to contain the whole of the reliable information available at the time of going to press. The old text has also been carefully revised and amended where necessary. In each case where it appeared that such a course would assist an intelligent comprehension of the matter, the recipes are accompanied by a detailed criticism. The author desires to repeat that every recipe in the book has been practically tested by himself, so that he can guarantee good results to every one who will use raw materials of good quality, and follow the recipe exactly. If anything goes wrong the manufacturer must always be sure that he has made no mistake in his operations and that his materials were of good quality before he blames the recipe. It often happens, with dye-extracts particularly, that the materials used would give a bad result with the best of recipes.

The continual increase in the use of the typewriter makes special dyes for the ribbons of those machines necessary. This book contains recipes for making these dyes, and for dyeing the ribbons, which, in view of the exorbitantly high prices charged for these ribbons, will be an addition to the work greatly appreciated by many of its readers.

The properties of all the raw materials entering into the composition of the recipes are accurately described, so that the reader is provided with a guide to assist him in purchasing them. The author concludes by expressing a hope that all persons skilled in any branch of the ink trade will assist him with any new recipes that have proved valuable in their hands for a new edition, and thanks them heartily in anticipation.

SIGMUND LEHNER.

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I.

INTRODUCTION.

Since human progress reached the stage of written communication of ideas, there has been a constant endeavour to simplify writing materials, just as in modern writing we have the tendency to simplify the forms of the symbols, and thus to facilitate the acquisition of the important art of writing.

The Assyrians wrote cuneiform inscriptions on tablets of clay, and the Egyptians chiselled hieroglyphics on granite, or painted them with the brush on the walls of their tombs and temples. The first impulse to the general practice of writing, however, came with the invention of papyrus, which stands in close relationship to paper. Modern writing material indeed derives its name from the word papyrus. Very many papyrus-rolls have come down to us from the ancient Egyptians, and show that a huge number of that race were able to write, especially as the papyri include memoranda of comparatively small importance, such as cookery recipes.

Long after the Chinese and Japanese had learnt the art of writing on paper with a brush, the Greeks and Romans were unacquainted with paper making and used tablets covered with wax, on which they wrote with a pointed stylus.

Writing inks have long been known. Pliny, Vitruvius, and other classical authors mention them, and Dioscorides gives a special recipe for making ink. It is a striking coincidence that the ink of the Greeks and Romans was practically the same as that of the Chinese, and consisted mainly of fine soot worked up in a vehicle. The printers' ink of to-day owes its colour to the same pigment.

The (German) word for ink (*Tinte*) comes through *tinge*, from the Latin *tingere*, to dye or to colour. Thus an ink means a liquid that will produce a colour.

Old deeds and other parchments show us that even in the early Middle Ages the art of ink making had been brought to a high degree of perfection. Letters 800 years old, indeed, are less faded in many cases than those of a much more recent date. When we see a MS. which has become almost illegible in fifty years or less, we are inclined to think that the knowledge of ink manufacture has gone backwards instead of forwards. We must not forget, however, that the durability of an ink depends not merely on itself, but also on the substance it is written on. Many of the substances now used in preparing papers, such as lime and chlorine, have, even when present in very small quantities only, a destructive effect upon an ink which if used on pure parchment would last as long as the monastic productions of the Middle Ages have done. All our bleached papers contain chlorine, which sooner or later destroys the paper. It is thus useless to write documents intended for long preservation with indelible ink if paper is used to write them on. Our modern books, printed without exception upon paper that has been bleached with chlorine, will disappear in a few centuries by the disintegration of the paper. This defect attaches particularly to a sort of paper much used now on account of its cheapness, that made from wood pulp. This in a few years turns brown, and becomes so brittle that it breaks when folded. Printing ink, on the other hand, which depends for its colour on carbon, is practically imperishable. People are now becoming alive to the disadvantages of such paper, and are printing important books on paper which is free from every trace of free chlorine. The durability of unbleached vegetable fibre is well exemplified by the linen wrappings of the Egyptian mummies. Woven four thousand years ago, it is now scarcely brown, and is still fairly strong. If the ancient Egyptians had written on such stuff with good ink the writing would be plain to this day.

The manufacture of ink has been carried on empirically until very lately. The first to apply scientific knowledge to the manufacture was Lewis, at the end of the eighteenth century. Since his time Berzelius and Bottcher have done a large amount of work at the subject.

Changes in the methods of manufacture of ink have been accompanied by two other movements which have had great influence on it. One of these is the substitution of smooth machine-made paper for the grey or brown hand-made paper. This glazed paper requires for its manufacture a very powerful bleaching of the raw material, with the result that it invariably contains chlorine or lime. It has thus become important to find inks that will resist the slow action of these substances. This may appear a very simple matter, but is in reality a difficult one. The second movement was the substitution of the steel pen for the quill. While in former times the goose-quill only was used for writing and the raven-quill for drawing, the steel nib is now almost universally employed for both. The substance of a quill is extremely resistant to chemical action. Steel, on the other hand, is readily corroded by very many things. Even very dilute acid in the ink will soon make a nib unusable. Before inks were invented which would not act on iron, many attempts were made to devise a protective coating for the nib, by covering it with copper, silver, or even gold. This coating, however, soon gets worn off the tip of the nib, even in using the smoothest paper.

We have called the manufacture of ink an art. Many may smile at the designation, but we shall adhere to our nomenclature. It is not easy to make an ink fulfilling every requirement that may be demanded of it, especially as we are even now to a large extent in the dark as to the exact chemistry of ink manufacture, although distinguished chemists have not thought it unworthy of them to work at the subject.

II.

VARIETIES OF INK.

By ink in general we understand a coloured liquid intended to make durable signs on any surface.

Inks may be classified according to their uses into several fairly distinctly defined groups, as follows:—

Writing Inks, for use with a pen, closely allied to which are the *Copying Inks*, also for use with a pen, but from which impressions can be reproduced. One of the latest species of copying ink is *Hektograph Ink*, which allows many copies to be made from an original written upon a specially prepared ground.

Ink Powders are powders which produce ink by mere solution in water.

Ink Pencils are closely allied to these. On slightly damp paper they make marks resembling those made with aniline inks.

Drawing Inks produce drawings by means of an ordinary pen or a drawing pen.

Lithographic Inks are used solely for writing and drawing on lithographic stone, and these must resist the corrosive fluids used by lithographers.

Marking Inks are used as a substitute for the old practice of embroidering names or initials on the garments.

Printing Colours include those used for marking guiding lines for embroidery, as well as those for india-rubber stamps, although the latter differ somewhat from most of

others. To printing colours, in the wider sense of the
'd, belong also the compositions used for typewriter
tape-machine ribbons. Many of them permit of copies
ıg taken, so that they are closely connected with the
ying inks.

ımong ink specialities we include gold, silver, and sym-
hetic inks, and every ink maker ought to know how to
ke these varieties, although they are not much in demand.
Ve can easily see that the number of inks and allied pro-
ɔts is considerable. If we were to produce all the recipes
t have come before us we should fill several volumes of
size of the present one.

Ɔur knowledge of ink making is almost purely empirical,
we are at present to a very large extent ignorant of the
ct chemistry of the subject. Most inks are combinations
metals with organic matter, especially with tannins. It
s formerly believed that only one of the substances con-
ned in a tanning material was able to produce the black
ɔstance the presence of which is essential to the constitu-
n of the ink, but we have now become aware that there is
rast number of such substances with most of which we are
ly very imperfectly acquainted. This explains the multi-
city of the recipes, and is the only possible reason for the
narkable fact that recipes vary enormously in the propor-
ns given, although the substances they name are exactly
e same. One recipe assigns a prominent place to an in-
edient which the other relegates to a very minor share in
e composition of the ink. In ink manufacture we have not
t beyond the recipe-making stage, and every maker will do
ell to experiment with the new recipes he may come across,
ıd try to improve them. There can be no doubt that there
a vast field for original research in ink making, and it
ould be highly remunerative. Few articles of daily use
'e sold at so high a profit as ink. Even a small sale will

keep a man comfortably. In view of the failures that we all experience sometimes in our ink making, it is quite certain that every step forward which we can make, be it ever so small, will be of material value to its discoverer and to the trade in general.

III.

WRITING INKS.

In considering these inks first, we must begin by setting forth clearly what properties are required in ordinary writing fluid. They are four in number, and will now be considered *seriatim.*

1. *Depth of Colour.*—The writing must at once or very quickly show a strong and decided hue of the colour which the ink is intended to produce.

2. *Freedom of Flow.*—The ink must flow readily from the pen, so that the finest lines and characters may be executed. The ink must not be thick, or form hard crusts when it dries upon the nib. This occurs sometimes with perfectly good ink, and is then merely a sign that the ink has become too concentrated by evaporation and requires dilution with water. If, however, the addition of water does not make matters right the ink is bad, whether it was so originally or not. This freedom of flow cannot of course be so perfect with a copying as with an ordinary writing ink. Copying inks are thicker and slower to dry than ordinary writing inks. Many complaints reach dealers from careless customers who have used copying ink when they had no intention of taking copies, and have found the two sides of a letter, for example, stick together so firmly that they were illegible when separated. Copying ink must always be diluted if it is to be used as a substitute for ordinary ink. It will not lose its special properties entirely even then.

3. *Durability.*—A good ink should keep its colour unchanged for a long time, even if the paper gets damp or wet. This is a quality which comparatively few inks possess. A good ink must gradually dry in the air to a brittle mass, and must not go mouldy, even after great dilution. This last condition is easily fulfilled. The main constituents of many inks are powerful antiseptics, and in any case antiseptics can always be added to them.

4. *Indelibility.*—For certain purposes, such as for documents that will possess a historical interest, it is necessary that the ink should be able to resist not merely the ravages of time, but also deliberate attempts to efface it. To secure absolute indelibility is impossible, for resistance to every agent that could possibly be employed is a property that no substance we know of, or are at all likely to become acquainted with, possesses. While no ordinary writing ink, however, offers any considerable resistance to chemicals, certain inks, especially those which owe their colour to carbon, are capable of withstanding them extremely well. Printers' ink, indeed, can only be destroyed by destroying the surface printed on as well. Printers' ink, however, can hardly be produced in such a condition as to be usable with a pen. Some dark-coloured substances of organic origin, also the so-called humus-bodies, play a very good second to carbon in respect of indestructibility.

The first three of these four qualities may be reasonably demanded of any ink professing to be a good one, and it is the business of our trade to make inks possessing good colour, freedom of flow, and a reasonable degree of durability, and no others.

We can classify writing inks either according to colour or to composition. The names red ink, blue-black ink, etc., are examples of the former method, and such appellations as chrome ink, hematoxyline ink, and others, illustrate the second. Several of these names, however, are misleading. Many inks are sold as alizarine inks, for example, when neither madder nor alizarine has been used in their manufacture. We have no intention in this work of binding ourselves to any particular classification too strictly, as we see no particular advantage to be gained by so doing. We shall describe the inks under their colours in an order depending partly on the method of manufacture and partly on similarity between the recipes. As black is the most important of all the writing inks, we shall devote more space and attention to it than to the rest.

BLACK WRITING INKS.

Black inks differ greatly in chemical composition, and can be divided into two sharply marked out groups—those containing tannin, and those not. The first class can be further divided, according to the raw material used, so that we have catechu-tannic acid inks, gall-nut (tannic acid) inks, etc. The inks free from tannin, or those which contain it with other substances, can also be divided on the same plan into chrome inks, logwood inks, and so forth. The differentiation of the two main classes is not, however, absolute, as inks made from dye-woods, which we have put in the second class, often contain tannin. The black writing inks which have been longest known and which are the most important are the tannin inks, and they are the cheapest to manufacture. In spite of this no maker should confine himself to such inks, as they have not, as a rule, the degree of durability that is now required of an ink. In fact they can already be regarded as antiquated, and as destined to be soon disused altogether.

TANNIN INKS.

In nearly every case these inks contain tannate of iron. Tannin being a very abundant substance in the vegetable kingdom, it follows that a very large number of plants can be utilised for ink making. It must be borne in mind, however, that although the various tannic acids of different plants are closely allied, they, and therefore the inks made from them, show well-marked differences in properties. Some of them give bluish compounds with iron, and some a characteristic greenish colour which only very slowly changes to the deep black which we are accustomed to in a good ink. Tannin inks which write a black at once usually cannot penetrate the paper, and have consequently no durability whatever.

The following may serve as a list of the chief raw vegetable materials used for making tannin inks: gall-nuts, valonia galls; barks of oak, sumach, poplar, willow, fir, and horse-chestnut; the wood of the elm and horse-chestnut, as well as sloes and buckthorn berries. This list makes no pretence of being complete, but only gives the more important materials. It is possible to use any plant or part of a plant for making these inks provided it contains tannin.

Before describing more minutely the properties of these tannin-containing bodies, we propose to make the reader acquainted with the chief chemical properties of the tannins themselves, as a necessary preliminary to the comprehension of the formation of the inks, and as a means of enabling him to make experiments and improvements for himself.

We proceed then to speak of the tannins or tannic acids as they occur in the form of definite chemical compounds.

TANNINS.

All the higher plants contain acids. All these acids are soluble in water, and many of them are characterised by a rough and astringent taste, and are called tannic acids. If the solution of one of them is mixed with one of gelatine a precipitate is formed, which consists of tannate of gelatine. Tannin behaves in a singular manner with egg albumen and also with fresh animal skins. If the hide of an animal is dipped into a solution of tannin it will gradually absorb the tannin, and acquire the property of keeping for long periods without putrefying, even when in contact with water. The hide is also made pliable and smooth, and is called leather.

Another property which all the tannic acids have in common is to form bluish-black or greenish substances when brought into contact with iron salts. These coloured bodies are very prone to decompose and become mouldy, so that a badly made tannin ink soon becomes utterly worthless.

Quercitannic Acid.

This is the commonest of all the tannins, and occurs in every part of the oak, but particularly in those morbid products of the tree known as gall-nuts. We also have quercitannic acid in Chinese galls, in sumach (*Rhus coriaria*), in sloes, and in the wood and bark of the pine.

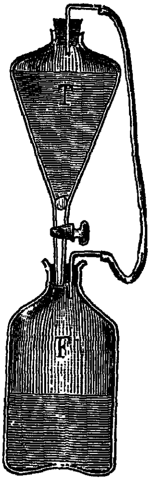

Fig. 1.

Quercitannic acid is freely soluble in water, spirit or ether, or in mixtures of them. In preparing it in a state of purity, however, it is best to use only ether as a solvent. Quercitannic acid is best prepared from gall-nuts as follows: The galls are coarsely powdered and put into a separating funnel stuck in the neck of a bottle as shown in Fig. 1, where T is the funnel and F the bottle. The tube shown permits air to pass from F to T, as liquid passes the other way. A filtering plug of cotton wool having been put into the neck of T, the gall powder is put into it and covered with ether. Care must be taken not to use ether near a naked flame as it gives off a highly inflammable vapour. The corks and tube are then fitted as shown, to prevent loss of ether by evaporation. When the ether has all drained into the bottle rinse the galls with as much water as will increase the bulk of liquid in F by one-half. There will now be two layers of liquid in F. The lower is brown and contains the tannin, while the upper layer is nearly pure ether and can be used again. This ether having been decanted, the tannin solution is poured into a shallow basin and left, with a sheet of paper as a lid to keep out dust, until the ether has dried up, and only a pale yellow powder remains, which is pure tannin plus a little water. The tannin is then dried under a bell-jar, which also contains a dish of concentrated sulphuric acid. The tannin finally becomes a nearly white amorphous powder, having an extremely astringent taste. Tannin does not crystallise, so that the expression "crystallised tannin," sometimes seen in price lists, is misleading.

If an aqueous solution of tannin is exposed to the air, it soon becomes covered with a thick crust of mould, and in time the tannin is all converted into gallic acid. Quercitannic acid, if heated dry, is partly carbonised and partly changed into pyrogallic acid which volatilises.

Gallic Acid.

This acid occurs in divi-divi, in mango kernels, and, to a small extent, in gall-nuts. If a decoction of a divi-divi in boiling water is allowed to cool, it deposits brown crystals, which, by solution in water, filtration through animal charcoal, and re-crystallisation, become white. It is, however, much better to make gallic acid from gall-nuts by crushing them and leaving them in a damp state until the mould, which rapidly accumulates upon them, has converted the quercitannic acid into gallic acid. This can then be dissolved out with water and purified by crystallisation.

Gallic acid is sharply differentiated from quercitannic acid by precipitating neither gelatine nor albumen. With ferrous salts it forms a deep blue solution, and on this property is based the value of gallic acid to the ink manufacturer.

PYROGALLIC ACID.

When gallic acid is kept at between 210 and 215 deg. C. it is gradually converted into pyrogallic acid. Distinctive properties of this are the precipitation of the metal from solutions of gold or silver and the formation of a bluish-black colour with proto-salts of iron.

CATECHU-TANNIC ACID.

Mimosa catechu, a tree indigenous to India, provides an extract known to commerce as cutch. The special tannin of cutch is prepared by boiling it in water and adding sulphuric acid to the decoction. A precipitate is formed, which is a compound of catechu-tannic with sulphuric acid. This precipitate is mixed with carbonate of lead and boiled in water. The sulphuric acid remains undissolved as lead sulphate, and the catechu-tannic acid can be crystallised from the filtrate. A simpler method is to extract the cutch with ether. Catechutannic is much like quercitannic acid, but is distinguished from it by giving a dirty green precipitate with solutions of iron salts.

KINOTANNIC ACID.

This occurs in gum kino, and is a brown substance very similar to catechu-tannic acid, and forms a blackish-green compound with ferric salts. Fermentation converts it into kino red.

MORITANNIC ACID.

This is deposited from a cooling decoction of fustic, the wood of *Morus tinctoria.* It has a sweetish astringent taste, and with ferrous salts gives a blackish-green precipitate. Heated it gives pyromoric acid, which has to it the same relationship that pyrogallic has to gallic acid. Moric acid is another acid present in fustic, and is probably related to moritannic acid in the same way that gallic acid is to quercitannic acid, and formed, like it, by fermentation.

The tannic acids hereby described are chiefly important by their action on solutions of salts of iron. Although this action is different with ferric and with ferrous salts, the difference is of little importance to the ink maker, for as all ferrous salts oxidise to ferric salts on exposure to the air, the final colour of the ink is always due to ferric iron. The following table shows the colours given by the various tannic acids:—

Acid.	Colour with Ferrous Salts.	Colour with Ferric Salts.
Quercitannic	—	Blackish-blue
Gallic	—	Dark-blue
Pyrogallic	Blackish-blue	—
Catechu-tannic	Dirty green	Dirty green
Kinotannic	—	Blackish-green
Moritannic	—	Dark-green

To get a deep black ink we must always use a gall-nut tannin.

Inasmuch as the chemically pure tannic acids are too dear to be used, in practice we shall never get any of the above-named colours in full purity, but always with a tendency to brown or black, owing to the action of the other substances present. This is, however, immaterial, as all that we require is that the colour should be very dark and also durable.

The tannin-containing bodies which we use come upon the market in many different qualities, so that we must describe the most important of them fully enough to prevent our readers from being cheated in purchasing. As iron salts are essential for making tannin inks, we shall describe those salts which we use, so that our readers may make them for themselves if occasion should arise.

IV.

RAW MATERIALS OF TANNIN INKS.

Gall-nuts.

Gall-nuts are morbid growths on the leaves of various kinds of oak caused by the sting of the gall wasp. The gall-nut is formed round the egg of the wasp which is laid by the sting, and the metamorphoses of the larva generally take place inside the gall, which is only deserted by the insect when it has reached its fully developed state; then it bites for itself a hole of escape. In trade, the chief distinction made with galls is into pale and dark, but they are classified also as white, yellow, green, blue, and black galls. The best galls are those from which the insect has not escaped, *i.e.*, which are unperforated, as those galls contain the highest percentage of tannin. Good black galls contain up to 27 per cent. of tannin, included in from 35 to 37 per cent. of soluble extractive. The form of the galls is nearly spherical, and their size varies from that of a pea to that of a small walnut. A good gall must be heavy and show a compact mass when cut through. If the gall is very light and filled with a crumbly mass it is of poor quality, as its content of tannin will be low. Experience has shown, too, that galls from southern countries are richer in tannin than those from the north.

The best galls are the Levantine galls, also called Aleppo galls. Next to them in quality are Morea, Smyrna, Marmora, and Istrian galls. In the third rank are the French, Hungarian, Italian, Senegal, and Barbary galls.

The signs looked for in the trade as denoting a good gall are almost perfect sphericity, a size not exceeding that of a cherry, a rough, unperforated exterior, and considerable weight.

Chinese galls have a smooth surface, often showing a reddish hue, and readily peeling off. Inside is a brown substance, full of the dead larvæ of insects. It is not yet known with certainty from what plant these galls come or what insect produces them.

KNOPPERN.

Ordinary galls are produced on the leaves and young stems of the oak, but there is a kind produced by the gall wasp stinging the immature cups of the acorns. The result is the development of a gall instead of an acorn.

Knoppern are misshapen brown masses. They are harvested mostly in August, and the chief place of production is Hungary. The Bakony forest, situated between the Lakes of Neusiedler and Platten, yields an enormous quantity of knoppern. Large amounts come also from the oak forests of Asia Minor.

Knoppern come on the market both whole and crushed. Chemically they are practically the same as the other galls, and, like them, contain a high percentage of tannin which secures them great employment in the leather, dye, and ink trades.

TANNERS' BARKS.

The crushed bark of the elm, oak, pine, poplar, willow, etc., is largely used in tanning. The bark, after having been once used, is spread out by the tanners and dried for use again. The dried bark ferments, and its quercitannic acid becomes gallic acid. Tanners are agreed that quercitannic acid makes much better leather than gallic, which has a tendency to produce brittleness. For ink making, however, they are of equal value, so that the once-used bark should be bought from the tanners by the ink maker.

GALL EXTRACT.

Gall extract, otherwise called tannin extract, is on the market in the form of shining blackish-brown masses, having a very astringent taste. It is made by boiling in water galls, knoppern, fresh bark, and other tanniniferous vegetable substances, and carefully evaporating the decoction to a syrup, which, on cooling, sets to a brittle mass. Tannin extract is now made on a large scale by boiling down the decoction in vacuum pans.

A good extract should consist of little besides tannin, and must dissolve completely in water without any carbonaceous residue, giving a very astringent solution. When it is not too dear it is a splendid material for ink making, and to be recommended especially to ink manufacturers who have no space for storing large quantities of galls. Besides, the use of the extract simplifies the ink making considerably.

It must be remembered that the extract is very prone to mould in damp air. It should be kept in a dry room in casks or boxes lined with strong paper and with well-fitting lids.

CUTCH AND GAMBIER.

This is also known as Japanese earth (*succus catechu* or *terra japonica*). It is obtained in the East Indies from the fruits and twigs of *Mimosa catechu* by boiling down a decoction of them. The chief cutch markets are Bombay and Calcutta, and it is divided into yellow and brown cutch.

Yellow cutch (gambier) is sold in dice-shaped pieces, which yield their colour to boiling water and give it a sweetish astringent flavour. It is better for dyers and ink makers than the brown kind.

Brown cutch is closer and heavier than the yellow variety, and the dark brown, shiny, sticky lumps yield a reddish-brown decoction.

Cutch contains catechu-tannic acid and variable quantities of japonic acid. There is more of this latter acid in brown than in yellow cutch. This is the reason why yellow cutch is better for our purposes, as japonic acid is of no use for ink making. The following is the percentage analysis of the two sorts:—

	Yellow.	Brown.
Tannin	54·5	48·5
Extractives	34·0	36·5
Mucilage	6·5	8·0
Insoluble matter	5·0	7·0

A purified cutch may be had but rarely. It is entirely soluble in water, and is to be preferred even to yellow cutch. The great demand for it caused the production of an adulterated extract in France. This rubbish is called *cachou épuré*, and consists of brown catechu mixed with 40 per cent. or more of its weight of ox blood.

Gum Kino.

This is a brownish-red, brittle solid, which gives a beautiful reddish-brown solution with water or alcohol. The chief ingredient is kinotannic acid. The following are the principal sorts found in commerce, with the name of the plant from which each is obtained:—

African kino	*Drepanocarpus senegalensis.*
East Indian kino	*Nauclea Gamber.*
Columbia kino	Unknown.
Australian kino	*Eucalyptus resinifera*
Jamaica kino	*Cocoluba nucifera.*

The first of these is the best gum, but it is very rarely to be met with unadulterated. To denote its purity more precisely it is also called Gambia gum.

Fustic.

This is the wood of *Morus tinctoria*, and is indigenous to the West Indies. It contains moritannic acid. The sumachs, *Rhus coriaria* and *R. cotinus*, probably contain the same or very similar colouring matters as fustic. The fustics are used for yellow dyeing and also (with iron salts) for dyeing black. They give dark blackish-green inks.

We thus see that the whole manufacture of tannin inks turns on the colours which the various tannins give with iron. Hitherto the expense of purification has prevented the use of pure tannins in ink making, and has hence made it impossible to determine exactly the proper proportions of iron salt and tannin.

Myrabolans.

Myrabolans is the trade name given to the dried fruit of various species of Indian *Terminalia*, the chief source being the *Terminalia Chebula.*

The ovoid fruit when perfectly dry is reduced to nearly half its original size.

During the drying process it becomes ridged, and then the outer layer of the pericap is hard enough to resist the blade of a peaknife.

A small percentage of the hirda, however, does not become ridged, and in such cases it is found that almost the whole of the interior of the fruit has turned into a black powder, which is much valued and used for making ink.

The best uniform qualities are the No. 1 Bhimley and No. 1 Rajah, both of which are very rich in tannin—35 to 38 per cent.

The low price of Myrabolans and the abundance obtainable have induced the makers of ink to use them freely.

Nitrous acid reacts on the red colouring of the fruit changing it to blue.

Therefore in the manufacture of blue and blue-black inks Myrabolans play an important part.

They are also found to be invaluable in other ways whereever tannin is used.

IRON SALTS.

The commonest of these is green vitriol, ferrous sulphate. The ferrous salts have for a base ferrous oxide, while that of the ferric salts, the sesqui-oxide, contains a larger percentage of oxygen. Ferrous salts have a sea-green colour, and pass into ferric salts by absorbing oxygen from the air. Ferric salts are brownish-red. Green bottle-glass contains ferrous, brown bottle-glass, ferric oxide.

GREEN VITRIOL.

This is offered for sale in the form of large and beautiful sea-green crystals, which have an unpleasant, metallic, astringent taste, dissolve easily in water, and, by long exposure, crumble to a rust-coloured powder of basic sulphate. Green vitriol is now so cheap, being a bye-product of several chemical manufactures, that it does not pay the ink maker to prepare it for himself. We may, however, describe how the salt can be prepared free from ferric iron if necessary. Pour dilute sulphuric acid on old nails, hoop-iron, or other scrap, and as soon as the evolution of gas has ceased, filter the solution while it is still warm (it becomes hot of its own accord), and mix the filtrate with its own volume of strong spirit. The spirit throws down a pale green powder, which is pure ferrous sulphate. The precipitate is filtered off, dried in filter paper, and kept in a closely stoppered bottle.

Inks made with ferrous sulphate in time contain ferric as well as ferrous tannate. Those made according to antiquated recipes, by mixing solution of iron in strong vinegar with decoction of galls, are also ferrous inks.

FERRIC SULPHATE.

This is prepared by mixing a solution of green vitriol with some nitric acid, and boiling. Unless too much nitric acid has been used, we get a rusty-looking precipitate, because ferric oxide requires more sulphuric acid to dissolve it than ferrous oxide. This precipitate is basic ferric sulphate. We can either filter off, or carefully add sulphuric acid and warm it until it redissolves. The addition of any excess of nitric acid is carefully to be avoided, as free nitric acid will gradually bleach ink made with solutions containing it.

These pure salts are only worth preparing for use in original experiments, as they cost too much to be used in preparing ink for sale. Such experiments should, however, be made by every ink manufacturer who wishes to improve his business, especially if he wishes to work with tanniferous material with which he is not familiar. Ferric sulphate should be free from excess of sulphuric as well as of nitric acid, as acid fluids behave to tannins very differently from liquids not containing an excess of acid.

V.

THE CHEMICAL CONSTITUTION OF THE TANNIN INKS.

The tannic acids are always used in the form of the vegetable raw material. Hence the iron combines not only with tannic acid, but with other substances present in the vegetable matter, whereby the colour and other properties of the ink are modified.

According to the extensive researches of Bostock, which, however, were carried out a considerable time ago, the following reactions take place when a decoction of galls is mixed with a freshly prepared solution of ferrous sulphate.

The ferrous oxide combines with quercitannic acid, gallic acid, mucilage, and with the extractives. The compounds with the acids are those which give the necessary colour, but the others deserve attention for several reasons. It is these which often make an ink flow too thickly, and which impart the tendency to mould. Moreover, an ink which contains combinations of iron with mucilage or extractives also quickly loses its colour, and deposits a black sediment consisting of those compounds. Its precipitation leaves the ink almost colourless, as it entangles and carries down with it the coloured particles of tannate of iron, which, while suspended in the liquid, give the colour to the ink.

Many experiments show that the tannic acid is the only constituent of gall decoction which is of any value to the ink maker. If, for example, a cold infusion of galls is made and then kept boiling for a long time, a flocculent precipitate i formed, which consists of extractives coagulated by the boiling If it is filtered off and the clear solution is exposed to the air it becomes very mouldy in a few days. The fungi feed on the solution, and thereby produce in it important chemical changes. They convert the quercitannic into gallic acid, and destroy the soluble extractives almost entirely. In a few weeks indeed the liquid may be regarded as a fairly pure solution of gallic acid. If we then filter, and boil to kill the spores, we obtain a liquid which gives with solution of ferrous sulphate a fine blue-black ink, which will keep for months in an open vessel without showing the least sign of mould. The ink will, however, gradually turn pale and deposit a black sediment, because the fluid is not dense enough to keep the tannate of iron in suspension. These experiments show that the tannate and gallate of iron are present in ink, not in solution but in the solid state. The liquid must therefore be dense enough to keep the particles from settling, and, if necessary, bodies must be added which, while without action on the colour, augment the density. For this purpose we use either gum-arabic or dextrine, and also, although it is a less suitable substance, sugar. Dextrine is much cheaper than gum-arabic, but has the great fault of being hygroscopic, so that the ink dries slowly on the paper. The use of sugar is unadvisable, not only on account of its price but because it favours the growth of mould, when the ink becomes a thick stringy mass and can no longer be used.

In writing with inks made with ferrous sulphate we observe that the letters are at first bluish or greenish, but turn to a deep black in time. This change of colour results from the oxidation of the ferrous to ferric tannate, which has a darker colour than the ferrous compound. If the ink is made with ferric sulphate it writes black at once.

On account of the variable amounts of tannin contained in the raw materials, it is impossible to calculate the amount of iron salt required for any given weight of galls, oak bark, etc. Hence we find in recipes great differences in the relative quantities given. In our opinion nearly all recipes direct the use of much too large quantities of ferrous sulphate, and thus when the writing turns yellow or rusty the cause is to be found in the presence of an excess of iron salt which gradually decomposes the black tannate, so that at last nothing is left on the paper but basic ferric sulphate. This substance is also the cause of the yellow marks seen on linen which has been stained with ink and then repeatedly washed.

According to experiments which have been made on the properties of various inks in connection with the relative amount of galls and ferrous sulphate used in their preparation, it has been found that equal weights of galls and ferrous sulphate gave a very fine black ink, but that the characters soon turned brown and rusty. With still larger quantities of the vitriol the ink is still black, but very deficient in keeping power. The reason of this is that such an ink contains green vitriol in an unchanged state. This oxidises on the paper, forming the brown basic sulphate. This brown can be easily got by simply writing with a solution of ferrous sulphate alone. The freshly dry letters are invisible, but exposure to the air soon converts them into the brown basic sulphate.

We shall find, on the other hand, that quantities of ferrous sulphate much less than the weight of the galls will still give a good deep black ink, for the extremely finely divided state of the tannate of iron gives it such great colouring power that a small quantity only of it is needed.

If we write on paper with only decoction of galls, the writing is at first hardly visible, but in time it will become brown, and easily legible. In one special case, however, to be presently described, the writing may disappear altogether. The tannins have the property of gradually turning brown, forming the humus-bodies which we see in the soil and in rotten wood. This change is greatly hastened by the presence of alkalies. Now paper always contains more or less lime, and this alkali helps the formation of the humus and the disappearance of the writing. If the writing done with gall decoction is wiped over when dry with a sponge just damp with solution of washing soda, the brown letters will appear very quickly. But when the paper contains free chlorine, the writing will develop feebly or not at all. Such paper will destroy the colour of even the very best ink in time, as no organic dye can withstand chlorine, not even indigo itself. Such badly made paper also contains the seeds of its own destruction.

It is thus not difficult to decide whether an ink should contain an excess of iron salt or an excess of tannin. In the first case it will turn brown, and become nearly illegible. In the second it will remain black for a very much longer period. It must not be forgotten, however, that an excess of organic matter makes the ink liable to mould, even after it has dried on the paper, so that the colour fades. Hence to such inks a disinfectant must be added.

The disinfectant that ink makers make the most use of is carbolic acid, which is very cheap and is an unsurpassable preservative for all inks.

Pure carbolic acid crystallises in long colourless needles, having a very penetrating odour, and easily soluble in water. The presence of as little as one-hundredth per cent. of carbolic acid will preserve even the most putrefiable liquid perfectly. As the acid evaporates slowly when exposed to the air, however, rather more than this proportion should be present in an ink, but never so much that its smell becomes perceptible. The acid may be made to contribute somewhat to the colour of the ink, as it forms a violet compound with ferric sulphate.

It is probable that the huge amounts of sulphate of iron which we find in nearly all the older recipes are intended to act partially for preserving purposes, as the salt is a disinfectant itself. We have, however, pointed out the very grave objections to using excess of iron salt in a tannin ink. No one nowadays, when we have such a perfect preservative as carbolic acid, will think of making the iron salt do the work of an antiseptic as well as that of a colouring agent.

Although the tannin inks are the most liable to go bad of any, carbolic acid should not be added to them alone, but to all inks, for they are all putrefiable to some extent. The expense of so doing is very trifling, and the value of the addition can be appreciated by any one who will reflect that it absolutely guarantees that none of the ink which he manufactures will go bad either in his hands or in those of his customers. An exception to this rule, though, is found in the case of the aniline inks, which require no disinfectant, the dye itself being one.

As regards the amount of carbolic acid to be employed, one pound will preserve 1,000 gallons of ink. For the sake of perfect safety, however, more is used, say from 4 to 8 lb. per 1,000 gallons.

VI.

RECIPES FOR TANNIN INKS.

N.B.—THE QUANTITIES GIVEN IN RECIPES IN THIS BOOK ARE IN PARTS *BY WEIGHT* UNLESS THE CONTRARY IS DISTINCTLY STATED.

Few recipes consist simply of tannin material, iron salt, and thickening. Most of them mention other ingredients, although it is often impossible to see what influence these can have on the colour of the product.

We proceed to give a collection of first-rate recipes, beginning with ferrous inks, which have long been made of first-rate quality, and proceeding to other tannin inks subsequently.

A.—PURE TANNIN-IRON INKS.

Brande's Gall Ink.

Aleppo galls	3
Crystallised green vitriol	2
Gum-arabic	2
Water	60

This ink is made cold. The crushed galls are placed in half the water, while the gum and the vitriol are dissolved separately in the other half. This solution is then poured into the vessel containing the galls. The resultant liquid can be used as ink at once, but it does not fully oxidise and acquire its deepest colour before the lapse of about two months. During this time it is occasionally stirred, and then, when the coarser particles have settled, the ink is bottled. The residue of the galls can be used again, and will make a good ink with—

Green vitriol	½
Gum	½
Water	15

This method of manufacture is extremely simple, but one or two modifications greatly improve it. As the presence of the woody fibre of the galls is injurious they should be placed in a bag, which should then be hung in the water with two-thirds of its bulk immersed. The extraction of the tannin then goes on very fast, and all insoluble matter remains in the bag.

We have also in the ink many other extractives from the galls, and it is very liable to mould and to thicken. When the latter phenomenon occurs the whole ink is converted into an oily, spinning mass, which clings to the nib and cannot be remedied by filtration, but in most cases it can be cured by boiling it up with one-twentieth of its volume of strong gall decoction for two or three minutes.

We have by means of numerous trials so far improved Brande's ink that it responds fairly well to all requirements which can be made of a cheap product. The ink must be regarded us a cheap ink only, but it is an excellent writing fluid if a very dark colour is not essential.

Improved Brande's Ink (Lehner).

Galls or knoppern	1,200
Ferrous sulphate	800
Gum-arabic	800
Water	24,000
Creosote	3

Cover the galls with part of the water, and dissolve the gum, vitriol, and creosote separately in the rest of the water. Pour the solution on to the galls, and cover up the vessel. Stir every day for about three weeks, when the ink will have reached its full blackness, and can be bottled off. This ink will keep for years.

Ure's Tannin Ink.

This is a very deep black and very durable.

Galls	18
Ferrous sulphate	8
Gum	7
Water	145

Add 130 of the water to the powdered galls in a pan, and boil with constant stirring, to prevent the ink from burning, for two hours, adding water little by little at intervals to replace that lost by evaporation. The decoction is then allowed to cool, and filtered through a linen bag, doubled or trebled if necessary, and sometimes with a filter paper inside. The bag is suspended by the frame shown in Fig. 2, the spikes going through the linen. While the filtration is proceeding we dissolve the vitriol and gum in the remaining 15 parts of water, and pour the solution into the filtrate.

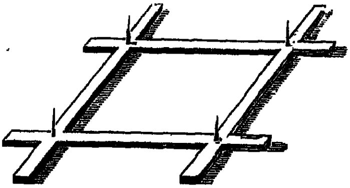

FIG. 2.

The ink does not develop its full blackness at once. To make it keep, a little carbolic acid should be added or some oil of cloves, or even a little gas-tar. Carbolic acid, however, is the best thing to use. Gas-tar was substituted when carbolic acid was expensive, but its use is now obsolete and to be avoided.

English Counter Ink.

Galls	20
Ferrous sulphate	5
Gum	5
Water	240

The water is divided into three parts—100, 80, and 60 respectively. The galls are boiled in the largest portion for 1½ hours. The decoction is poured off, and the second lot of water is boiled on the galls for an hour. It is then replaced by the smallest lot of water, which is boiled on it for half an hour. The first two decoctions are mixed, and the third is used to dissolve the vitriol and the gum. The whole is then mixed.

This practice of boiling the galls with several lots of water is highly to be recommended, as it ensures complete extraction. The ink is finally mixed with a little carbolic acid, and stirred once a day for a week. The ink becomes clear in a few more weeks and is then bottled.

To tell when an ink has cleared, *i.e.*, that nothing remains suspended but the necessary colouring matter, mix some of it in a tumbler with water till it is transparent. No solid particles must then be visible to the naked eye, and on long standing a black sediment should form at the bottom of a pale yellowish-brown liquid.

American Counter Ink.

Gall	24
Ferrous sulphate	5
Gum	5
Water	200

The peculiarity of this ink consists in the fact that some of the vitriol is oxidised by roasting the whole of it before use. This is done over a fire in an iron, or better in an earthen, pan. The vitriol first loses its water of crystallisation and becomes white. It afterwards turns yellow from the formation of ferric sulphate. Over-heating converts some of this into the basic sulphate, which, being insoluble, is waste. We have therefore modified the roasting process somewhat with the best results. We mix two parts of water with one of concentrated sulphuric acid, and pour the mixture over twenty parts of ferrous sulphate. The whole is then slowly heated to the fusing point of lead. We thus obtain a substance perfectly soluble in water. Care must be taken that the heat expels all excess of sulphuric acid from the mass or the ink will corrode steel nibs, and be useless.

Karmarsch's Gall Ink.

Galls	18
Ferrous sulphate	7
Gum	7
Water	64

The solids are powdered and left for a week in three-quarters of the water, with one daily stirring. The rest of the water is then added, and the ink is fit for use.

This ink is very good and cheap, but readily ferments, and should therefore be mixed with carbolic acid or with oil of cloves. The latter is an antiseptic and has a pleasant smell.

Gall inks attack nibs when not quite free from acid. Hence some recipes contain an alkali. An example of these is—

Link's Steel-Pen Ink.

Galls	224
Ferrous sulphate	96
Gum	80
Water	3,200
Ammonia	2
Spirit	128

The ammonia is to neutralise the free acid, and the object of the spirit is to prevent mould and to hide the smell of the ammonia. We think the spirit quite superfluous, as it not only adds to the prime cost of the ink, but makes the ink dry up. We have improved the ink as follows:—

Link's Steel-Pen Ink (Improved by Lehner).

Galls	112
Ferrous sulphate	48
Copper sulphate	2
Gum	40
Water	1,600

When the ink is made it is treated with carbonate of ammonia so long as a strong effervescence is caused. The reason for adding the copper sulphate is that this salt covers a new nib dipped into the ink with a coating of copper, which protects it, as copper is much less easily corroded than steel. At least, we thereby guarantee the surface of the nib from rust, but the point very soon loses its copper coating through friction against the paper.

B.—GALLIC ACID INKS.

The gallic acid inks combine with a beautiful blue-black colour the valuable property of being far less liable to decomposition than those made from quercitannic acid. The speciality of the manufacture consists in the preliminary conversion of all that acid into gallic. This is done by simply allowing the galls or their decoction to ferment spontaneously. It is, however, often very inconvenient to have a big vat of decoction standing fermenting for weeks together. Hence we give the following very practical method of simplifying the work. A vat is nearly filled with the coarsely powdered galls or bark, and just enough water at from 20 to 25 deg. C. is then poured on to cover the mass. The contents of the vat mould with great rapidity, and the fungus fills the inside of the mass with a whitish felt and covers it with a green crust. The whole conversion into gallic acid is completed in from 8 to 10 days, when, to prevent further action, boiling water is poured over the mass to kill the ferment. The solution of gallic acid is then drawn off by means of a cock. It gives ink of a fine blue-black colour and of great durability.

The names under which these gallic acid inks come on the market are as various as the recipes for making them. We here give some of the best :—

First Quality Gallic Acid Ink.

Gall-nuts	50
Ferrous sulphate	10
Gum	10
Water	2,000
Carbolic acid	2

The crushed galls are soaked in the water and allowed to ferment. This often takes some time, especially in the winter. It is a good plan to inoculate the mass with the mould from a piece of mouldy bread or leather. The fermented liquid is filtered, and the other ingredients dissolved in it.

Runge's Gallic Acid Ink.

Galls	8
Water	64
Ferrous sulphate	4
Gum	2

The larger part of the water is poured boiling over the crushed galls, which are then allowed to ferment for two months. The liquid is then drawn off, and the residue is rinsed with the rest of the water. The two solutions are filtered together and the gum is dissolved in the filtrate. The vitriol is then added in the form of concentrated solution.

Bolley's Inks.

Bolley, formerly professor at Zurich, has published the following recipes, showing great diversity in proportions :—

1.

Galls	125
Ferrous sulphate	24
Gum	24
Water	1,000

This, according to our experience, gives a good ink, but contains galls in excess.

2.

Galls	66
Ferrous sulphate	22
Gum	19
Water	1,000

Here the proportion of vitriol to galls is correct.

3.

Galls	62
Ferrous sulphate	31
Gum	31
Water	1,000

In this there is an excess of iron salt, and ink made from the recipe turns yellow sooner than those made from the first two.

STARK'S INK.

Boil 100 oz. of Aleppo galls with 8 gallons of water, and dissolve in the decoction from 33 to 50 oz. of gum. When cold add 66 oz. of ferrous sulphate, 66 oz. of indigo-carmine, and 1 oz. of carbolic acid. This is a beautiful ink, but the indigo-carmine makes it an expensive one.

Cheap Gallic Acid Inks.

1.

Galls	100
Logwood	30
Dextrine	40
Alum	12
Ferrous sulphate	45
Soft water	1,000

2.

Galls	58
Dextrine	40
Ferrous sulphate	45
Soft water	300

3.

Japan galls	180
Dextrine	120
Ferrous sulphate	85
Indigo-carmine	90
Water	2,500

4 (*School Ink*).

Japanese galls	30
Water	720
Dextrine	36
Ferrous sulphate	10
Pyroligneous acid	2
Logwood extract	28

EXTRA CHEAP IRON INKS.

Leather cuttings can be used with great advantage for the manufacture of glue and ink. The cuttings are covered with water containing ½ per cent. of hydrochloric acid, and left for a week. The liquid is then run off, and as much as possible is squeezed out of the leather. The leather is then treated for another week with another lot of dilute acid. The solutions are filtered and mixed, and enough ferrous sulphate is added to make letters written with the ink turn a deep black in a few hours. The ink is then exposed to the air for several weeks, to darken it, and finally bottled. The leather residues are first soaked and then boiled in water, and will yield a very good if rather dark-coloured joiners' glue, for which it may be possible to find a market.

VII.

LOGWOOD TANNIN INKS.

Logwood or Campeachy Wood.

Logwood is a medium-sized tree, indigenous to the West Indies and the greater part of tropical America, and known by the name of *Hæmatoxylon campechianum.* The wood is red or dark brown, from the presence of a special colouring matter called hæmatoxylin, which is extracted by boiling water.

The decoction is dark red, and gives an intense dark blue-black with iron salts. Hæmatoxylin has a great affinity for ammonia, and forms with it crystals which are green to reflected and red to transmitted light.

Logwood comes upon the market in fairly large pieces, sometimes with the white sapwood still adhering to it, but sometimes freed from it. It is very easy to extract the colouring matter from ground logwood, and this is therefore preferred by ink makers; but wrongly, as it is so extensively adulterated with foreign woods and water that it can only be safely bought by an expert.

Logwood Extract.

This can be highly recommended for use by the ink manufacturer, as it is very convenient, and its relative price is very small when we consider that the trouble and expense of preparing it are avoided. It can be roughly estimated that the extract is equivalent to four times its weight of the wood.

Commercial logwood extract occurs in the form of irregular pieces or flat plates with a shining dark-brown surface, and readily soluble in water, leaving, if the extract is good, very little residue, which consists of substances coagulated by the heat of the evaporation.

Although logwood decoction or a solution of the extract will make ink with an iron salt and without any third substance, yet logwood is preferably used as an addition to tannin inks which are not black enough without it.

The logwood may either be boiled or macerated with the galls, or the two decoctions may be made separately and then mixed. If logwood extract is used it is dissolved in the least possible quantity of hot water, and added to the solution of the other ingredients separately made.

The logwood tannin inks have a splendid blue-black colour and fair freedom of flow. They also have the great advantage that they attack the nibs less than pure tannin inks, as the logwood probably forms a varnish on the pen when it is laid aside, which excludes the air and prevents rust.

CAMPEACHY INK.

Galls	9
Ferrous sulphate	9
Logwood shavings	9
Gum	9
Water	180
Vinegar	180

Dissolve the gum, the vitriol, and the galls in the vinegar, and make a decoction with the logwood and the water. Then mix. The water which evaporates during the making of the logwood decoction must be replaced.

CAMPEACHY EXTRACT INK.

Galls	36
Ferrous sulphate	36
Logwood	9
Gum	36
Water	300
Vinegar	60

Proceed as above, and filter the finished ink.

RIBANCOURT'S CAMPEACHY INK.

Galls	16
Logwood raspings	8
Ferrous sulphate	8
Copper sulphate	2
Gum	6
Sugar	2
Water	200

The logwood is boiled with the water till half the liquid is evaporated. The decoction is filtered hot, and the other ingredients are dissolved in it. As soon as ink is cleared, which takes about three days, it is run off from the sediment and bottled.

CAMPEACHY GALLIC ACID INKS.

These much resemble the inks last described, and practically the only difference is that they contain gallic instead of quercitannic acid.

FIRST QUALITY.

Galls	20
Campeachy wood	30
Ferrous sulphate	20
Gum	30
Water	130

Crush the galls, and let them ferment with 80 of the water for a fortnight. Then draw off the liquid, and rinse the residue with enough water to make the liquid and washings up to 100. The remaining 50 of the 130 of water is boiled on the logwood raspings till the solution only weighs 30. It is then filtered hot, and the vitriol and gum are dissolved in it. It is then mixed with the gallic acid solution. In a few days there will be a considerable precipitate. The supernatant liquid is an excellent ink of a pure black colour.

HÆMATOXYLIN INK.

This differs from the last chiefly in name. The following is the recipe :—

Galls	40
Logwood	50
Ferrous sulphate	30
Gum	25
Water	200

Leave the powdered galls with part of the water for at least three months in a uniformly warm room.

We differ here from the recipe, for a fortnight is certainly ample for the complete conversion of the quercitannic into gallic acid. If a longer time is allowed other changes set in, and the gallic acid is itself altered and much of it converted into substances quite useless for ink making. This is quite irrespective of the waste of time and capital involved in substituting thirteen weeks for two. Even if there were a little quercitannic acid left, that would not matter in the least. The logwood is then boiled for some hours with the gallic acid solution, adding water so as to keep the volume constant. The vitriol and gum are then dissolved in a little of the liquid, which is then added to the main mass.

VIII.

FERRIC INKS.

As already stated, many inks only acquire a deep black colour a considerable time after the writing has been done. The change is due to the oxidation of the ferrous to ferric tannate. As a necessary consequence of this many attempts have been made to use ferric salts only in the manufacture, so as to get an ink which will write a deep black from the first. The chief method is to roast the ferrous sulphate, *i.e.*, to oxidise it by heating it in the air before it is used. Our experiments, however, have shown that inks containing ferric iron only are of very little value. We prepared the ferric sulphate by boiling a solution of the ferrous salt with nitric acid or by dissolving the sesquioxide in sulphuric acid.

On adding to the ferric salt a decoction of galls, fermented or unfermented, and with or without logwood, an ink was obtained which wrote at once with a faultless lustrous black, but in time the characters lost their lustre and became of a brownish hue. Worse than all, however, the ink adhered so loosely to the paper that with a little care the writing could be entirely erased with a damp sponge. It was only after some years that the ink withstood the sponge to some extent. Probably the ferrous compounds penetrate the paper more deeply than the ferric salts, so that when the persalts are formed on the paper they are formed below the surface, and are hence protected by the fibre from removal with water.

The browning of the writing done with a ferric ink is probably due to separation of part of the sesquioxide; this in the free state shows the reddish-brown colour which is so familiar in rust.

JAPAN INK.

This long-celebrated ink principally consists of ferric tannate. It is made by roasting green vitriol at a moderate heat and then treating it with logwood extract and decoction of galls. It is of a deep black at first, but has all the drawbacks above noted as belonging to ferric inks. Like all other ferric inks, too, it does not flow very freely, and the nib must be carefully cleaned after use or it will soon be so encrusted as to be unusable.

The best iron inks are those made from ferrous sulphate. The writing soon comes to have the necessary amount of ferric oxide in it to make the writing black by spontaneous oxidation on exposure to the air.

IX.

ALIZARINE INKS.

If the name shows anything these inks should contain alizarine. Alizarine is a red colouring matter occurring in madder (*Rubia tinctoria*), but it is now always prepared artificially. It is very largely used in dyeing, especially in Turkey-red dyeing. Nevertheless, most of the so-called alizarine inks contain neither alizarine nor any other constituent of madder. We do not exactly know how such inks came to be called alizarine inks, but seeing that real alizarine inks are most excellent ones, we have little doubt that the name was adopted for fraudulent reasons, and to deceive chemists as well as the general public.

The inks so far described owe their colour to the presence of suspended and very finely divided quercitannate or gallate of iron. The sole object of adding gum is to keep the coloured precipitate in suspension, and if it is omitted a black precipitate will soon form in the ink. The formation of this sediment can, however, be completely prevented by adding to the ink an acid which will dissolve it. For this purpose acetic acid is specially suitable, and we have here the secret of what are called alizarine inks. They are simply iron inks in which any precipitation of tannate of iron is prevented by acidification with acetic acid, or occasionally with sulphuric. The solution has generally a rather pale greenish or brownish colour, and the writing is at first green, turning in a few hours to a fine black. The process of blackening is a double one; the acetic acid evaporates in part, leaving the solid matter it had in solution behind it. Another part of the acid is neutralised, partly by the lime in the paper, but chiefly by the ammonia of the atmosphere. There is always lime in paper, from the water used in its manufacture. If a wet writing with an alizarine ink is put under a bell-glass with a dish of ammonia, the writing becomes black almost instantly.

Of course an ink which contains so strong a free acid as acetic or sulphuric must corrode steel nibs rapidly, but that only happens the first time the nib is used. If the ink is then allowed to dry on the nib it forms a protective coating which prevents further action. Naturally all excess of free acid should be avoided in the manufacture, if only for the sake of economy. An ink which has been accidentally made too acid may be brought to the right point by the cautious addition of ammonia. If too much alkali is added the object of adding the acid is lost, for it all becomes neutralised and solid matter appears in the ink. More of the too acid ink can be mixed in in this case. The best plan of all is to divide the ink which is too acid into two parts. One is then made neutral with the ammonia, and mixed with the other.

The "alizarine" inks have become very favourite writing inks, partly because they leave no sediment, even when they have stood for years in bottle, and partly because they flow very freely from the pen—a matter of great importance for quick writing. The great objection to them is their pale colour. In some cases the fresh writing is barely visible. This can be got rid of by adding just enough of a solution of a very powerful dye, which is, in its turn, concealed when the ink turns black. Before the discovery of the water-soluble aniline dyes, indigo-carmine was the only substance available for this purpose. Until the artificial dyes were invented indigo- and cochineal-carmines had the greatest colouring power known, and both were therefore much used by the ink maker in spite of their high price. In fact no other dye is so suitable for his purpose as indigo-carmine, but we have now artificial dyes which will serve our purposes even in smaller quantities than will suffice of indigo-carmine, and they have therefore replaced it to a large extent. It is nevertheless suitable for every kind of ink, and in addition forms in itself an excellent ink both for writing and for stamping. We must hence describe it carefully.

INDIGO-CARMINE.

Indigo is the splendid blue dye obtained by a fermentative process from *Anil indigofera*, a plant indigenous to India. Very many kinds of indigo come upon the market, and Bengal indigo is considered the best.

Indigo has a deep dark-blue colour and a characteristic coppery lustre. The following infallible tests of good quality should be carefully noted:—

The pieces must be light, and of a uniform colour, and show a uniform fracture. Sand and pebbles must be absent, and on rubbing with the finger-nail the coppery lustre must appear distinctly. The pieces must not feel damp. They are often sprinkled with water to add to the weight.

To prepare indigo-carmine we must dissolve the indigo in sulphuric acid. This can only be done in the fuming or Nordhausen acid, and only when the indigo is quite dry. Having powdered our indigo fine (it is a mistake to buy indigo ready-ground, as it is then usually adulterated), we dry it with the greatest care at a temperature which must not exceed 120 deg. C. at the highest. The acid is then poured on to the indigo while it is still warm. The quantity needed depends upon the purity of the indigo and on the strength of the acid. It is usually about four times the weight of the dry indigo.

The acid must be added slowly with constant stirring with a glass rod, and the indigo must be in a roomy earthen basin, because the act of solution is accompanied by much frothing. When all the acid is in, the basin is left covered up for twenty-four hours. By that time the conversion of the indigotin into sulpho-indigotic acid is complete, and the latter compound must be at once converted into indigo-carmine of inferior quality, as it would be mixed with substances previously mixed with the indigotin which have been carbonised by the sulphuric acid. To get pure indigo-carmine we dilute the liquid with 10 or 12 times its volume of pure water and allow it to stand for a few days, till all the insoluble matter has settled to the bottom. The clear solution then looks black in large masses, but slender columns of it are transparent and of a splendid blue colour. It is decanted and evaporated without boiling, and at the same time neutralised with carbonate of potash. As soon as the effervescence due to the escape of carbonic acid has ceased we have a solution of pure indigo-carmine, which is potassic sulpho-indigotate. This salt can be got in the solid state by very cautious further evaporation, but it is more usual to precipitate it with carbonate of soda, on the addition of which the indigo-carmine, being less soluble in alkaline solutions than in water, is thrown down. It is filtered off and dried, when it shows an efflorescence of the excess of soda.

Indigo-carmine when dry has a deep blue colour with a strong coppery lustre. It is extremely soluble, and a very small quantity of it gives an intense blue colour to the water. It is with difficulty soluble in alcohol or in saline solutions.

For ink making it is quite unnecessary to evaporate down the solution of indigo-carmine. As soon as the neutralisation with carbonate of potash is finished, the solution should be concentrated and preserved in bottles. It is, however, required in a solid state for water-colour painting and as a laundry blue or for india-rubber stamps. The above-mentioned efflorescence spoils the look of the solid substance, and can be prevented by adding glycerine to the mass. The hygroscopic qualities of the glycerine prevent the soda from crystallising, and make the dark blue of the indigo-carmine appear to the fullest advantage.

COUNTER ALIZARINE INK.

Galls	20
Ferrous sulphate	12
Gum	2
Acetic acid	200
Indigo-carmine solution	40

This green, readily flowing ink is made by soaking the powdered galls in the acetic acid, drawing off the solution after a few days, and dissolving the vitriol and the gum in a part of it, which is then added to the rest. Finally the indigo-carmine is added. It is best not to weigh it, but to add it gradually till the ink writes a fine bluish-green at once. The ink is bottled as soon as this point is reached, and forms a clear dark-green solution.

Many ink makers use sour beer instead of vinegar, and thus get an ink which soon moulds on exposure. To avoid this, and at the same time save expense, crude pyroligneous acid should always be employed. The carbolic acid in this prevents any mould from growing.

FIRST QUALITY ALIZARINE INK.

Galls	40
Iron solution	15
Indigo-carmine	5
Gum	10
Pyroligneous acid	10
Water	100

This, which is the best of all alizarine inks, and has no action on steel, is prepared from the above hitherto unpublished recipe, as follows:—

The galls are powdered and soaked in the water and half the acid for a week. The quercitannic acid is thus completely extracted, but none of it converted into gallic, as the pyroligneous acid prevents any fermentation. The iron solution is prepared from pyroligneous acid and scrap iron, left together for a week. This solution must contain enough acid to keep the acetate of iron in solution. To test this point a sample of the gall infusion is mixed with one-tenth of its volume of the iron solution. The thin column of the mixture should be clear and of a dark-green colour, but if the column is black and opaque more acetic acid is necessary, and the additional amount required must be ascertained exactly by adding measured quantities of pyroligneous acid, with constant stirring, till the liquid assumes the appearance described. From this the extra amount wanted for the whole lot of ink can be calculated. Any necessary extra acid is then added to the gall infusion, the gum is dissolved in it, and the iron solution is then put in. Enough indigo-carmine is then added to give the required shade.

ALIZARINE INDIGO INK.

The following is Prollins and Bley's recipe:—

Galls	20
Indigo	2
Fuming sulphuric acid	8
Iron filings	4
Chalk	4
Water	160

Boil the crushed galls with the water till the infusion weighs 40. Dissolve the indigo in the acid, add 40 of water to the solution, and then put it into the gall infusion. Then put in the iron filings, where they dissolve with evolution of hydrogen, the ferrous sulphate reacting with the quercitannic acid. The excess of sulphuric acid is then precipitated as sulphate of lime by means of chalk. A still better plan is to dissolve the iron in the indigo solution first, neutralising them with chalk, and adding the gall infusion after decantation from the sulphate of lime. The reason is that in the method first mentioned the calcium sulphate carries down with it some of the colouring matter of the ink. This method is simpler but more expensive than using sulphate of iron ready made.

AMERICAN ALIZARINE INK.

Powdered galls	40
Ferrous acetate	15
Gum	10
Pyroligneous acid	10
Indigo-carmine	5
Water	100

We could give many more recipes for these inks, but they simply vary from those given and about to be given in the proportions of the ingredients, without giving any better inks.

REAL PATENT ALIZARINE INK.

Aleppo galls	84
Dutch madder	6
Indigo-carmine	2
Ferrous sulphate	10
Pyrolignite of iron	4

The galls and madder are boiled with water down to 240 of solution, and the other ingredients are added after filtering. The addition of the madder makes very little difference to the beauty or the durability of the ink, and it is now very difficult to get madder.

HAGER'S ALIZARINE INK.

In a roomy earthen dish (to allow for frothing) put 12 of fuming sulphuric acid, and add to it, little by little, 2 of indigo. Twenty-four hours after the indigo is all in, dilute with 16 of water, and dissolve in the solution 6 of clean iron filings. In the meantime boil 24 of Chinese galls with 300 to 400 of water, and dissolve 6 of gum and 3 of sugar in the decoction. Then add the other solution and a little carbolic acid for preservative purposes.

As good results can be obtained with very various proportions of tanniniferous materials and iron salts, it is possible further to multiply recipes for iron inks. Every intelligent maker can soon discover wherein any recipe which he uses is faulty, and a few experiments will then quickly show him what the best proportions are, both as regards the cost and the quality of his ink, of the particular materials which he uses or has at his command.

X.

EXTRACT INKS.

The fact that gall-nuts are usually directed in ink-recipes as the ingredient for providing the tannin is owing to an old but erroneous idea that they contained a sort of tannin absent from all other vegetable matter. It must be regarded as a great step in advance that we have learned to use other vegetable substances to prepare inks which are in no way inferior to those made from galls. An ink maker who knows his trade can get his tannin very cheaply indeed, by using some of the materials to be presently named. In the first rank of these are the unripe fruits of the sloe (*Prunus spinosa*), of the bird-cherry (*Prunus padus*), and of the black elder—any fruits, indeed, which have an astringent taste or intense colour.

Most of the barks of our forest trees, also, contain notable quantities of tannin. We may mention specially oaks, pines, elms, and willows. The sumach, the plum, the poplar, the horse-chestnut, and the elder contain tannin in the young twigs as well as in the bark. These vegetable matters also contain extractives which affect the colour of the ink. Some of them give a green ink with ferrous sulphate, some a brown, and many a purple. We seek for ink-making purposes such dark colouring matters as will make what the dyers call lakes.

If we add solution of alum to certain vegetable decoctions the colour of the solution changes, and if caustic potash or ammonia is then added we get a precipitate of coloured alumina, which is called a lake. In ink manufacture this lake is not, of course, to be produced in the ink itself. The flocculent precipitate would not remain in suspension. It is a question of having the lake in solution, which is effected by having free acid present. If we write with an ink so made, we shall see that the writing gradually darkens. The ammonia in the air and the traces of lime in the paper co-operate to precipitate the lake, and thus make the writing more distinct.

The amount of alum to be used can only be known by experience, as it depends upon the nature and the degree of concentration of the decoction. The nature of the decoction depends, too, not only on the plant it was obtained from, but on the age of the plant and the time of year at which it was gathered. When once the right proportion has been hit upon, on adding ferrous sulphate we shall obtain an ink of a particular colour, and we have in indigo-carmine an excellent means of bringing that colour to black, blue, or violet, as may be required. We use gum-arabic or dextrine as a thickening, and add as well a little antiseptic, such as carbolic acid, as these inks are very liable to go mouldy, which must always be particularly guarded against.

Although it is impossible to give recipes for all the substances which can be used for ink making, we give below a sufficient number to act as a guide to the manufacturer.

Elder Ink.

The berries of the common elder (*Sambucus ebulus*) contain a large quantity of a reddish-blue dye, and give a capital ink. The writing is at first violet, but soon turns to a deep black.

Elder berries	100
Ferrous sulphate	5
Alum	2
Vinegar	5

Crush out the juice of the ripe berries and mix it with the vinegar. Then add the alum and the iron salt dissolved in hot water.

SLOE INK.

Sloes	200
Ferrous sulphate	10
Alum	4
Vinegar	50
Water	125

Crush the unripe berries and boil them in the water. Strain, and add first the vinegar and then the alum and the vitriol both dissolved in a little hot water. A little carbolic acid is added to all these inks.

CHESTNUT INK.

The prickly shells of the fruits of the horse-chestnut (*Tesculus hypocastanum*) give, with boiling water, an excellent extract for ink making.

Green chestnut shells	400
Ferrous sulphate	4
Alum	2
Water	2,000.

Boil the shells for a few hours in the water, strain, and add the alum and the vitriol. The bark of the young twigs of the horse-chestnut can also be used instead of the fruit.

CATECHU INK.

Catechu	10
Ferrous sulphate	10
Gum	2
Water	100

Dissolve the catechu in the water boiling, let the solution clear, decant it, and add the iron. In this way a splendid ink can be very quickly made. A small percentage of strong vinegar is a great improvement.

WALNUT INK.

The pulp of the fruit of the walnut (*Juglans regia*) contains an extractive which quickly turns brown on exposure to the air, and is sometimes used to dye the skin a deep brown. This pulp gives a very durable ink of a fine black colour.

Green walnuts	200
Ferrous sulphate	8
Alum	2
Water	800

XI.

LOGWOOD INKS.

Logwood (*Hæmatoxylon campechianum*) contains a colouring matter soluble in water and showing several very characteristic reactions. A decoction or an aqueous infusion made at ordinary temperatures is red, but alkalies turn it blue. The pure colouring matter is called hæmatoxylin, and forms yellow crystals. When the wood is exposed to the air it changes into hæmateine, which is red.

Hæmateine gives a violet compound with ammonia. Treated with solution of alum or lead acetate, and then with ammonia, it gives a blue or violet lake.

The most important property of logwood decoction for our purpose is that of forming very dark liquids with neutral chromates. These liquids can be used as inks or dyes, or for painting. On this account logwood and its extract are much used by ink makers, and rightly so, for the inks so made have a fine colour, are very durable, and cost little to make.

English Logwood Ink.

Galls	100
Logwood	120
Ferrous sulphate	35
Gum	100
Vinegar	400
Water	500

This ink can be got by putting all the ingredients into a vat. Stir every day for about a fortnight. The ink will then be a deep black, and can be bottled. The residue of galls and logwood is then treated with —

Ferrous sulphate	15
Gum	30
Vinegar	100
Water	150

and gives a second lot of ink of good second quality. Even a third lot of ink may be got by adding half the quantities last mentioned to the residue after the second ink has been drawn off.

It is, however, a better plan to put the solid ingredients into a bag, which is hung, two-thirds immersed, in the vinegar and water. We thus get an ink that requires no filtering. A wooden ring round the mouth of the bag greatly facilitates the filling and emptying.

The only drawback to this very convenient way of making ink is the liability of the liquid to mould. It is thus advisable to substitute crude pyroligneous acid (which contains carbolic acid) for the vinegar, or if vinegar is used, to add a little carbolic acid.

If it is desired to prepare these inks well in a few hours, the bag should be steeped in the liquid ingredients at the boil, the galls should be well crushed, and the logwood either in the form of extract or of sawdust or very thin shavings.

French Logwood Ink.

Galls	55
Logwood	30
Ferrous sulphate	30
Cupric sulphate	8
Alum	2
Gum	20
Water	1,500

Boil the crushed galls and the logwood shavings in the water till the liquid is evaporated to about half. Then strain boiling, and stir in the gum and the metallic salts in the state of fine powder. The ink is then fit for use, but it is better to allow it to settle a few days. The sediment is put to the residue remaining from the first decoction, and mixed with—

Ferrous sulphate	10
Copper sulphate	2
Gum	8
Water	500

Boil for two hours, and strain boiling hot. A second lot of ink is thus obtained, which, although inferior to the first, is better than many common gall inks. It shares with all logwood inks the manifest advantage of containing no free acid, so that it does not injure the nibs. A nib which had been used for this ink till the point had become so worn by friction that it was impossible to make a fine stroke with it appeared, when cleaned with water, perfectly polished, and showed no signs of corrosion.

Germania Ink.

Galls	200
Logwood extract	30
Ferrous sulphate	60
Alum	4
Vinegar	10
Carbolic acid	2
Water	2,400

The powdered galls are mixed with 2,000 of the water, and left in a covered vessel for fourteen days. In the meantime the logwood extract is dissolved in 200 of the water, and the metallic salts in the remaining 200. When the gall infusion is drawn off—it is usually very mouldy—it is mixed with the vinegar and the carbolic acid, and finally with the solution of vitriol and alum. The result is an ink of the very deepest colour, which flows freely and penetrates the paper well. It resists chemicals strongly, and is very suitable for important documents which have to be preserved for long periods.

GALLIC ACID AND LOGWOOD INKS.

Although the Germania ink just described is partly a gallic acid ink, as the gall decoction is used in a mouldy state, the process can be also so managed that an ink is obtained which unites the advantages of a good alizarine ink with those of a logwood ink. The following is the recipe for securing this result:—

Galls	200
Ferrous sulphate	60
Vinegar	1,600
Carbolic acid	2

The galls are soaked with part of the water and left to ferment for three weeks. At the end of this time all the quercitannic acid will have become gallic acid. The vinegar is then added, and the liquid is strained. The residue is rinsed with water till the liquid and washings weigh 800. In a part of it we dissolve 40 of logwood extract and 2 of alum, and then put it back to the rest. The addition of the carbolic acid finishes the ink.

As appears from the description, we get first an acid ink, which, if used at that stage, gives pale green writing which gradually turns black in the air. The addition of the logwood makes the ink write a fine blue-black from the first, which soon becomes a deep lustrous black.

All the logwood inks hitherto described have, besides great cheapness of production, the additional advantage that they penetrate the paper very deeply, a circumstance which, of course, greatly increases the durability of the writing. We possess writings executed with them many years ago, some of which have been purposely stored in damp cellars. The writing is as black as ever, while those done with ordinary logwood inks, which have been treated in the same way for the same time, have turned distinctly brown.

LOGWOOD CHROME INK.

So far we have described only inks owing their colour to a very finely divided black precipitate suspended in a colourless solution, or those in which the black is in solution in an acid. In reality, however, none of these inks consists of a black solution which would give no sediment on standing. Such a solution, however, exists without any suspended matter whatever. It was discovered by Runge, who found that *neutral* chromates gave with infusion of logwood a very black, clear liquid.

Runge found that the best salt for the purpose was the yellow potassium chromate (K_2CrO_4). Although it is not a rare salt, it is sold at an exorbitant price, and the ink maker who uses it in large quantities will find it advantageous to make it himself by the following process:—

PREPARATION OF POTASSIUM CHROMATE.

Dissolve commercial bichromate of potash in ten times its weight of water, boil up, and add powdered carbonate of potash till all effervescence ceases. A slight excess of the carbonate does no harm. The liquid during the process gradually changes from red to yellow. It is then evaporated to about half its bulk in an earthen dish, and then allowed to cool with constant stirring. The chromate then crystallises out in small yellow crystals. The mother liquor is poured off, and the crystals are dried on blotting-paper. The mother liquor can be used instead of water to dissolve a fresh lot of bichromate.

In the bichromate half the chromic acid is less firmly combined than the other half. This seems to be the reason why an ink made with it has the drawback of changing its pure black colour to brown with time, a change probably due to that half of the chromic acid having been set free. If the monochromate is used the black does not change. We do not at present know the nature of the reaction between logwood dye and monochromate. Some chemists think that the chrome combines with the dye. Although we are aware of the existence of various compounds of organic dye stuffs with metallic oxides we do not think there is much foundation for this opinion, for a very small amount of potassium chromate will convert a large quantity of logwood infusion into ink, and the proportion of chrome to hæmateine present is so insignificant that we do not think it likely that there is combination between the two, although it is, of course, possible. We have also found that the amount of monochromate required to convert a given quantity of infusion into ink varies greatly, probably on account of the variable amounts of colouring matter present in different kinds of logwood. We have also found that it is of great importance to take just the right quantity of chromate. If too little is used the colour is not full enough, and if too much, the black, although satisfactory at first, will turn brown like that got with bichromate. Although it is impossible to give the exact proportions for all kinds of logwood, yet it will be found that a solution of 2 lb. of chromate in 2 gallons of water when added to a decoction of 40 lb. of logwood in 24 gallons of water will always give a satisfactory ink.

The logwood is broken very small, and boiled with the water till the solution is down to 20 gallons. The decoction is then strained, and the chromate solution is added in very small portions, with constant stirring. After a time a sample should be taken. If it is transparent and writes red or violet, more chromate is wanted. Enough has been added when the liquid is black and writes a blue-black. The quantities used and the brand of the logwood should be noted for future reference.

LOGWOOD EXTRACT CHROME INK.

It is simpler and better to use the extract than logwood itself.

Logwood extract	2,000
Potassium chromate	10
Water	100,000

Dissolve the chromate in the water, and hang the extract in a bag in the solution.

These logwood inks are all very cheap, very black, and very durable. They penetrate the paper very deeply, and after a few days will resist all attempts to destroy them chemically.

VIOLET LOGWOOD INK.

Logwood	100
Alum	5
Gum	10
Water	500

Boil the logwood with the water, dissolve the gum in the hot decoction, and finally add the alum previously dissolved in a little hot water. If a more purple shade is desired, reduce the alum to two-thirds or a half of the above quantity. If, however, the ink is to be blue-black with a violet tinge, add carefully a solution of chromate till the wished-for colour is reached.

FREE-FLOWING LOGWOOD INK.

Solution of logwood extract	440
Dextrine	80
Water	1,080
Alum	72
Sulphuric acid	6
Potassium chromate	3

The sulphuric acid is added before the chromate and the alum.

ORDINARY LOGWOOD INK.

Logwood extract	1,110
Dextrine	30
Alum	600
Water	80,000

To the solution of the extract add first the alum and then the dextrine. The alum is hung in the solution in a bag till it is all dissolved.

VIOLET LOGWOOD INK.

Solution of logwood extract	300
Alum	12
Dextrine	15

The alum is dissolved by heating it in part of the extract solution. Finally one and a half parts of finely powdered acetate of copper is hung in the ink in a bag.

RED LOGWOOD INK.

Solution of logwood extract	50,000
Dextrine	2,500
Alum	2,500
Acetate of copper	20

The finished ink is carefully reddened with small additions of sulphuric acid, stirring vigorously each time. This ink does not attack steel nibs so much as might have been expected, especially if the ink is allowed to dry on the pen after the first using.

XII.

COPYING INKS.

It is unnecessary to enlarge upon the importance of copying inks, especially as we have now succeeded in making copying inks that require no press or any other mechanical contrivance.

The essential feature of a copying ink is to dry slowly, so that the writing may be copied even after a considerable interval. This property is given by mixing the ink with hygroscopic substances, that is to say, such substances as keep moist by absorbing water from the atmosphere. The hygroscopic bodies which we use are sugar, grape-sugar, dextrine, glycerine, or chloride of calcium. The hygroscopicity of the last substance is so great that it has to be used in very small quantities. Excess of any of these bodies causes the writing to remain too damp and apt to be effaced.

Any of the inks already spoken of can be made into a copying ink by adding to it the proper quantities of thickening and hygroscopic substances, but inks in which there is a suspended precipitate are less suitable for copying inks than those in which the colouring matter is in solution. The reason of this is that the latter inks penetrate the paper more deeply than the former, and hence remain copyable longer than inks in which only the liquid parts penetrate and the coloured precipitate remains upon the surface, where it is only retained by the thickening substance.

A very simple experiment will convince anybody how different the precipitate-containing inks are from the others. The dry writing of one of the former can be washed away in great part with a damp sponge two or three hours afterwards, and even made quite illegible. This is quite impossible when the ink used had its colouring matter in solution.

A copying ink with a suspended colouring matter will generally give one copy only, and that a bad one, while the original will be nearly obliterated. When, on the other hand, a copying ink has its colour in solution, the latter penetrates the paper, and hence the characters consist of liquid of a particular depth. The lowest part of it adheres so to the paper by capillary attraction that it cannot be removed. The surface of the paper may, however, be likened to a soaked sponge, for when another porous body is pressed on to it, it gives up to it part of the liquid it contains, and gives a sharp copy without injuring the original. When the copy is removed there is enough liquid left to give, with a somewhat stronger pressure, a second copy as sharp as the first. By the use of moistened paper and a still greater pressure a third or even a fourth copy can be taken from the same original. The amount of pressure and its duration must be greater for each successive copy, and the pressure is best applied with a copying press.

Before speaking of copying presses we may say a few words about the paper to be used for taking copies. It must be unsized and of a high degree of porosity, so as to suck up the ink freely. It must also be so thin that the copy penetrates it through and through. It is often necessary to hold the copy up to the light before it can be read, especially if it is the third or the fourth copy. These are always pale, even when a very good copying ink is used. It is a good plan to keep the copying paper in a tin box with a cup of water. This will keep it damp, and it will then take more copies than a perfectly dry paper, even with a moderate pressure,

COPYING PRESSES.

The object of these is to get a uniform pressure all over the paper. To assure this it is necessary not only to have the original and the copying paper between two unyielding plates, but also between two others having a certain amount of softness and elasticity. Hence the boards of the press consisted in the old forms of strong wooden boards covered with several layers of soft paper. In the newer forms we have iron instead of wood, and the paper coating of the plates is replaced by india-rubber. The use of iron avoids the trouble caused by the warping or splitting of the wood in the old presses.

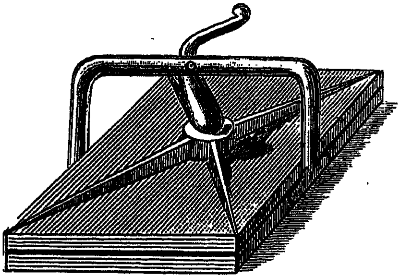

FIG. 3.

The old arrangement for applying pressure is a screw, but the use of a lever is simpler and more convenient. (See Fig. 3.)

The writing to be copied is laid on the lower plate, and covered with the copying paper, and this with blotting-paper. The upper plate is then brought down upon the three. The amount of pressure required depends on three circumstances—the nature of the ink, the time that has elapsed since the original was written, and the degree of dampness of the copying paper. The more deeply the ink of the original has penetrated the paper, the fresher the characters are, and the nearer the paper is to the right degree of dampness, the less will be the pressure wanted, the sharper the copies and the larger the number of them possible. The pressure causes the copying paper to take up a part of the ink from the original, and the copy is visible on both sides of the paper. Care must be taken in removing the copy, which will, of course, adhere to the original to some extent.

If more copies than one are wanted, the others should be taken as quickly as possible after the first. The longer the time, the more the ink of the original dries and the less distinct does the copy become.

It is possible to obtain copies if the original is damped on the back by means of a wet sponge long after it has become impracticable to get any without resorting to this device. The wet, of course, soaks through the paper to the ink on the other side and brings it back, at least in part, to the liquid form, when sufficient pressure, after the water has been allowed time to act, will often result in the production of one perfectly good copy at least.

Copying Books and Skins.

At the present time the copying process has become so simplified that the copying sheets are bound into books containing 500 or 1,000 each. These books are used by placing a skin under the leaf to be used, which is then wetted with a sponge and dried by pressure under blotting-paper till it ceases to shine. The original is then placed on it and covered with a skin. The book is then shut, and a moment's sharp application of the press gives a faultless copy.

The skins are made by soaking white or yellow cartridge paper in fused paraffin. When cold the paper is run through smoothing rolls. It is then quite impervious to water.

Single Gall Copying Ink.

Galls	120
Ferrous sulphate	30
Gum	20
Grape-sugar	10
Water	1,000

Here the grape-sugar is the hygroscopic agent. As it easily ferments, whereby the ink would be spoiled, some carbolic acid must also be added. If the ink turns out too sticky, mix it with some more which has been made without either gum or grape-sugar.

DOUBLE GALL COPYING INK.

Galls	7
Ferrous sulphate	7
Logwood	16
Gum	5
Grape-sugar	2
Water	60
Vinegar	10

The logwood may be replaced by about one-tenth of its weight of logwood extract. A little more does no harm, as it is itself hygroscopic and hence contributes to the copying properties.

LOGWOOD COPYING INK.

Logwood extract	200
Ferrous sulphate	4
Copper sulphate	2
Alum	24
Grape-sugar	16
Potassium chromate	2
Indigo-carmine	38
Water	1,000

The extract, the indigo-carmine, and the sugar are dissolved in 800 of the water. The other ingredients are dissolved in the rest of the water, and the two solutions are then stirred together.

GLYCERINE COPYING INK.

Logwood extract	200
Ferrous sulphate	8
Potassium chromate	2
Indigo-carmine	16
Glycerine	20
Water	1,000

This excellent ink is made by dissolving the extract, the iron salt, and the chromate simultaneously in the water, and then adding the glycerine and the indigo-carmine. The glycerine does not thicken the ink very much, and the ink flows therefore freely enough for the finest hair strokes to be made with it. In spite of this great advantage the ink will give many copies, as it dries very slowly and penetrates the paper very deeply.

N.B.—It must not be forgotten that in all cases when potassium chromate is included in an ink recipe that salt must be used, and not the bichromate.

BOTTGER'S COPYING INK.

Logwood extract	64
Carbonate of soda	16
Potassium chromate	2
Glycerine	64
Gum	16
Water	270

Dissolve the soda and the extract together in the water, then add the gum and the glycerine, and lastly the chromate dissolved in the smallest possible quantity of hot water. The ink is then ready for immediate use. This ink will give three copies merely with the pressure of the hand, and two more afterwards in the press.

LOGWOOD COPYING INK.

Logwood extract	70
Vinegar	1,000
Water	1,000
Ferrous sulphate	40
Alum	20
Gum	35
Sugar	60
Glycerine	5

BIRMINGHAM COPYING INK.

Logwood extract solution	5,200
Dextrine	240
Alum	265
Verdigris	2
Oxalic acid	16
Glycerine	56-168

The amount of glycerine used is according to the time during which the ink is to remain copyable after writing.

ALLFIELD'S COPYING INK.

This is intended for use without a press. It is made by evaporating 10 gallons of ink down to 6, and then making up to the original volume with glycerine. The copying is done by mere contact of the copying paper, but the copy is very easily smudged.

KNAFFL'S COPYING INK.

The following preparation is of the greatest value to architects and engineers, as it gives two or three copies without any wetting of the paper, and of such sharpness that the finest lines of the original are faithfully reproduced. It is rather expensive, but that is of small importance, as its use saves all the great time and labour involved in making a copy of a plan or working drawing by hand.

Solution of pyrogallic acid	240
Copper sulphate	4
Iron chloride	10
Uranium acetate	2

Pyrogallic acid is now so much used in photography that it can be bought fairly cheaply. The uranium acetate is dearer, but since uranium compounds have come into use for black painting on porcelain their price has fallen considerably. The iron chloride is easily made by saturating 10 lb. of commercial hydrochloric acid, adding 1 lb. of strong nitric, and evaporating till crystallisation begins.

To copy a drawing made with this ink a sheet of thick, well-glazed paper is laid on the original (Bristol board answers excellently), and then a smooth board, and the whole is uniformly weighted, but not excessively, with books. In from 3 to 5 days the copy will be ready. Since the invention of hektographs, chromographs, polymillegraphs, etc., copying inks have lost part of their importance in certain directions. By using these apparatuses with suitable inks we can obtain not merely two or three copies, but 60 or even 100, although with the latter number the last copies are certainly rather pale.

Valuable as the hektograph is when a large number of copies is required, it will never cause the disuse of the ordinary copying process as already described, inasmuch as for business purposes, one copy of a letter or invoice is usually enough, and the somewhat troublesome hektograph process is therefore unnecessary.

XIII.

HEKTOGRAPHS.

The consideration of hektography may be divided into three parts—the preparation of the hektograph, the manufacture of the ink, and the making of the copies. These points we now proceed to consider in order.

If a solution of glue which has been boiled down till it would set to a firm mass if allowed to cool is mixed with a certain amount of glycerine, it will then set, indeed, but will remain permanently sticky and very elastic. This property of a mixture of glue and glycerine has caused it to be used for years for printing rollers.

If we cast the glue-glycerine mass into a flat plate, and write on paper with a very thick-flowing ink containing a very powerful colouring matter, such as an aniline dye, either dissolved or in solution, and also glycerine, and then lay the paper, writing downwards, on the gelatine mass with gentle pressure, a large part of the ink will be retained by the gelatine, which will therefore show a reversed copy when the original is taken off. If we then replace the original by a blank sheet of paper, a moderate hand pressure will convert it into an exact copy of the original, and in this way from 60 to 100 copies can be successively obtained. To prepare the gelatine for a fresh writing the old one must be erased with a damp sponge, which removes the upper part of the preparation together with the ink in it. The rest can be used again as soon as it is dry. The "graph" is kept shut up when not in use to prevent its surface from becoming contaminated with dust.

The Preparation of Hektograph Compositions.

With regard to this very simple matter a whole range of recipes has been published, and all of them give a usable product. A very simple and yet very good method is to take a good quality glue—it is quite superfluous to use gelatine for this purpose—and to soak it in cold water for twenty-four hours. When taken out it will be much swollen, and it is then fused in an enamelled pot over a gentle fire. When all the glue is quite liquid, the glycerine is added and mixed with it perfectly by careful stirring. The mixture is kept hot till it flows thinly, and so that all the bubbles produced by the stirring may rise to the surface and break. Any scum that may rise is carefully removed with a shallow spoon. The mass is then cast into plates.

The only way to tell whether the preparation is of the right consistency is to take copies with it. If it contains too little water through overheating, and is therefore deficient in elasticity and stickyness, the ink will only give a few copies. It must therefore be mended by stirring hot water into it. If, on the other hand, it has not been evaporated enough, it will be very elastic and so sticky that the paper can only be taken off it with great difficulty, and the copies will smudge and be indistinct. In this case, of course, the mass must be further heated.

Many recipes direct the addition of white powder to the glue and glycerine. The object of these is simply to whiten the mass and make the reversed copy more distinct. They can always be dispensed with.

RECIPES FOR HEKTOGRAPHS.

Simple "Graphs".

A.

Glue	100
Glycerine 28 deg. B.	500

B.

Glue	100
Glycerine 28 deg. B.	400
Water	200

Mix the glue and glycerine as above described.

CHROMOGRAPHS.

The ink written on a hektograph can be more easily removed when done with if inactive bodies are added in the shape of fine powder. One of the best to use is sulphate of barium. To prepare this, precipitate a solution of chloride of barium with oil of vitriol, and wash the precipitate repeatedly with water, pouring off each lot of water when the white sulphate has settled to the bottom. The sulphate is used after the last washing in the form of a thin paste.

A.

Glue	100 grammes
Barium paste	½ litre
Dextrine	100 grammes
Glycerine	1,000-1,200 ,,

The mass is warmed and stirred till all the glue and dextrine are dissolved, and then cast. Test a sample of the mass by copying from it as above directed (p. 72).

B.

Glue	100 grammes
Barium paste	½ litre
Glycerine	1,200 grammes

C. (*Recommended by the French Ministry of Public Works.*)

Glue	100
Glycerine	500
Finely powdered heavy-spar or levigated pipe-clay	25
Water	375

As ink for this chromograph a concentrated solution of aniline violet is recommended.

In our opinion the simple hektographs are the best. By varying the proportions of glue and glycerine we can regulate the number of copies procurable and the ease with which the writing is removed from the gelatine at pleasure.

XIV.

HEKTOGRAPH INKS.

As already mentioned the function of a hektograph ink is in the first place to adhere to the composition and to be gradually transferred to the copies. The copies get fainter and fainter until, when the retentive power of the gelatine becomes equal to the absorptive power of the paper, the copying comes to an end, although the writing is still distinct upon the gelatine. One of the first requisites for a hektograph ink evidently is that it should contain a very deep and powerful dye and enough glycerine to make it resemble a very slowly drying copying ink.

Of all known colouring matters the aniline dyes go the farthest, and hence they alone are used in the manufacture of hektograph inks. Those at present in the market are not particularly satisfactory products. They do not flow freely enough for use with the pen. The chief reason of this is that most of the aniline dyes require alcohol to make strong solutions of them, and in use the alcohol evaporates so fast that the ink becomes thick before the pen is empty.

There are, nevertheless, aniline dyes which are sufficiently soluble in water, and among them we have blues and reds which make excellent ink. There is no difficulty in writing with them, and, in fact, only water-soluble anilines should be used for hektograph inks. We can, however, by artifice incorporate anilines which are insoluble in water with the inks with the use of so little spirit that the ink does not dry too fast. The process is as follows:—

The glycerine and dye having been weighed out, the former is heated to about 50° C., and rubbed up with the dye. The coal-tar colours are soluble in glycerine, especially with the aid of heat. If the mass is too tough to be handled it is diluted with hot water to the consistency of a syrup. When no more solid particles can be felt with the pestle the dye can be brought perfectly into solution by carefully adding about 50 per cent. of spirit. By this method very good hektograph inks can be got even with methyl violet.

BLUE HEKTOGRAPH INKS.

Lehner's Recipe.

Water-soluble blue (Mainz Fabrik)	10
Glycerine	10
Water	50-100

Mix with the aid of gentle heat. The amount of water should be taken between the limits stated according to the number of copies required. This ink will be found excellent for every requirement, and to copy the finest strokes perfectly.

METHYL VIOLET INKS.

A.

Methyl violet	10
Dilute acetic acid	5
90 per cent. spirit	10
Water	10
Glycerine	5

B.

Methyl violet	10
Alcohol	10
Gum	10
Water	70

The ingredients are kept together for about two hours at 50 to 60 deg. C., and then filtered hot through flannel.

RED HEKTOGRAPH INKS.

A.

Diamond magenta	20
Alcohol	20
Acetic acid	5
Gum	20
Water	140

B.

Diamond magenta	10
Alcohol	10
Glycerine	10
Water	50

These inks are prepared like those with methyl violet. The second recipe gives a very good ink.

VIOLET HEKTOGRAPH INKS.

Any shade of violet can be got by mixing blue and red inks in different proportions. Specially serviceable in this connection are the blue inks made with water-soluble blue and the red ink last given.

GREEN HEKTOGRAPH INK.

Water-soluble blue	10
Picric acid	10
90 per cent. spirit	30
Glycerine	10
Water	30

Different shades can be got by varying the amount of picric acid.

BLACK HEKTOGRAPH INKS.

Aniline black or nigrosine is insoluble in water, and black hektograph inks are got by rubbing up a mixture of a very dark methyl violet and nigrosine with alcohol and glycerine.

Methyl violet	10
Nigrosine	20
Alcohol	60
Glycerine	30
Gum	5

This ink is always very thick on account of the nigrosine in it being in the solid state. It is therefore little used. We shall return to this important subject when speaking specially of the aniline colours.

TYPEWRITER INKS.

In a typewriter, when a key is pressed, a lever, on the end of which a letter is cut, is raised, like the hammer of a piano, and, striking an inked ribbon, presses those parts of it which correspond to the relief of the letter on to the paper, which is thus stamped with that particular letter. It is of course necessary that the whole of the ribbon should be soaked with a powerful dye and should retain the proper amount of moisture. It is easy to see then that inks for typewriter ribbons closely resemble hektograph inks, so that this is the proper place to discuss them.

The simplest method of making a typewriter ink is simply to rub up a solid dye in glycerine. We have prepared the following ink in this way, and it has been used for years for typewriter ribbons.

LEHNER'S TYPEWRITER INK.

Heat pure glycerine, and add to it in small portions its own weight of water-soluble blue. On cooling the mass becomes sandy, as part of the dye separates out again in the solid state in the form of minute crystals. Now add cautiously and with constant stirring just enough water to redissolve these, and no more. The finished ink will then be a thick bluish-black liquid. The ribbon, which is made of thin silk, is run through it, and then subjected to heavy pressure between smooth rollers. In this way a ribbon is got which will give a deep blue writing for many months, even with constant use.

PATENT INKS, FOR TYPEWRITER RIBBONS, RUBBER STAMPS, ETC.

Inks (Gall-Nut) for Typewriter Ribbons, etc.

(German Patent 229,467, E. Beyer, Chemnitz.)—In the original patent (224,637) to which the present is an addition, oil, glycerine, or an aqueous solution of shellac was mixed with the condensation products of ammonium, ammonio-ferro or ferri-gallate (or analogous substances) with aldehydes (formaldehyde). It has now been found the ketones, *e.g.*, acetone, will furnish with the same complex gallates compounds suitable for making inks for typewriter ribbons, rubber stamp pads, Indian ink, etc. The above ammonium salt, for example, is dissolved in hot water, and acetone is stirred into the warm solution. The resulting condensation product, though soluble in water, can be precipitated by an excess of acetone, and when dried forms a deep black powder suitable for making copying inks.

Ferrogallic Inks for Rubber Stamps, etc.

(German Patent 224,637, E. Beyer, Chemnitz).—Ammonium ammonio-oxyferrigallate (*e.g.*, 500 parts) is dissolved in water (25,000 parts), and treated with 40 per cent. formaldehyde (1,000 parts), the precipitate being washed with water and dried at 70° C. This deep violet-black powder is perfectly insoluble in water, and is ground with oils or fats, and glycerine, for the production of stamping and typewriter inks. It may also be made into Indian ink by grinding with an aqueous solution of shellac, a little coal-tar dye, lampblack, etc., being added. Other aldehydes, *e.g.*, benzaldehyde, may be used

XV.

SAFETY INKS.

Chemists have long endeavoured to discover inks which are absolutely indelible except when the material written on is also destroyed. The value that such an ink would have is self-evident. Paper when properly made and kept—in air-tight boxes, for example—is so durable that we do not yet know how long it can last, and documents written on such paper with such an ink would not only resist the tooth of time for thousands of years, but would offer an insuperable barrier to falsification. Unfortunately, there is no known recipe which will yield an ink capable of withstanding all exterior influences. A skilled chemist, who is prepared to devote the necessary time and care to the work, can efface any ink whatever, and leave no trace of its former presence. It is true that free carbon bids defiance to all chemical agents and is insoluble in all our solvents. Ink made with any form of carbon, however, whether lampblack, soot, or charcoal, does not carry the carbon inside the paper. The black particles are simply mechanically attached to the surface, whence they can be perfectly washed off by a skilled hand. Printers' ink alone is an exception. In this important substance lampblack is mixed intimately with boiled oil, which carries the carbon into the pores of the paper. With very porous paper it is impossible with the greatest skill and patience to efface entirely the characters by any means. Unfortunately printing ink is much too thick to be written with.

Of all the black pigments consisting of carbon, Indian ink contains that element in the most finely divided state. Direct experiments, however, have shown us that even after the lapse of years the writing done with the purest Indian ink can be removed by soaking in water and repeated delicate treatment with a soft sponge. According to our experience the permanence of a writing depends less upon the resisting qualities of the ink than upon the depth to which it penetrates the paper. Hence easily flowing inks used on soft porous paper will give a much more permanent writing than inks owing their colour to solid matter. Ordinary alizarine inks, which contain considerable amounts of indigo-carmine, are very difficult to erase, and when the paper is so porous that the ink penetrates it from side to side its removal is practically impossible.

The inks which consist mainly of vegetable extractives rich in humus are of extraordinary durability. If we write with a solution of grape-sugar mixed with 1 per cent. of caustic potash or soda, the letters are at first a pale brown, but gradually darken, and resist acids or alkalies, and even chlorine, with great energy. The only effect, indeed, of these bodies is to set free more carbon from the humus substances, and so to increase the blackness of the writing.

There are many compositions extolled as safety inks, and some of them are fairly good, but none of them can resist the skill of a trained chemist. We give a few of the best.

DOCUMENT SAFETY INK.

Ruby shellac	15
Borax	8
Gum	8
Soot	10
Water	130

The shellac is powdered and boiled with the borax and water till dissolved. The solution is filtered. In the meantime the gum and the soot are intimately mixed, put into the vessel in which the shellac was boiled, and boiled with part of the clear filtered solution. When the gum is dissolved the rest of the shellac solution is gradually stirred in. The finished ink is allowed to stand for a few days that the coarser particles of soot may settle to the bottom, and is then decanted or siphoned off.

Shellac-resin forms with the boric acid of the borax compounds of a dark brown colour, which resist chemical agents so well that the writing cannot be effaced completely without their effects upon the paper being clearly visible. The only object of adding the soot is to make the ink more legible, and the ink is just as permanent without it. It may be replaced by a little indigo-carmine or a very concentrated chrome-logwood ink.

Read's Safety Ink.

This ink is characterised by its essential constituent being Prussian blue. It is a solution of that pigment in oxalic acid. The purest blue must be chosen, as the inferior qualities are always largely adulterated with chalk and other foreign substances.

In order that the Prussian blue may dissolve readily in the oxalic acid it must undergo a preliminary treatment. This consists in keeping it for a week in an earthen dish with its own weight of sulphuric acid. The acid is then poured off and the pigment is repeatedly washed by decantation with water until the wash water has no sour taste. When the last lot of wash water has been drained off from the Prussian blue the wet sediment is dissolved in solution of oxalic acid. The usual proportions are 1 lb. of oxalic acid dissolved in 5 lb. of water to every 5 lb. of Prussian blue. The resulting solution is decanted and mixed with its own volume of a good logwood-chrome ink.

Writing executed with this ink penetrates very deep, and is hence very difficult to efface.

COLOPHONY SAFETY INK.

Colophony	10
Soda crystals	10
Soot	2
Gum	4
Water	100

The colophony is dissolved by boiling with the water and the soda. A clear solution is got more quickly if three of the ten of soda crystals are replaced by one of caustic soda. The gum and soot are mixed and stirred into the solution.

WATER-GLASS INK.

This is an excellent safety ink. Baudrimont, its discoverer, made it by mixing soot with ten times its weight of silicate of potash. The silicate of potash is bought in the form of a thick solution, which must be kept from the air or it will set solid, by the liberation of silica from it by the carbonic acid of the air. The soot is first mixed with a little of the water-glass by long rubbing, and the paste when quite uniform is stirred into the rest of the silicate. The ink must be bottled up air-tight as soon as it is made. When it is used the carbonic acid of the air acts upon it as above described, and the silica, enclosing carbon within it, is set free in the pores of the paper. Both the silica and the paper thus protect the carbon from mechanical removal. As, however, the carbonate of potash also formed might injure the paper it should be rinsed out with weak vinegar, which in its turn should be removed by rinsing with water.

CARBON SAFETY INK.

This is a kind of liquid Indian ink prepared from soot.

Soot	10
Gum	10
Oxalic acid	5
Water	200

The solid ingredients are rubbed up with the water, which is added to them a little at a time, until a perfectly uniform paste is got which can then be stirred into the rest of the water. This ink, however, like all such inks, penetrates the paper very slightly. Hence although the carbon they contain enables them to offer successful resistance to attempts to efface them by chemical means, they can be easily and completely removed with care by mechanical processes.

VANADIUM INK.

This is one of the discoveries of Berzelius. It is prepared simply by adding ammonium vanadate to a filtered decoction of galls. The vanadate is still an expensive salt, and is not purchasable everywhere. It has, however, a far more energetic action than that of potassium chromate or decoction of logwood. A few drops of solution of ammonium vanadate will convert a large quantity of decoction of galls into a deep black ink, which has the advantage of flowing very freely. The ink cannot be destroyed completely by any known means. The writing always remains readable, and the ink is undoubtedly the best of all safety inks. If vanadium were cheaper it would be extensively used.

LEHNER'S SAFETY INK.

Mix concentrated sulphuric acid with twenty times its weight of water, and colour the solution with a little indigo-carmine or water-soluble blue. The colouring matter is added merely to make the writing visible from the first. Write with a quill on good paper. In a few days the sulphuric acid will have become strong enough, by the evaporation of the water, to carbonise the paper. As soon as the writing turns black the paper is soaked for a few days in a 5 per cent. solution of carbonate of soda, then rinsed several times with plain water and dried. The black characters will then last as long as the paper itself, and cannot be effaced. If the neutralisation with soda is delayed the paper will be eaten into holes by the acid, but if it is done at the right moment that will not happen.

XVI.

INK EXTRACTS AND POWDERS.

Frequent attempts have been made to bring inks upon the market in concentrated forms which would yield a good ink directly they were mixed with water. Although many of these preparations really give good results they are very little used, as writers will not take the trouble of making the solution.

INK EXTRACTS.

Ink extracts can be very easily made by evaporating inks to a certain concentration and then bottling them. The process is, however, difficult according to whether the ink owes its colour to dissolved or suspended matter. With the latter kind it is best to concentrate the gall decoction by itself in a shallow pan, but without boiling it, down to about one-quarter of its original volume. The other ingredients are then dissolved in it. The result is a syrupy liquid which gives a good ink with from five to eight times its volume of water.

If an extract for an alizarine ink is wanted the ink is made according to one of the above recipes, and carefully evaporated. For this purpose earthenware vessels should be used, as those of iron or copper are attacked by the acetic acid in the ink. When, too, the ink during evaporation becomes turbid owing to loss of acetic acid, a little of the strong acid should be put in. By observing this precaution and also by evaporating at a low temperature the ink can be got very concentrated indeed, and can then be bottled and diluted with water for use.

Logwood-chrome inks and horse-chestnut inks can be evaporated to very thick syrups without their quality being in the least impaired or the readiness with which the extract gives an ink with water being affected.

INK POWDERS.

These powders make ink when mixed with water. Most inks may be obtained in the form of powder by various simple devices.

TANNIN AND GALLIC ACID INK POWDERS.

The galls, either fermented or unfermented, are extracted with boiling water in the quantities and in the manner directed above. The filtered decoction is carefully evaporated to a syrup. At this stage, constant stirring is begun, and kept up until the contents of the pan are quite dry. The temperature must be kept as low as possible to avoid burning the ink. In the meantime the ferrous sulphate and the gum are made perfectly dry, and are ground together to a fine powder. They are then mixed in the same way with the dry gall decoction. The brown mixture obtained is filled at once into well-stoppered bottles, as it is very hygroscopic. A pinch of this powder converts water in which it is stirred up into ink immediately.

LOGWOOD CHROME INK POWDER.

This is made by carefully evaporating the ink to dryness, or more simply by finely powdering very dry logwood extract and grinding it up with potassium chromate.

All ink powders should be put on the market and kept in bottles with ground-in stoppers, or in air-tight packets, for although their quality is not deteriorated by the absorption of moisture from the air, they form lumps which are difficult to get out from the receptacles.

Paper Boxes for Ink Powders.

The following process for making paper boxes which will protect ink powder perfectly from damp can be confidently recommended: Heat paraffin to about the temperature of boiling water, and fill the box and its lid with it, and then pour it out at once. The sides of the box thus become perfectly air-tight, so that it will keep ink powder quite dry, even in a damp room.

The chief points in the manufacture of ink powder are to keep the temperature of evaporation and drying so low that no burning can possibly happen, and to see that the ingredients are in a state of perfectly uniform mixture. We will now give some recipes which can be depended on for good results.

Frick's Ink Powder.

Gall powder	42	All well dried.
Ferrous sulphate	30	
Gum	15	
Alum	6	

The galls are ground fine with the alum. The gum and the vitriol are powdered separately, and then mixed with the rest. The powder is at once packed or bottled. The ink made by adding this powder to water gives a black sediment, from which it must be decanted. We can nevertheless make an ink powder which is entirely soluble by infusing the galls with water, evaporating the solution to dryness, and grinding up the residue with the other ingredients. The object of the alum in the recipe is to prevent moulding. If it is replaced by boric or salicylic acid, the acid chosen need only be about one-tenth per cent. of the powder.

Precision Ink Powder.

Gall extract	150
Ferrous sulphate	25
Copper sulphate	5
Alum	10
Gum	10

These ingredients, made absolutely dry and perfectly mixed together, give a powder which produces with water a very fine black ink of the very highest quality.

Logwood Ink Powder.

Logwood extract	500
Potassium chromate	1

Make the extract into a syrup with hot water, and stir in the chromate in concentrated solution in hot water. Evaporate to dryness with constant stirring, grind, and pack while still warm.

Ink Tablets.

Ink tablets are solid masses which dissolve in water, forming ink. The best inks for tablet-making are those in which the colouring matter is in solution. Chrome and horse-chestnut inks answer very well for the purpose. They are made by evaporating the ink to the right point, and then pouring it into tin trays with perpendicular sides about half an inch high. When the mass has set it is cut up with a sharp knife into square pieces, which are wrapped up in tinfoil. To gauge when the ink is sufficiently evaporated let a drop of it fall on a cold iron. If it sets at once to a pasty mass, the ink is ready to be cast. Ink tablets have the advantage that indigo-carmine can be included in their composition, which on account of the pasty nature of the indigo-carmine, cannot well be done with ink powders.

Chrome Ink Tablets.

1.

Logwood extract	500
Potassium chromate	1
Alum	10
Gum	20

This gives a violet ink. Only as much water is used as is indispensable to obtain a perfect mixture.

2.

Logwood extract	100
Potassium chromate	1
Gum	10
Indigo-carmine	20

This gives a beautiful ink. The writing changes from a blue to a deep black.

HORSE-CHESTNUT INK TABLETS.

Chestnut extract	100
Ferrous sulphate	10
Alum	2
Gum	5
Indigo-carmine	5

The extract is made from the green husks of the horse-chestnut or from the young twigs, and evaporated down to the consistency of a paste.

XVII.

PRESERVING INKS.

In former days the liability of every ink to mould was accepted with resignation as an unavoidable evil. The visible moulding of an ink is, however, only a symptom, and is attended by many undesirable changes. For example, an ink to which sugar has been added instead of gum to get a lustre often becomes so tough that long threads spin from the nib, and it cannot be written with. This results from the fermentation of the sugar, and can usually be cured by shaking the ink with a freshly prepared gall decoction, and then allowing it to stand. In a short time a tough black precipitate forms, and if the supernatant liquor is decanted it will be a useful black ink.

The fermentation processes which result in the formation of lactic acid have a much more serious effect upon ink, as they gradually destroy the colouring matter. If we find that the ink becomes pale and acquires a strongly acid taste, we may be sure that it will soon be useless. If the process is carried out in time, the ink can be saved by boiling it with some clean iron nails. The ferment is thus killed, and the lactic acid is brought into combination.

When an ink becomes mouldy it gradually gets covered with a green, felty layer of greyish-green fibres, which grow again as fast as they are removed and with such speed that the whole surface will be re-covered in a single night. Even if we throw away the ink and kill the germs adhering to the vessel by boiling it in water, the remedy is only temporary. When the vessel is refilled with fresh ink, it will soon get more germs from the air, and the growth will get as thick as ever, and for a long time no means of combating the evil was known. It was certainly found that an excess of ferrous sulphate had a preservative action, but with the result of increasing the cost of manufacture, and causing the ink gradually to deposit a sediment and to produce characters which quickly turned brown. Additions of alum, too, were found very effectual in preventing mouldiness, but cause the ink to corrode steel nibs, and in the absence of considerable amounts of acid precipitate the colouring matter in the form of an alumina-lake. This not only makes the ink pale, but makes it flow less freely, as may often be noticed in logwood inks containing alum.

It was long since noted that alizarine inks made with ordinary vinegar were very apt to mould, while those made with pyroligneous acid rarely or never went mouldy. The reason of this certainly rather striking fact is that the pyroligneous acid contains a certain amount of carbolic acid, which is an extremely powerful disinfectant and hence an efficient preventive of mould. It is better to preserve the ink by adding carbolic acid to it than by using pyroligneous acid in its manufacture. Carbolic acid is very cheap, and the ink is perfectly preserved by one-thousandth of its own volume, or even less. The acid possesses, however, a very penetrating odour, which is plainly perceptible even when the acid is highly diluted, and which, as we have reason to know, has brought even very excellent inks into disfavour. We possess, at the present time, another splendid antiseptic which is perfectly odourless, in the shape of salicylic acid. It has no bad effect on human beings, and cannot be too strongly recommended to manufacturers of ink. According to our results it will completely preserve from 5,000 to 10,000 times its weight of ink. A little of it put into the ink-vat will prevent moulding for good and all. The salicylic acid can be added solid or dissolved in a little spirit.

Boric acid is another preservative not less to be recommended. It occurs in the form of mother-of-pearl-like shining crystals, soluble in cold water with some difficulty, but easily in hot. This body, too, will preserve 1,000 times its weight of ink and upwards from mould. The best plan of using it is to hang it in a bag in the ink, so that it will gradually dissolve.

Many antiseptics, the often recommended corrosive sublimate for example, seem to us very ill-suited for ink preserving. Corrosive sublimate, in particular, is very poisonous as well as expensive, and we have in salicylic acid a completely innocuous and in every way suitable substance, which, for our purpose, is as powerful an antiseptic as the mercury salt.

Ethereal oils in general, and clove oil in particular, also possess antiseptic properties, and we therefore find the addition of a few cloves or a few drops of the oil to an ink recommended in many recipes. But an ink to which oil of cloves has been added necessarily acquires its smell, which is a disagreeable one to many persons. Besides the preservation by clove oil is only evanescent. In time exposure of the ink to the air resinifies the oil, and it loses its antiseptic power completely.

We thus conclude from a general survey that salicylic and boric acids are the antiseptics which offer the greatest advantages to the ink maker, and which should therefore be universally used.

XVIII.

CHANGES IN INK AND THE RESTORATION OF FADED WRITING.

The preservative agents we have just been discussing have only come into use very recently. We cannot, therefore, form any judgment as to the durability of characters written with inks preserved by their means, and must confine ourselves to considering the behaviour of the ancient inks, which were exclusively iron and tannin inks. Under certain conditions these inks are extremely durable. In a place which is dry and free from ferment spores the writing may remain a full black after the lapse of many centuries, as certain old documents amply prove. These two conditions are, however, very rarely combined. It is very difficult to exclude moisture completely, and even the best preserved writings betray the presence of spores under the microscope. These only demand the access of a little more moisture to develop and destroy the writing.

When a writing is destroyed by mould or damp, or by their joint action, the black colour gradually changes to brown, and finally to a pure rust colour. The ink is then entirely destroyed, and nothing remains but basic ferric sulphate. If the paper is then repeatedly wetted through the characters become paler and finally illegible.

When it is a question of restoring the legibility of a faded MS. we must go to work with the greatest care, for unskilful treatment with chemicals may result in the absolute and irremediable destruction of the characters instead of their reproduction. One of the best means of deciphering characters made with an iron ink and which have become illegible, is to convert the iron compounds still adhering to the paper into ferrous sulphide. As this is black, the characters at once reappear. This appearance, however, is only temporary, as the sulphide is oxidised by the air, and the iron returns to the form of basic sulphate. After many attempts we have succeeded in so modifying this process that the letters will remain revived for at least a few days, so that if necessary the document may be copied. We use a cardboard box about 4 in. high, and of length and breadth corresponding to the sheets of paper containing the faded writing. The box has no lid, but can be closed by laying a sheet of glass on the top of it. Half-way up it a frame is placed horizontally, and carries a netting of fine white silk or cotton threads. On the bottom of the box we place two earthen dishes containing yellow ammonium sulphide. We then put in the frame, place the MS. on the netting, and cover the box with its glass lid. The MS. is damped with a sponge before being placed in the box. Care must be taken not to wet the paper too much, especially if the writing is on both sides, as then the letters are liable to soak through to the other side of the paper. No rubbing is, of course, allowable.

The yellow ammonium sulphide can be bought, or we can make it ourselves by dissolving sulphide of iron (FeS) in dilute sulphuric acid and passing the gas through a solution of ammonia until the solution turns yellow. It is then exposed to the light for a few days in a well-stoppered bottle, and turns dark yellow. In a short time after the MS. has been shut up in the box, the letters turn brown, and the colour eventually passes to black. As long as the MS. remains in the box the vapour of the ammonium sulphide will prevent any oxidation of the sulphide of iron, so that the MS.

can be copied at leisure. It can also be removed from the box and photographed between glass plates.

In many cases the restoration can be made permanent by the following process :—

The MS. is dipped in a mixture of pure hydrochloric acid with 100 volumes of distilled water. The immersion must be momentary only, so as not to wet the paper below the surface. The hydrochloric acid used must be absolutely free from iron. The paper is then allowed to dry completely in the air, and the writing is then dusted over with finely powdered ferrocyanide of potassium from a pepper-caster, covered with a glass plate and slightly weighted. After a few hours the plate is removed and the paper is dried. The yellow powder is then brushed off. If the paper had the proper amount of moisture when it was sprinkled, the characters will now be distinctly visible and of a blue colour, owing to the formation of Prussian blue by the action of the ferrocyanide on the iron of the ink which has been dissolved by the hydrochloric acid. The paper must now be freed from all traces of hydrochloric acid, which would in time efface the letters. To this end it is floated for twenty-four hours in a 2 per cent. solution of sodium carbonate crystals, and then rinsed in running water. The restored MS. must be kept in the dark as much as possible, or the light will fade the writing again.

It is much more difficult to restore parchment than paper MSS., for the prepared skin contains substances which produce coloured compounds when subjected to the restorative processes. The process given by Moride consists in soaking the parchment in distilled water until it has swollen up, but all stirring or movement is carefully avoided. When thoroughly swollen, the parchment is drained, and dipped for five seconds in a 1 per cent. solution of oxalic acid in distilled water. It is then dipped in clean water, and then into a 1 per cent. solution of gallic acid. Here it remains until the writing comes out clearly. The parchment is then rinsed with several lots of distilled water, and dried between folds of blotting-paper as quickly as possible.

The oxalic acid makes the iron salt still existing in the bleached ink soluble, so that it can form a fresh lot of black ink with the gallic acid. Unfortunately, the parchment itself often contains so much iron that the gallic acid makes it black all over, when the writing cannot be made out. The same discoloration happens when the parchment is very mouldy, for the gallic acid then turns it brown. Hence it is important to restrict the quantities of chemicals used to the absolute minimum possible, and solutions are used still more dilute than those above given, and the process is repeated with them if necessary. In particular the use of oxalic acid requires the greatest care, for if it acts too long, or in too strong a form, the writing, instead of being restored, will disappear for ever, as the iron of the original ink will pass from the paper into the solution. If it is a question of restoring valuable documents it is always advisable to experiment with a small portion first. We then find out how the whole will behave, and how far the use of reagents may be carried.

We have tried the experiment of exposing old parchments to the vapour of acetic acid, then letting them dry, and finally spreading them out on a glass and applying solution of gallic acid to the written surface, and have always obtained results at least equal to those achieved by the processes described above. For this process, also, the parchment must first be swollen by soaking in water, or better, by exposure to steam, as long immersion often injures the parchment.

XIX.

COLOURED INKS.

Although among writing fluids black inks are the most important, as being those most largely used, there is also a demand from the public for inks of other colours. The origin of this demand is partly a desire to make distinctive appearances in different parts of a MS., and partly fashion and a preference on the part of individuals for coloured rather than for black inks.

In the present state of chemistry it is not difficult to prepare inks of any desired colour. Since the discovery of the coal-tar dyes we have been able to prepare coloured inks very easily by simply dissolving the appropriate dye. All possible colours can, however, be obtained in inks without coal-tar colours, and many of these inks are in great demand. No coloured ink, be it observed, except, perhaps, real indigo-carmine ink, can compete with the black inks as far as durability is concerned. Writings made with most of them turn pale in a few months, and documents for long keeping should always be written with a good black ink. We proceed to give processes and recipes for making coloured inks, putting inks of the same colour together.

XX.

RED INKS.

In the preparation of red inks we generally use redwood, cochineal, or an aniline dye. Magenta can always be had in satisfactory quality, while both redwood and cochineal vary considerably in quality, and require much care in selection. We must therefore describe both of them rather minutely.

Redwood.

This is also called Brazil or Pernambuco wood. The tree (*Cæsalpinia echinata*) is indigenous to tropical America, especially to Brazil, which indeed owes its name to the appearance of the wood, *brasil* being the Portuguese word for glowing coals. The fresh wood is pink, but changes to a dark red on exposure to the air.

Several sorts are known in commerce. The best and richest in colouring matter is known as Pernambuco wood, after which come Sapan, Jamaica, Braziletto, and Bahama woods.

Redwood contains a colouring matter soluble in water, which gives very fine red lakes with alumina or tin. It is therefore much used by dyers and ink makers, although the colour is inferior to those obtainable with cochineal.

Cochineal.

This colouring matter consists of the dried bodies of an insect which feeds on various cacti, especially the nopal plant. Indigenous to Mexico, both the insect and its food-plants have been acclimatised elsewhere, and nearly all tropical countries now produce quantities of cochineal.

The dried insect appears in the form of silver-grey grains, the nature of which is easily recognised with a lens. The silver-grey sort is the best, and rubs-down to a brown powder. The black cochineal is inferior.

Great experience is necessary in buying cochineal, as it is so expensive that the most flagrant adulteration is often met with. A common occurrence is for cochineal from which most of the colouring matter has been exhausted to be resold as fresh goods. In many cases, too, the form of the insect is imitated with flour-paste, and the masses are coloured with a little cochineal and offered for sale.

A simple test of the goodness of cochineal consists in rubbing it up and treating the powder with a little caustic ammonia. If the cochineal is good, a very deep red solution of the dye will be immediately produced.

Before the aniline dyes were known, the finest red inks were those made from cochineal, but those made from anilines now dispute priority with them.

Redwood Inks.

Red Brazil Ink.

Pernambuco wood	280
Tin salt	10
Gum	20
Water	3,500

The wood is boiled in the form of thin shavings with the water in a roomy vessel for about an hour. The decoction is then filtered. The tin salt is dissolved in a little water. If the solution should be turbid from the presence of basic salt, it is cleared by boiling it with a few drops of hydrochloric acid. The gum is now dissolved in the filtered redwood solution, and the tin solution is added. The ink is now finished, unless the colour of the writing with it is too weak, in which case it must be concentrated by evaporation. The tin salt forms a red lake, which remains dissolved unless too much tin is added. If this is the case some of the lake precipitates.

PERNAMBUCO INK.

Pernambuco wood	8
Alum	2
Gum	2
Water	60

Alumina forms a red lake with redwood, like tin salt. The wood is boiled with the water, and the gum and alum are dissolved in the filtered decoction. If this ink has a violet hue, which is likely to be the case, add powdered tartaric acid to it while it is boiling, putting it in a little at a time, until the desired pure red is produced. After each addition of tartaric acid boil for a few minutes, stir well, and try the colour by writing on paper.

BRAZIL EXTRACT INK.

Pernambuco extract	15
Alum	3
Tin salt	2
Tartaric acid	2
Water	120

Pernambuco wood comes on the market in solid masses like logwood extract. It gives a beautiful red solution in water which answers as well for ink making as the decoction of the wood, and with the additional advantage of saving much time and trouble. Moreover, the solution can be made so strong that after-evaporation of the ink is unnecessary. Although very good, these redwood inks have been almost entirely superseded by cochineal or aniline inks, which are far superior to them in colour.

COCHINEAL OR CARMINE INKS.

Inks can be made direct from cochineal itself, and will be of great beauty and warmth of colour, but for the very best inks the cochineal must first be converted into carmine. The labour of so doing is richly rewarded by the unsurpassable excellence of the resulting ink, and most of the trouble of making the carmine is made up for by the actual preparation of the ink from carmine being easier than from cochineal.

PREPARATION OF CARMINE.

Powder the best silver-grey cochineal as finely as possible, and boil it for three hours in water. Filter the hot solution quickly through a thick linen cloth. Boil up the filtrate again, and add the substances needed to form the lake. Many such substances may be used, but only two can be thoroughly depended upon, and they should both be used together. These two are alum and tin salt, and if necessary, warmth may be given to the colour by the cautious addition, drop by drop, of hydrochloric acid. The alum must be absolutely free from iron, or it will be impossible to get more than a very unsatisfactory product. The best proportions are :—

Cochineal	20
Water	500
Alum	2
Tin salt	2

The alum and tin salt are added at the boil, which is kept up till everything is dissolved. The clear solution is then exposed in shallow dishes covered with sheets of glass for several weeks in a very bright sunny place. By this time the dark-red liquid will have lost nearly all its colour, and the carmine will have been deposited in the solid form, partly on the dish and partly on the surface of the liquid. It is separated by filtration, and carefully dried with blotting-paper. To get a fine and warm red it is absolutely indispensable that the dishes should get plenty of sun, so that the manufacture is impossible in any but the most favourable weather.

To get absolutely pure carmine, the product already described is dissolved in caustic ammonia. The solution is filtered, and the carmine is reprecipitated with acetic acid. We now give some recipes for carmine inks.

BEST QUALITY CARMINE INK.

Carmine	4
Caustic ammonia	500
Gum	10

Pour the ammonia on the carmine and gum, and heat on the water-bath nearly to boiling. Maintain the heat for ten minutes longer, and bottle the solution the moment it is cold, closing the bottles with good sound corks. If the ammonia is allowed to evaporate the carmine will precipitate, as it is insoluble in water. The carmine can, however, be re-dissolved by adding a little ammonia and shaking.

The solution of carmine in ammonia is sold as soluble carmine, carmine solution, etc., and is much esteemed for water-colour painting.

It must be remembered that commercial caustic ammonia is not always of the same strength, and that an excess of ammonia makes the carmine solution purple or violet. Hence the ammonia should be added with care. If in spite of every precaution too much is put in, the right colour can be obtained by the very cautious addition of dilute hydrochloric or acetic acid.

SUPERFINE COCHINEAL INK.

Cochineal	40
Carbonate of ammonia	2
Alum	2
Water	200

The carbonate of ammonia is dissolved cold in the water, and the solution is poured on to a mixture of the alum and cochineal both finely powdered. Shake every quarter of an hour for 3 or 4 hours. By that time the extraction of the colouring matter of the cochineal will be complete, and nothing remains but to filter the ink.

The alum is required to precipitate from the ink other substances which are extracted from the cochineal together with the colouring matter, and which would otherwise decompose in the ink. When this happens, the ink turns thick and rapidly moulds, at the same time emitting such a disagreeable odour that many persons would throw the ink away long before it became unusable.

INDELIBLE SILICATE-CARMINE INK.

This peculiar compound is made by rubbing up carmine with water-glass solution to a thick paste, to which more water-glass is then added till the ink has the desired colour and consistency. This ink, which was invented by Bottger, must be kept in well-closed bottles, and only so much must be poured out as is required for immediate use. Exposure to the air makes the ink first gelatinise, then solidify to a glass. This ink is distinguished not only by its beautiful and permanent colour, but by being the most indelible of all red inks. When made of the proper degree of thinness it penetrates deeply into the paper, and can only be removed by caustic alkalies. Even these do not efface it completely.

ODOURLESS CARMINE INK.

Cochineal	80
Crystallised carbonate of soda	160
Tartar	500
Alum	40
Gum	80
Water	1,800
Spirit	100
or Salicylic acid	2

Dissolve the soda in 1,600 of the water, and soak the cochineal, finely powdered, in the solution for several days, with frequent stirring. The whole is then boiled up, and the alum and the tartar are added in powder. This causes the liquid to froth very much, so that the boiling vessel must be roomy, and the powder must be put in a little at a time. After half an hour's boiling the liquid is filtered, and the remaining 200 of water poured boiling through the residue on the filter. The gum is then dissolved in the total filtrate. The alcohol or salicylic acid is used as a preservative, as the ink is very decomposable. Salicylic acid leaves the ink without smell and unalterable. As this ink is free from poisonous metallic salts it can be used for dyeing confectionery.

PATENT RED INK.

Cochineal	10
Tin salt	2
Sal ammoniac	2
Water	200

The colouring matter is fully extracted from the cochineal by boiling it in the water. While the liquid is still warm it is treated with ammonia and filtered. The filtrate while still warmed is mixed first with the sal ammoniac and then with the tin salt.

CHEAP COCHINEAL INK.

Pernambuco wood	60
Tartar	15
Alum	15
Gum	15
Water	500
Cochineal	5
Strong spirit	60

Boil the Pernambuco wood with the water for 1½ hours. Then add the tartar and the alum, and boil for another hour and a half. The gum is then added, and then the alcohol with which the cochineal has previously been exhausted by a week's digestion.

If the residual wood is treated with all the other ingredients again, but with one-fourth of the quantity prescribed for each in the above recipe, a fresh lot of ink will be obtained, which can be mixed with the first.

PURPLE INK.

Logwood extract	15
Crystallised verdigris	10
Alum	50
Gum	30
Water	800

The four solids are dissolved separately, and the four solutions are then mixed. Should the shade be too bluish, a few drops of very strong vinegar or of a carmine ink will correct it.

CARMINE PURPLE INK.

This is made by carefully adding solution of indigo-carmine to a carmine ink, whereby the pure red of the latter may be changed to violet or purple as required.

PURPLE CARTHAMINE INK.

Safflower-carmine	200
Gum	750
Cream of tartar	30
Sugar	75
Water	6,000
Carbolic acid	5

RED MAGENTA INK.

Magenta, which is so largely used in dyeing, makes very beautiful red inks. It is sold in green crystals which form a dark red solution in spirit.

Magenta	2
Gum	5
Spirit	10
Water	100

The magenta is dissolved in the spirit, which must be as strong as possible, 90 per cent. at least, with the aid of gentle heat. In the meantime, the gum is dissolved in the water, and the solution is filtered and heated. As soon as it is boiling the magenta solution is poured into it in a thin stream, with constant stirring.

Eosine Ink.

Eosine is a splendid scarlet dye. Red inks made with it do not surpass the magenta inks in beauty, but have advantages in the brilliance of the written characters. They are made from the crystalline powder, of which commercial eosine consists, exactly in the same way as a magenta ink.

Coal-tar Dye Inks in General.

We have coal-tar dyes from which inks may be made of every conceivable colour, in the same way as above directed for magenta ink. Since we have learned to make coal-tar dyes which are readily soluble in water, the manufacture of coloured inks has been vastly simplified. All we have to do is to dissolve the dye in just so much water that the solution shall write of the proper colour. Care must be taken that the solution is not too concentrated, or the writing will have a metallic lustre, and to add enough gum, and also glycerine in the case of a copying ink, to give the right consistency.

The high price of these dyes hardly affects us, as it is compensated for by their enormous intensity of colouring power. In this they so far exceed all other colouring matters that they make remarkably cheap inks. Inks made with coal-tar dyes excel in purity of colour, and can be used with advantage instead of water-colours for retouching photographs, steel engravings, etc. They have also been proposed as colourings for liqueurs and pastry, but although they give very fine colours many of them contain poisonous compounds of arsenic and other metals, and only those which are quite free from metals should be used for colouring articles of food.

XXI.

BLUE INKS.

The blue inks which deserve most attention are the solutions of water-soluble blue or indigo-carmine. They are the most deeply coloured, and penetrate so deeply into the paper that they are difficult to efface.

INDIGO-BLUE INK.

Indigo-carmine	10
Gum	5
Water	50-100

First dissolve the gum in water and then the indigo-carmine, and then add more water till the writing is of the proper colour.

PRUSSIAN BLUE INKS.

Indigo-blue does not show so well on paper as Prussian blue. This, as sold, is insoluble, and although it can be used as such, does not give such good ink as the soluble Prussian blue. Soluble Prussian blue is also much used as a washing blue, and the ink maker should therefore make it for himself.

MANUFACTURE OF SOLUBLE PRUSSIAN BLUE.

Mix crude hydrochloric acid with one-tenth of its weight of nitric acid, and then add a weight of distilled water equal to that of the hydrochloric acid. Saturate the mixture with pieces of iron. As soon as it has dissolved as much of the metal as it can, which will take a few days, decant the solution of chloride of iron through a filter. In the meantime a weight of ferrocyanide of potassium equal to that of the hydrochloric acid has been dissolved in ten times its weight of distilled water, and is now gradually added to the iron solution until no more blue precipitate is formed. No notable excess of either ferrocyanide or chloride should be used. The precipitate is washed several times with water by decantation, and finally filtered off. The paste from the filter is rubbed up with one-tenth of its weight of crystals of oxalic acid, and water gradually added till a clear sky-blue solution is obtained, which can be used at once for ink making.

The trouble of making the iron solution can be avoided by using bought ferrous sulphate, but that salt must first be converted into ferric sulphate by contact for a few days, in solution, with one-tenth of its weight (as a solid) of nitric acid. The solution is then used as above directed for the solution of chloride of iron. In either case, the Prussian blue must not be allowed to dry before treatment with oxalic acid.

If the ink maker buys his Prussian blue he must buy the best, usually called Paris blue, and must prepare it for solution in oxalic acid in a way to be presently described. The bought Prussian blue, being dry, requires far more oxalic acid to dissolve it than it would do had it not been allowed to dry. The result is an ink costing much more to make, and by virtue of the large excess of acid which it contains attacking steel nibs vigorously. To prepare the purchased pigment for solution we mix it with its own weight of concentrated sulphuric acid, and leave it for from 24 to 36 hours in it. We then pour the whole lot into a large excess of water, and wash the precipitate with water by decantation until the wash waters give no blue coloration with solution of potassium ferrocyanide, and are therefore free from iron. The precipitate is then rubbed up wet with oxalic acid as above described. Under these circumstances the oxalic acid will dissolve six times its own weight of Prussian blue, or eighteen times as much as it will dissolve of the dry commercial pigment.

Blue Post Ink.

Dissolve 17 of potassium ferrocyanide in 54 of water, and 17 of ferrous sulphate in 1,540 of water. Mix and treat the blue precipitate with a mixture of—

Nitric acid	10
Hydrochloric acid	5
Water	500

After 24 hours pour off the liquid, and rub up the precipitate with 3½ of oxalic acid. Then add 4,000 of water containing 160 of white gum in solution.

Blue Aniline Ink.

Dissolve water-soluble blue in water so that the writing is a good blue without metallic lustre, and thicken with gum. If a copying ink is wanted, add glycerine as well.

XXII.

VIOLET INKS.

We now wish to describe some violet inks made differently from those previously discussed. One way of making a violet ink is to mix a red ink with a blue one; and in any case aniline dyes give inks of a much better colour than the violet inks already mentioned. The latter, however, have the advantage of being very cheap.

VIOLET ANILINE INK.

This is prepared by dissolving methyl violet in spirit. The alcoholic solution need not be boiled for the necessary dilution with water as is the case with magenta, but the water must nevertheless be added with care. The moment any precipitate begins to appear the addition of water must be stopped, and the liquid made clear again with a little spirit. The necessary amount of gum is then dissolved in the liquid.

The violet aniline inks, although very beautiful, are not particularly durable, and can be easily and completely effaced by chemicals. The following recipe gives a more durable ink:—

VIOLET INDIGO INK.

Make a solution of indigo-carmine strong enough to be used as a blue ink, and add to it the proper amount of gum. Then add gradually a very thick solution of carmine, when the ink passes through purple to violet. The ink should be tested from time to time during the making by writing with it.

A still finer but less durable ink is made in the same way from solution of Prussian blue and carmine.

VIOLET COPYING INK.

1.

Glycerine	10
Oxalic acid	5
Logwood extract	40
Alum	30
Water	800

2.

Bichromate of potash	5
Dissolved in water	100

Make solutions 1 and 2 separately, and then mix them. Boil up the whole then in a copper pan, add 50 of pyroligneous acid, and bottle.

XXIII.

YELLOW INKS.

A full yellow ink can be made in several ways, the simplest of which is to dissolve picric acid in hot water. Picric acid is sold in yellow crystals, which are very bitter and poisonous. Picric acid ink must therefore not be used for colouring foods.

Picric Acid Ink.

Picric acid	10
Gum	2
Water	100

Boil all together. The water must be distilled water.

Yellow Gamboge Ink.

Gamboge is a resin which can be emulsified with water, although it will not dissolve. Heat 10 of gamboge in fine powder with 10 of spirit, and then mix it with 5 of gum-arabic first made to a very strong mucilage with water. Then mix with 30 of water.

Imperial Yellow Ink.

Persian berries	280
Alum	28
Gum	36
Water	1,000

Boil the crushed berries with the water for an hour. Then add the alum and boil another hour. Then filter and dissolve the gum in the hot filtrate.

XXIV.

GREEN INKS.

Green, like violet, is a mixture, in this case of blue and yellow. Hence by mixing a blue and a yellow ink in different proportions every imaginable shade of green can be obtained. The best mixtures are picric acid with either indigo-carmine or solution of Prussian blue. The following, however, are some recipes for some green inks which are not mixtures:—

Klaproth's Green Ink.

Crystallised verdigris	4
Tartar	2
Water	16

The three ingredients are boiled together, filtered and bottled.

Green Chrome Ink.

We are able to prepare from bichromate of potash a green which has not only a lively green colour but is very durable.

Bichromate	10
Hydrochloric acid	10
Spirit	10
Gum	10
Water	30

Mix the bichromate, finely powdered, with the acid, and let it stand for an hour. Into the red solution thus obtained the spirit is slowly poured, with constant stirring. The reaction is very vigorous, and the liquid froths and gets very hot, and gradually turns to a dark green. If the action gets too violent, a little cold water is put in. To avoid boiling over, it is best to add the spirit in portions, waiting till the frothing after each addition is over before adding the next. The next step is to add carbonate of soda till all effervescence has ceased and a greenish precipitate just begins to form. The liquid is then left covered up for a week, filtered from the salts which have crystallised out, and diluted to the desired colour. Finally the gum is dissolved in it. This ink penetrates the paper deeply, and gives green writing which is absolutely permanent and is very difficult to efface.

STEIN'S GREEN INK.

1.

Indigo-carmine	120
Gum	200
Water	3,000

2.

Picric acid	15
Boiling water	720

Make solutions 1 and 2 separately, and then mix them.

XXV.

METALLIC INKS.

In ornamental writing it is customary to use inks which produce characters with a metallic colour and lustre. Such inks can be made in two ways. We can either use the metals themselves or certain dyes which, under particular circumstances, acquire a metallic lustre. If an unalterable metallic ink is wanted, it must be made from a precious metal, gold or silver, for all other metals oxidise in time and change their colour. This is particularly true of copper.

Real Gold and Silver Inks.

To produce these the metal, in the form of tinfoil, is rubbed up with gum and water in a mortar till even a strong lens shows no sign of metallic lustre. Water is then added, but the ink must be left thick or the metal would rapidly settle to the bottom. As it is, the ink must always be well shaken every time it is used. In the case of gold it is better to dilute with solution of picric acid than with water. Then much more water can be added, and the writing will nevertheless have a fine gold colour and lustre. This use of picric acid lessens, too, the extreme costliness of the ink.

Copper Ink and Bronze Ink.

These are got in the same way, using the proper foil. The writing turns dull, and in damp places green.

IMITATION GOLD INK.

This is made from aurum musivum, which is rubbed up with a gamboge ink. This ink, although not so beautiful as the real gold ink, has the advantage over bronze ink that it keeps its colour.

IMITATION SILVER INK.

For this tinfoil is rubbed up with the gum, but a better imitation can be made with aluminium foil or filings. The aluminium keeps its silver colour permanently.

COLOURED INKS WITH A METALLIC LUSTRE.

It is possible to combine any colour whatever with a metallic colour when coal-tar dyes are used. The solution of the dye is thickened with gum, and rubbed up with real or imitation silver, when we get an ink having a metallic lustre and the colour of the dye used. For yellow, red, and brown we use gold or a golden yellow alloy and a very concentrated alcoholic solution of magenta. The writing is a dark red, and in certain lights shows the green and gold lustre of the crystallised magenta.

We have now exhausted the subject of ink in the narrow sense of the word, but there are other liquids which are applied to special purposes, such as Indian ink, used for perpetuating lead pencil drawings, lithographic and chemical inks, marking inks, and, lastly, sympathetic inks, which are the inks which disappear, or become visible, or change their colour under special treatment. While the sympathetic inks must be reckoned more or less as toys, the remaining kinds just named are widely used, and their manufacture is very remunerative.

XXVI.

INDIAN INK.

The Chinese, Japanese, and other Asiatic races write with a brush with a solid ink rubbed up with water like a pigment. This Chinese or Indian ink is remarkable for the durability and lustre of its colour. These properties have caused it to be extensively used by architects and engineers, and in general by people who have to make permanent drawings.

Although we have made enormously greater progress in chemistry than the Asiatics, they still surpass us so much in the manufacture of certain articles that the imported product always receives the preference over that made in Europe. One of these articles is Indian ink, and the real Asiatic product is always preferred to the European, as it has a deeper black colour and a greater lustre. Most European-made Indian inks are distinctly brown when diluted to any great extent.

We do not know exactly what method of manufacture is adopted in China. There are reports, which, however, cannot be regarded as very reliable, that the process consists in burning certain plants in a limited supply of air, and passing the smoke through very long paper tubes. The soot deposited in those parts of the tubes which are farthest from the fire, *i.e.*, the finest particles, is selected for making the ink. Other accounts say that the smoke used is got principally by burning sesame oil. This is so burnt in lamps that it gives a very smoky flame. It appears to us not impossible that a product which is manufactured over such an extensive area may be made from various raw materials and in various ways.

When we examine real Indian ink we find that it consists mainly of carbon in a state of excessively fine subdivision, with a binding material probably consisting of gum, but also containing camphor (up to 2 per cent.) and musk. The special smell of real Indian ink is certainly due to the presence of musk, of which only very minute quantities are needed to produce it.

The points to be noticed in real Indian ink are two in number. The carbon is pure, *i.e.*, free from tarry matter, and is in a state of extraordinarily fine subdivision. Now we have devised a process by which such carbon can be prepared without much difficulty. We burn a fuel rich in carbon, such as petroleum or purified oil of turpentine, in lamps with a feeble supply of air. The smoke is passed through a zinc tube at least 100 feet long, and with a slight upward inclination from the lamp, so as to produce the necessary weak draught. The soot which accumulates in the parts of the tube near the lamps can be used with advantage for articles less expensive than Indian ink. It makes excellent printers' ink, for example. That which is gathered from the most remote part of the tube is quite fit for the finest Indian ink, after it has been purified from the traces of tarry matter which adhere to it, and which impart the brown colour to inferior inks. This purification is effected by making the soot into a thick paste with nitric acid by means of a glass or porcelain spatula. This is then made to the consistency of honey by adding a little distilled water. The mass is then heated in a porcelain basin till thick fumes of nitric acid are evolved. In this way a large part of the tarry matter is completely destroyed, and moreover produces finely divided carbon by its destruction. The mass is now largely diluted with water, and allowed to settle. The dilute acid is then poured off, and the washing with water is once repeated. The sediment is next boiled for half an hour with a strong solution of caustic soda. This destroys the rest of the tarry matter, and the carbon left, after repeated washing with water, is in a state of the finest possible subdivision and practically chemically pure. It is then dried in vessels covered to keep out dust, and made into a paste with clear solution of gum. This paste is thickened by stirring and heating till it sets quite hard on cooling. Just after it has been removed from the source of heat a little tincture of musk is stirred into it. The mass must then be cooled slowly in a warm place. When it begins to crack it is kneaded into a lump which is rolled out into a flat plate and dried further till it can be cut into the usual quadrangular sticks, and will take a clean impression of a stamp. The sticks are formed in metal moulds, having Chinese characters on the inside and representations of dragons, etc. The overflow from the moulds is cut off with a sharp knife, and the rods are ejected by inverting the mould and tapping it. Then they are perfectly dried, and, if wished, wrapped partly or entirely in gold or silver leaf. If any cracks appear in them, these are filled with fresh paste and smoothed over. The pieces must be hard, have a lustrous pure black surface, and show a perfectly uniform and compact fracture.

Indian ink prepared as above directed and in which care has been bestowed on the moulding as well as on the manufacture cannot be distinguished from the Asiatic-made article, even by experts. In uniformity, colour, and lustre it yields to no Chinese manufacture, and surpasses some genuine Indian inks.

A somewhat inferior article can be made from ordinary soot by boiling it with caustic soda lye, washing, and mixing with gum as above directed, and then moulding the paste in the usual way.

XXVII.

LITHOGRAPHIC INKS AND PENCILS.

Lithographers require special inks or pencils, according to the particular method of procedure. If the stone is polished the drawing is executed in lithographic ink on it with a pen or brush. When the stone is then treated with a dilute acid the ink protects the parts it covers, which therefore become raised above the etched part of the stone, and the sheets can then be printed from it. When, however, MS. is to be reproduced by lithography the MS. is written on prepared paper with lithographic copying ink. The paper is then laid, writing downwards, on the smooth stone, and the ink is transferred to the stone by pressure. The acid is then used as before.

When the lithography has to be done on a rough stone, pencils and solid ink are employed.

The inks and pencils used for lithography must always contain acid-resisting bodies, and must be capable of giving a number of impressions. Such bodies are fat, rosin, and wax when converted into a soap.

LITHOGRAPHIC INK.

Water	140
Gum lac	100
Mastic	30
Rosin	10
Tallow soap	70
Soot	32

To use this recipe we require a copper boiler with a lid and a copper pan with a spout. We first melt together all the ingredients, except the wax, in the pan, and get a uniform mixture by thorough stirring. The wax is heated by itself in the larger vessel until it can be ignited. This is then done, and the contents of the pan are stirred into the burning wax. As soon as all the ingredients are in the boiler, the wax is put out by putting on the lid, and the heat is moderated till the mass only keeps in fusion. It is then ladled out into metal moulds which give it the same shape as the rods of Indian ink.

This ink is written with after rubbing up with warm water, just like Indian ink. Any ink rubbed up which is to be left overnight should be covered up to keep it moist, for if it has to be rubbed up again it will very likely form lumps which will spoil the work, more particularly if a brush is used.

It has been recommended to dissolve the ink in hot water and bottle it. Although this saves constant rubbing up, the practice is not good, as the rubbing up each time gives a more uniform and reliable writing liquid.

French Lithographic Ink.

Shellac	30
Mastic	6
Carbonate of potash	6
Hard tallow soap	6
Soot	2

Melt the soap with the shellac and the mastic, and stir the carbonate and the soot into the fused mass. As soon as the mixture is uniform it is cast in the moulds.

VIENNA LITHOGRAPHIC INK.

Wax	18
Soap	18
Shellac	14
Rosin	6
Tallow	10
India-rubber	2
Oil of turpentine	5
Lampblack	6

Fuse the first five ingredients together, and heat till the mass begins to bubble. Then stir in the lampblack and also the india-rubber, previously dissolved in the turpentine. When the smell of the turpentine has nearly disappeared cast the mass into sticks.

MUNICH LITHOGRAPHIC INK.

Wax	20
Tallow	10
Shellac	20
Soap	20
Carbonate of soda	30
Soot	10

Fuse all together at a strong heat, and stir thoroughly.

ENGLISH LITHOGRAPHIC INK.

Virgin wax	12
Tallow	12
Hard tallow soap	12
Shellac	24
Mastic	16
Venice turpentine	2
Lampblack	22

Heat the turpentine, and add to it the shellac, the mastic (both finely powdered), the tallow, the wax, and the soap in the order named. Finally mix in the lampblack intimately. The tough mass produced on cooling is rolled out and cut up and shaped.

LITHOGRAPHIC CHALK.

This is used for drawing on the stone. It must be dense enough to take a sharp point without breaking, like a good lead pencil, and give a uniform stroke with a light pressure.

LONDON LITHOGRAPHIC CHALK.

Wax	30
Tallow	25
Soap	20
Shellac	15
Lampblack	6

Fuse all together, and heat till the mass can be set fire to. It is then allowed to burn for a time, which requires some experience to judge it. The condition of the mass can, however, be judged of at any time by extinguishing it by putting the cover on the boiler, and then making a stick of the mixture and trying how it will write. If the stick will not bear a sharp point, having some elasticity and writing a uniform black line, the mass in the boiler must be set fire to again, and again tested a few minutes later. The finished mass is rolled out on a hard surface, and made into pencils the thickness of a goose quill and about 3 in. long.

FRENCH LITHOGRAPHIC INK.

Tallow	100
Soap	85
Shellac	70
Mastic	10
Lampblack	10

Fuse together and ignite, and proceed altogether as directed under the last recipe.

AUTOGRAPHIC INKS.

These are intended for transferring a writing or drawing to the stone, so that the latter can be printed from directly it has been etched. Here we have a means of securing a number of copies, which is very important for circulars, letters, plans, etc.

It is undeniable that certain difficulties attend the preparation of these inks, for it is necessary to prepare a liquid which besides possessing the properties of an ordinary ink, will cling fast to the stone and give copies for a considerable time. The paper used may be any usual paper, provided it is not too rough, for common work such as a circular, but if fine work is necessary, as in preparing copies of a pen-and-ink drawing or of an architect's plan, prepared paper only is usable.

Preparation of the Paper.

By following strictly the recipe about to be given the finest line or point can be faultlessly reproduced in the copies. The stone can be etched immediately the transfer has been made, and many thousands of good copies can be printed off.

A fine, strong, unsized printing paper is spread out on a smooth board, and poured over first with a 10 per cent. solution of gelatine. The board is then tilted and the gelatine run off, and a 5 per cent. solution of tannin is next poured on. The paper is again drained and dried. The two processes and the drying are then repeated a second or a third time, and the paper is finally calendered. This paper will not only transfer as above stated the finest lines of a drawing, but will also take the minutest details of a copper or steel plate, and transfer them to the stone.

When the drawing or writing has been laid on the stone the two must be forcibly pressed together several times. The paper is then carefully taken off. The repetition of the pressure is made necessary by the fact that the stone takes an appreciable time to take the ink so strongly that it will not be affected by the etching.

BEST AUTOGRAPH INK.

Wax	110
Tallow	30
Soap	110
Shellac	50
Mastic	40
Rosin	10
Soot	30

These are fused together in an iron vessel, and the temperature is then raised until disagreeable vapours are largely produced. The mass is then cast into moulds or rolled into cylinders.

The autographic inks can also be used very well for ordinary writings with a steel pen, so long as the letters are not too small.

AUTOGRAPHIC DRAWING COPYING INK.

Ground Mass.

Wax	70
Tallow	75
Soap	60
Copal	45
Shellac	70
Mastic	70
Pitch	10
Linseed oil	10
Sulphur powder	10

The copal is first fused with the linseed oil, and so strongly heated that thick, strong-smelling fumes appear. The soap is then added, then the tallow, then the wax, and then the other resins. The whole is next strongly heated and set fire to. During the combustion the sulphur is sprinkled on to the mass, which is continually stirred. The combustion must be maintained until about three-quarters of the mass has been burnt away. The fire is then put out by covering the vessel with its lid.

AUTOGRAPHIC INK No. 1.

Ground mass	12
Distilled water	100
Indigo-carmine	5

The ground mass is boiled with the water till the liquid is reduced to one-half. The clear brown liquor is then poured off, and the indigo-carmine is dissolved in it. The ink is then bottled.

If the ground mass has not burnt long enough the ink will not copy well, as it will dry too quickly. If, on the other hand, the combustion has been unduly prolonged, the ink will not adhere properly to the stone. It must also be remarked that when the writing is transferred to the stone, the back of the paper must be well damped to facilitate the transfer of the ink from it to the stone.

AUTOGRAPHIC INK No. 2.

Wax	200
Soap	60
Tallow	32
Shellac	16
Black pitch	8
Lampblack	40

The ingredients are all fused together and stirred to a uniform mixture, which is gradually heated till it fumes strongly. As soon, however, as the mass catches fire the cover of the vessel is put on, as the burning must not be allowed to continue. The finished ink is then cast into sticks and for use is rubbed up with warm water.

Autographic Ink (Andés).

1.

Shellac	6
Wax	2
Fat	14
Mastic	8
Soap	6
Soot	2

2.

Refined mutton tallow	100
Yellow wax	125
Soap	16
Shellac	150
Mastic	125
Turpentine	16
Soot	30

3.

Soap	100
Wax	118
Fat	50
Mastic	50
Soot	50

4.

Wax	6
Mutton tallow	11
Soap	12
Shellac	11
Mastic	90
Venice turpentine	2
Soot	20

Carbon Papers.

These are used for producing a copy of a writing while the writing is being executed. To prepare them, strong, smooth paper is covered on one side with an intimate mixture of yellow wax and an equal weight of the finest Paris blue with ten times the weight of purified tallow. The mixture is well fused and stirred, and is applied to the paper hot. The prepared paper is laid between two unprepared sheets, and the sheet which is in contact with the uncoated side of the prepared paper is written on with a blunt pencil, whereby the writing is copied on the lowest sheet as it is made on the uppermost one.

PHOTOGRAPHIC COPYING OF DRAWINGS.

Certain chemical compounds are altered by light, and can therefore be used for copying writings or drawings made on one side only of the paper by photography. We will describe the process known as Cyanotypy, which consists in soaking paper in the dark-room with a solution of 10 oz. of ferric chloride and 5 oz. of tartaric acid in 100 oz. of water, or with a solution of 10 oz. of ammonia-citrate of iron and 10 oz. of potassium ferricyanide in 60 oz. of water. The paper is then dried and exposed to the sun for an hour under the copy. The paper is then developed with a 10 per cent. solution of ferrocyanide of potassium, thoroughly rinsed and dried. The writing, etc., will then show white on a blue ground.

COPYING PROCESS FOR INDIAN INK DRAWINGS AND ENGRAVINGS ON COPPER OR WOOD.

Dissolve oxalic acid in cold water, boil up, and add as much molybdic acid as the boiling solution will dissolve. The solution is then kept in bottles of black glass. Paper is soaked with this, and then dried in the dark-room, and then exposed under the photograph, drawing, or engraving in an ordinary printing-frame. The copy is then obtained white on a dark-blue ground. If the paper of the engraving, etc., is very thick, the passage of light through it must be facilitated by lightly rubbing it on the back with petroleum.

XXVIII.

INK PENCILS.

It is unnecessary to enlarge on the usefulness of these articles, which combine the convenience in use of a lead pencil with the production of ink-writing with its special appearance and durability. The manufacture of ink pencils has received a great impulse from the discovery of the coal-tar colours, but although many makers put them on the market, certain faults have restricted their use within somewhat narrow limits. They are either too soft, so that they absorb water from the air and make smudgy writing, or so hard and brittle that they break whenever any attempt is made to sharpen them. The question is one well worthy of the attention of manufacturers, and we proceed to give some recipes. The prime conditions of making a really usable ink pencil are to have the ingredients in a state of the finest possible subdivision, and to bring them into sufficiently dense rods by high pressure. We consider that it is advisable to cover the point when the pencil is not in use by a metal cap, and to keep the paper to be used in a damp place. The characters then come out strongly, with gentle pressure on the point of the pencil. The aniline dyes which should be used are magenta for red, water-soluble blue and methyl violet for their respective colours, and nigrosine for black.

FABER'S INK PENCILS.

	Aniline Dye.	Graphite.	Kaolin.
1.	100	75	25
2.	46	34	24
3.	30	30	40
4.	25	24	50

The three ingredients are thoroughly mixed, and the mixture is then forced through holes in a plate, so as to form it into rods, which are finally dried. No. 1 is very soft, No. 4 very hard.

According to another recipe 10 lb. of best logwood are boiled with 100 lb. of water. The decoction is evaporated down to 100 lb., and a solution of chromium nitrite is added till the precipitate at first formed has redissolved to a bluish-black liquid. This is evaporated on the water-bath till it can be formed into rods, after being mixed with from 3 to 4 times its weight of fat-clay and solution of gum-tragacanth. This recipe seems to us faulty, and gives results very inferior to those obtained with the aniline dyes.

PENCILS FOR WRITING ON GLASS, PORCELAIN, AND METAL.

The ingredients are thoroughly mixed, and shaped into sticks by hydraulic pressure. The sticks are then encased in wood like pencil-leads. Their use requires a fair amount of pressure, but the writing cannot be washed away with water.

1. *Black.*

Soot	10
Wax	40
Tallow	10

2. *White.*

Chalk	40
Wax	20
Tallow	10

3. *Pale Blue.*

Prussian blue	10
Wax	20
Tallow	10

4. *Dark Blue.*

Prussian blue	15
Gum	5
Tallow	10

5. *Red.*

Cinnabar	20
Wax	60
Tallow	20

6. *Yellow.*

Chrome yellow	10
Wax	20
Tallow	10

PENCILS FOR WRITING ON GLASS.

1.

Water	16
Red lead	8
Tallow	2-4

The ingredients are thoroughly mixed and fused together, and cast into sticks. The variation in the amount of tallow enables the pencils to be made harder or softer.

2.

Tallow	5
Wax	10
Tallow soap	10
Red lead	10

The red lead is stirred in after the other three ingredients have been fused together. The mass is shaped into cylinders before it is quite cold, after having been stirred to the last possible moment. The sticks tend to become brittle with age, and should therefore be kept in a warm place.

XXIX.

MARKING INKS.

These are the inks used for writing on garments. It goes without saying that they must resist washing, and must be capable of immersion for weeks on end without change. They have, however, to resist also the various substances used in laundries. It is often required of them in addition that they should be still distinctly visible when the place marked has been dyed and then bleached again.

Only a few substances are known which answer fully all the requirements made in respect of a marking ink, and only those which depend for their colouring matter on free carbon are absolutely indelible.

Solutions of the precious metals, gold, silver, platinum, and iridium (a rare metal closely allied to platinum), have the property of being decomposed by organic matter, the metal being separated out in an extremely finely divided state, and forming a very distinct writing.

Silver compounds are decomposed by light alone, and turn black by the separation of very finely divided metallic silver. This circumstance, as well as the fact that silver is the cheapest of the precious metals, makes silver the most suitable for metal marking ink. (Gold is fifteen times the price of silver, and platinum seven times.) We know, however, organic dyes which can be brought into a form in which they are soaked up by a fabric, and form with it insoluble compounds. Such a substance, for example, is indigo-white, which is almost entirely indelible on animal fabrics such as wool and silk. The organic marking inks have here a great advantage over those prepared from metals, for writings made with any metallic salt can be eradicated without leaving any trace and with comparative ease. Silver can be removed by solution of cyanide of potassium, and gold and platinum by chlorine water. Writings done with indigo-white and carbon, on the other hand, are practically indestructible, for even after the indigo has been got rid of the carbon adheres to the fibres with such tenacity that it cannot be removed without radically injuring the fabric.

METALLIC MARKING INKS.

A.—SILVER INKS.

There is a large number of recipes for marking inks of which the basis is silver, and we shall presently give the more important of them. In all cases without exception the salt of silver used is the nitrate. On account of the price of this salt, those who use it in anything like large quantities should make it for themselves, especially as it can be done very easily.

Preparation of Silver Nitrate.

The first condition of suitability for marking inks of nitrate of silver is freedom from copper, and a perfectly pure salt can be got as follows :—

Pour nitric acid over some silver in a glass vessel. The metal dissolves rapidly with evolution of suffocating fumes of nitrous acid. The solution obtained will be more or less blue, according to the amount of copper present. It is diluted with distilled water and precipitated with hydrochloric acid. The white, curdy precipitate settles quickly, and when the further addition of hydrochloric acid produces no more of it the supernatant liquid is decanted through a filter, on to which the precipitate is received. Here it is washed with distilled water until the filtrate gives no blue colour with ammonia, a sign that all the copper has been washed away.

The precipitate is then put, together with strips of zinc, into somewhat dilute hydrochloric acid. The colour of the chloride of silver soon changes to a peculiar metallic grey as it becomes reduced to the metallic state. After some days the mass is filtered off, and the pure silver on the filter is washed with distilled water until a sample of the filtrate remains perfectly clear on the addition of ammonia. The silver is then dissolved in nitric acid, which must be free from hydrochloric acid, or some of the silver will return to the state of chloride and remain undissolved. The solution is then evaporated down, but is not allowed to boil for fear of loss by spirting. As soon as the contents of the dish are solid the heat is raised till the salt fuses, and then immediately removed. We shall then get the nitrate of silver in the form of a colourless crystalline mass. It gradually blackens when exposed to the light, and should be kept in the dark or in orange-coloured bottles. It should leave no residue on solution in water.

A simpler method of preparation is to dissolve the impure silver-containing copper in pure nitric acid, evaporate the solution down, and heat the residue. This then turns dark and evolves fumes of nitrous acid, for the nitrate of copper decomposes at a lower temperature than the nitrate of silver into nitrous fumes and black oxide of copper. The secret of success in this method is therefore to work with such a temperature that the nitrate of copper is decomposed, but not the nitrate of silver. The process is regulated by occasionally taking a sample of the fused mass on the sharp point of a glass rod. This sample is dissolved in water and tested with ammonia. As soon as this ceases to produce a blue colour the decomposition of the copper salt is complete, and the mass is at once allowed to cool. The grey solid then obtained consists of nitrate of silver mixed with finely divided cupric oxide, which is removed by dissolving the nitrate of silver in distilled water and filtering off the solution for use.

Whichever of these two methods of preparing silver nitrate is adopted, it is necessary to fuse the salt obtained to get rid of the last traces of the nitric acid, which would otherwise damage the fabric by passing into the marking ink.

Preparation of the Fabric for Marking.

It is, of course, possible to write with a mere solution of nitrate of silver, but the writing will then run, and will, besides, not adhere strongly to the fibre. But if the fabric, whether linen, cotton, silk, or wool, is first prepared at the spot to be marked, we can use the plain nitrate of silver as a marking ink, either with the pen or with a rubber stamp, and get perfectly sharp letters. We dissolve equal weights of soda crystals and gum-arabic in a weight of water equal to ten times the weight of either, and filter the solution. The place to be marked is soaked with this solution and dried, and when quite dry smoothed with a hot iron. The solution of nitrate of silver being colourless it must be coloured with some inactive colouring matter to make the writing visible from the first.

Silver Marking Ink.

Nitrate of silver	4
Water	40
Gum	4
Soot	2

Dissolve the gum by itself in half the water, and rub the solution carefully with the soot. Then dissolve the silver salt in the rest of the water, and mix the two lots by thorough shaking. Other indifferent colouring matters may be substituted for the soot, *e.g.*, finely powdered indigo or a solution of sap green, or of any soluble aniline dye, such as water-soluble blue, taking in each case only enough to make the writing legible from the first.

When the marking is done it is left exposed to the light, if possible to the direct rays of the sun, when the writing blackens by the formation of metallic silver. The nitric acid which is set free at the same time is neutralised by the soda used in preparing the fabric. If this preparation has been omitted, delicate fabrics would be worn into holes by the acid. As soon as the writing ceases to darken, the marked place is rinsed in warm, soft water. After that the garment may be washed in the ordinary way without injury to the marking.

It must be remarked that steel pens must not be used with metallic marking inks or the silver will be precipitated on the nib, some of the steel of which will dissolve to take its place. Not only do the marked letters thus become paler, but often acquire a rusty edging due to the presence of oxide of iron. A quill should always be used. It will be blackened the first time it is used with a silver ink, and browned with a gold ink, but subsequent employment of the same pen will not entail any further loss to the ink, especially if the pen is rinsed in soft water each time it is used.

Ammoniacal Silver Ink.

If caustic ammonia is added to a solution of nitrate of silver in water, a precipitate of silver oxide is at first formed, but soon dissolves if more ammonia is added. In this way we get a solution which always remains clear and deposits no sediment, while the non-ammoniacal silver inks always give a black deposit of silver on keeping, and thus gradually become so weak as to be useless.

Normal Ammoniacal Silver Ink.

Nitrate of silver	6
Gum-arabic	6
Soda	8
Distilled water	15
Ammonia	12

Dissolve the nitrate in the water in a stoppered bottle, then add the ammonia, and finally the gum and the soda. The bottle is then heated in hot wâter till the colour of the liquid is so dark that it will write legibly. The stopper is left out during the heating. Care must be taken not to overheat, or so much ammonia will be lost that the ink will precipitate. For the same reason the finished ink must be kept well stoppered up, and must also on account of the action of light on silver inks and metallic inks in general be kept in the dark. The foregoing ink is particularly suitable for writing and drawing with the pen. If it flows too thinly, add more gum to it.

Silver Stamping Ink.

Nitrate of silver	10
Ammonia	20
Soda	20
Gum	25
Water	80

Dissolve the silver in the ammonia, and the soda and gum in the water. Then mix the two solutions, and heat till the at first turbid liquid becomes perfectly clear and of a fine brown colour. For use with the pen the ink is now ready, but for use with a stamp the amount of water used should be less, so that the ink may be thicker and give sharp letters with the stamp.

For large establishments where the weekly washing is heavy, such as hotels, hospitals, etc., there is no better marking ink than this. With the stamp especially, it gives the finest lines and details with great distinctness and durability with a very moderate amount of pressure.

Cheap Silver Ink.

The silver inks already given are somewhat dear, as the nitrate of silver must be used in the form of concentrated solution in order to get a deep black writing. But if we combine the silver salt with copper salts a dark black can be got without much silver.

When ammonia is added to a solution of a copper salt we get first a pale blue precipitate of hydrated oxide of copper, which dissolves in an excess of ammonia, forming a magnificent dark-blue solution of cuprate of ammonia. If writing executed with this ink is heated, say with a flat iron, a deep black results from the formation of black oxide of copper.

Hence, if we make ink of a mixture of argentate and cuprate of ammonia, we can get a black and durable writing with a comparatively small amount of silver. Take

Nitrate of silver	15
Sulphate of copper	35
Ammonia	50
Gum	20
Carbonate of soda	20
Soft water	80

Dissolve the metallic salts in half the water, and add the ammonia to the solution. If the amount of ammonia above indicated does not give a clear solution, add more till the liquid is clear. The gum and soda are next dissolved in the rest of the water, hot, and the two solutions are then mixed. This ink is of so dark a blue that no dye need be added to it. It is excellent for linen and white silk and wool. For thin fabrics the amount of gum must be somewhat increased.

It must be here remarked that when a marking ink containing gum and soda is used no preliminary preparation of the fabric is needed.

Silver Drawing Ink.

For executing drawing on fabrics with silver ink, it is advisable to make the inks from special recipes, to ensure the production of the finest lines. The same recipes give excellent stamping inks, and we proceed to give a few of them.

Nitrate of silver	20
Soda carbonate	30
Water	100
Tartaric acid	7
Litmus	5
Gum	40

Dissolve the nitrate of silver in 40 of the water and the carbonate of soda in the remaining 60, and add the soda to the silver as long as a precipitate of carbonate of silver is formed. This white precipitate is filtered off, washed on the filter with distilled water, and rubbed up in a mortar with some water and the tartaric acid. The mass effervesces owing to the escape of carbonic acid. Ammonia is now added cautiously to dissolve the tartrate of silver, and the litmus is next added, and turns the ink blue. The gum in solution is now mixed in, and the finished ink is diluted with water if necessary. Water-soluble blue can be substituted for the litmus, the object of either being to make the writing legible from the first.

Red Silver Drawing Ink.

Nitrate of silver	48
Tartaric acid	60
Gum	40
Carmine	2
Water	80

Rub the nitrate of silver and the tartaric acid together in a perfectly dry state and then add the ammonia to them, using no more, however, than will give perfect solution with diligent stirring. The clear solution is mixed with the gum in solution and diluted, if necessary, with water.

Kindt's Green Silver Ink.

Nitrate of silver	11
Ammonia	22
Carbonate of soda	22
Water	12
Gum	50
Sap green	2

Dissolve the silver salt in the ammonia and the soda in the water separately. Boil the latter and pour the silver solution into it. Then add the gum, and colour with the sap green.

According to our experience the following process is better: Dissolve the silver salt in the ammonia, and add next the dry soda, and finally the sap green and the gum.

This ink only gradually blackens in the light, but the blackening can be hastened by ironing the dry writing.

Chloride of Silver Ink.

A.

Nitrate of silver	8
Water	80
Gum	16
Indigo-carmine	2

B.

Common salt	2
Gum	5
Water	10

These solutions are made and kept separate. The fabric is prepared with B, and when dry is written on with A. When he writing is dry, it is exposed to the sun, and soon turns a leep black by the action of the light on the chloride of silver ormed from the nitrate by the common salt.

B.—GOLD INKS.

Gold, which is very easily evaporated in the metallic state rom any of its compounds by organic matter, can be used vith great advantage for marking inks. With it we can get t pleasure black characters, characters with a metallic lustre, r of a splendid purple colour. The markings are very difficult o efface, and it is unfortunate that the cost of such inks should e so great.

Black Gold Ink.

Reade has recommended a process for preparing this ink vhich contains iodide of ammonium. According to his recipe, however, that salt is made in a way which entails great risk of the formation of iodide of nitrogen, which is very dangerous on account of its great explosiveness. A method of preparing the iodide which involves no such danger, however, is to saturate ammonia with sulphuretted hydrogen made by dissolving ferrous sulphide in dilute sulphuric acid. The iodine is put into the ammonium sulphide so prepared. The iodine dissolves with precipitation of sulphur, so that the liquid becomes turbid. The colourless solution of ammonium iodide is filtered off from the precipitated sulphur, and more iodine is dissolved in it. We now dissolve gold leaf in the saturated solution, whereby we get a solution of the double iodide of gold and ammonium. If we write with this solution we get brownish-black letters, which can be made quite black by mixing the ink with one of the foregoing ammoniacal silver inks.

Purple Gold Ink.

This consists of two separate liquids. A is used for the preparation of the fabric, and B for the subsequent writing.

A.

Tin salt	2
Water	200
Gum	20

B.

Chloride of gold and sodium	2
Water	20
Gum	2

Dissolve gold in strong hydrochloric acid by adding the necessary amount of nitric acid in small portions. The usual amount of nitric required is one-quarter of the weight of the hydrochloric. The impure gold solution containing copper is evaporated nearly down to dryness to get rid of the excess of acid, diluted with water, and precipitated warm with a solution of oxalic acid, which throws down a brown precipitate of metallic gold. This is washed, and again dissolved in aqua regia. Common salt is added to the solution, which on evaporation gives crystals of double chloride of gold and sodium. With this ink we write on the fabric previously prepared with solution A, whereupon Cassian purple is formed. The tint may be made as delicate as desired by using the solutions in a sufficiently dilute state.

Gold Ink with Metallic Lustre.

Here again two solutions are used, A for the preparation of the fabric, and B for the subsequent writing.

A.

Oxalic acid	2
Gum	4
Water	10

B.

Chloride of gold and sodium	2
Gum	4
Water	20

When the writing appears it is ironed and then washed.

C.—PLATINUM INKS.

When platinum is dissolved in aqua regia (the abovementioned mixtures of 4 parts hydrochloric and 1 part nitric acid) and the solution is evaporated, we get a residue of tetrachloride of platinum. If this is used alone for writing on linen we get a dead black writing, but if the fabric has been prepared with tin salt the characters will be red. As before, A is the preparing, B the writing liquid.

A.

Oxalic acid	3
Gum	3
Water	10

B.

Tetrachloride of platinum	2
Gum	4
Water	20

As soon as the writing is dry and quite distinct, wash the marked place thoroughly.

D.—VEGETABLE MARKING INKS.

As above stated several organic bodies can be used for making marking inks, and their use is to be preferred to that of metallic salts, as the inks are not only cheaper but are, under certain conditions, more durable. Writings executed with gold, platinum, or silver salts can be gradually entirely effaced by careful treatment with cyanide of potassium or dilute acid.

It would be very easy to get any colour on a fabric with organic matter. All that is required is to mordant the fabric with alumina or tin salt, and then to write on it with a solution of the organic dye, such as cochineal, madder, logwood, etc. The result is that the characters appear in the form of a coloured lake. For fabrics which have not to be wetted this principle is taken advantage of in producing designs, and is known as textile printing, but the method does not answer for marking, as the soap and other substances used in washing clothes rapidly destroy the writing.

Of organic matters which will give an ink that will stand washing the most important are indigotine, aniline black, and the colouring matter of *Anacardium longifolium.*

INDIGOTINE MARKING INK.

Indigotine, the blue colouring principle of indigo, has the property of being convertible into a colourless substance called indigo-white. This substance, however, rapidly becomes indigotine again when exposed to the air, by absorbing oxygen.

Indigotine will not dissolve in anything but fuming sulphuric acid.

Indigo-white is prepared from the following recipe :—

Gum	40
Finest powdered dry indigo	40
Ferrous sulphate	80
Caustic soda	80
Water	400
Litmus	2

Mix the indigo and the sulphate in a bottle, and then pour in the soda dissolved in the water. Cork the bottle lightly, and leave it for several days, shaking it occasionally. When all blue colour has disappeared the reaction is finished. Then place the gum and litmus in another bottle, in the state of very fine powder, and rapidly pour the indigo-white upon them, and then cork the bottle immediately. When the gum has dissolved the ink is ready.

Use it by dipping a pen into the bottle and writing on the fabric, which need not be specially prepared, and cork the bottle again quickly. The writing soon turns green and finally blue, and can only be destroyed by nitric acid or chlorine. The ink in the bottle gradually forms a deposit of indigotine, which can be used for the preparation of more indigo-white.

ANACARDIUM MARKING INK.

There are two sorts of cashew-nuts on the market, one from the Asiatic tree *Anacardium longifolium*, the other from the American *Anacardium occidentale*. The fruits of *A. longifolium* are heart-shaped, flat, and grey or black in colour; those of *A. occidentale* are oval, greyish-green, and very lustrous. The colouring matter of both is partly of the nature of an essential oil, partly of a resin. It can be extracted from the crushed nuts with alcohol and ether, but better by means of petroleum ether, by shaking in a well-stoppered bottle. The solution is finally filtered into a dish, where it is allowed to evaporate spontaneously to a syrup, under a sheet of paper so that no dust can get in. The resulting extract is thick enough to be used with a pen or a rubber stamp without any gum. The letters are at first brown, but are quickly changed to a deep black by alkalies. To fix and fully bring out the colour the place marked should be held for a short time over the surface of some ammonia, the alkaline fumes from which rapidly produce the desired result. The writing will then resist washing, even when chloride of lime is used, and also dilute nitric acid.

Black Copper Marking Ink.

Completely precipitate a solution of chloride of copper with one of caustic potash. Pour off the supernatant liquid and dissolve the precipitate in the smallest possible quantity of ammonia. Then add enough dextrine to enable characters which will not run to be written with a quill. When the writing is dry iron it and it will turn black.

Aniline Marking Ink.

Aniline black makes a most excellent marking ink. The use of other anilines for marking purposes, although beautiful colours are obtained, is unadvisable, on account of the want of permanence displayed in the majority of cases by the writing. The coloured aniline marking inks are especially loose to alkali, the very agent with which they are brought into contact in the laundry. We proceed to give the best of the known recipes for aniline marking inks.

Copper Aniline Marking Ink.

This consists of two solutions which are not mixed until just before use.

A.

Chloride of copper	15
Sal ammoniac	10
Chlorate of soda	20
Water	100

B.

Hydrochloride of aniline	25
Gum	20
Glycerine	5
Water	50

For use a small quantity of A is mixed with five times its weight of B. The result is a green liquid which turns black in a short time, and is then unfit for use. As it is, the ink has to be fixed on the dried fabric, at once, by holding it over boiling water till it is thoroughly soaked. No washing with soap will then efface the writing, which even resists chloride of lime for a long time.

JACOBSON'S MARKING INK.

This also consists of two liquids, which are mixed just before use, A being added to four times its weight of B.

A.

Crystallised copper chloride	85
Chlorate of sodium	106
Sal ammoniac	53
Distilled water	600

B.

Glycerine	30
Gum	20
Dissolved in water	40
Hydrochloride of aniline	60
Dissolved in water	90

The ink is green at first, but the writing soon turns to a black which is fast to washing. This ink is known as Jetotine.

BLUE MARKING INK FOR GALVANISED WARE, ETC.

Dissolve in 1 gallon water 1 lb. shellac, ¼ lb. borax; then stir in the requisite quantity of ultramarine blue.

ANILINE STAMP INK.

This again is a two-fluid ink. For use B is mixed with four times its weight of A. The writing must be fixed by leaving a hot iron on it for a few minutes.

A.

Chloride of copper	2
Ammonia	80
Common salt	2

B.

Hydrochloride of aniline	40
Gum	·15
Glycerine	15
Water	30

BLACK ANILINE MARKING INK.

Aniline black	1·75	grammes
95 per cent. spirit	42·0	„
Hydrochloric acid	60	drops
Gum-arabic	2·5	grammes
Water	170·0	„

The aniline is first rubbed up with the spirit and the acid. The gum is then rubbed in after being dissolved in the water. The result is an intensely black ink, which, however, is easily washed out. In order to be able to use it for marking clothes requiring washing we must substitute 2·5 grammes of shellac dissolved in 170 of spirit for the gum solution.

This ink can also be used for writing on wood, glass, metal, leather, and india-rubber, and is unaffected by water.

Since the discovery of the vegetable marking inks the demand for the much more expensive metallic marking inks has been greatly reduced, but the latter still deserve the preference so far as resistance to the alkalies used in washing is concerned. To these they are quite unsusceptible, so that the writing can never disappear. They can, however, be completely effaced by solution of cyanide of potassium, and writing done with silver inks can be destroyed with very dilute nitric acid. Gold and platinum can only be effaced by solutions which contain free chlorine.

A writing which is absolutely indelible can be got by writing on the fabric with a fine glass point wetted with concentrated sulphuric acid. The instant the writing turns brown, the marked place is thoroughly rinsed. In this way a part of the fibre is carbonised, and a permanent marking is secured. This method requires a good deal of practice, as the fabric is easily eaten into holes by unskilful treatment.

STENCIL INKS.

Liquid.

A high-class ink for wooden cases, etc., is made by grinding ivory black (bone black), tinted by a little ultramarine blue, into a good copal varnish or other drying medium, thinning the mass with turps or white spirit to the right consistency for application with the stencil brush.

Solid.

A black, soluble stencil ink for marking chests and bales is made by allowing 80 parts of good glue to swell up in water for twelve to twenty-four hours, and then dissolving it, on a water-bath, in 450 parts of fresh water, along with 16 parts of yellow commercial dextrine, 6 of sugar, 22 of glycerine (crude, 28 deg. B.), and 26 of water nigrosine. The solution is then incorporated, by stirring, with 400 parts of lampblack, to form a paste, which is then thickened by further heating on the water-bath, until a small sample is found to set hard on cooling. All the superfluous water being thus evaporated, the mass is pressed in greased moulds. The addition of a little ox-gall will help the ink to run freely when used on greasy material.

XXX.

INK SPECIALITIES.

Certain industries require particular liquids for writing on metal, leather, wood, ivory, and other materials requiring inks varying in properties.

Ink for Metal.

Lustrous Black Ink for Metal.

Copal	10
Oil of turpentine	12
Soot	2

The copal is fused in an iron pot, and then further heated till dense fumes come off, and the copal begins to decompose. Keep the cover of the pot handy, in case the copal should catch fire. When the copal has wasted down to about four-fifths of its original weight let the pot cool a little and stir in the turpentine gradually, and finally the soot. Care must be taken that the pot is not too hot when the turpentine is put in or it will be thrown out again. The finished mass is thinned with more oil of turpentine, if necessary, till it can be written with. The ink must be kept in well-closed bottles as it dries up quickly.

We can write with this ink upon any metal, and the writing adheres best when the surface is quite clean and somewhat rough. It should be sand-papered and then written on.

Lustrous Red Ink for Metal.

Copal	20
Oil of turpentine	24
Cinnabar	2

Proceed as directed under the last recipe, except that less turpentine must be used, as the ink must be kept thick enough to prevent the cinnabar, which is very heavy, from settling.

Lustrous Coloured Inks for Metals.

By substituting other pigments, such as ultramarine, Prussian blue, chrome-yellow, aniline violet, etc., for the cinnabar in the last recipe, ink of any desired colour may be made.

Dull Black Ink for Metals.

Copper sulphate	10
Vinegar	2
Gum	4
Soot	2
Water	10

Fine dead black writing can be done on clean iron, zinc, or brass with this ink, but not on copper or tin. For these two metals we use the following recipe :—

Sulphate of copper	10
Hydrochloric acid	4
Sal ammoniac	8
Soot	2
Gum	4
Water	10

Ink for Writing on Silver.

Dissolve the double chloride of gold and sodium in fifteen imes its weight of water. The solution writes a beautiful olden brown on silver. If this colour is to remain the silver s dipped into ammonia and rinsed. If the writing is exposed o the sun instead, the colour soon passes into black. Black vriting on silver can also be executed with a solution of tetrahloride of platinum made as above directed. If we follow ngraved lines on the silver with this ink, the effect known as iello is produced.

BLACK INK FOR ZINC.

Sulphate of copper	2
Chlorate of potash	2
Water	72

On using this solution with a quill the writing is at once black. When dry, rinse with water, and go over the letters with an oiled rag.

BLACK INK FOR LEATHER.

This consists of two separate fluids. The place to be written on is painted over with A, allowed to dry, and then written on with B. The ink writes a fine black, and penetrates deeply, especially if the back of the leather is wetted before the other side is written on.

A.

Galls	20
Gum	2
Water	200

B.

Ferrous sulphate	4
Gum	8
Indigo-carmine	2
Water	40

BLACK INK FOR LINEN, COTTON, WOOL, AND SILK.

The place to be marked is prepared with solution of alum, and then, when dry, with decoction of galls. It is written on with the solution marked B in the last recipe. A slight increase in the amount of indigo-carmine makes the writing more permanent.

WATERPROOF BLUE INK FOR GLASS.

Bleached shellac	10
Venice turpentine	5
Oil of turpentine	10
Powdered indigo	5

Dissolve the shellac and the Venice turpentine in the oil of turpentine over hot water. Then stir in the indigo.

LABORATORY INK.

Nigrosine	10
Ruby shellac	20
Borax	30
Ammonia	15-30
Water	400

Boil the shellac and the borax in the water till both are dissolved. Then filter, and add the nigrosine and the ammonia. This ink resists laboratory fumes for a long time.

IVORY INK.

It is possible not only to write indelibly in black on ivory, but by a simple process to execute on the material very beautiful drawings in every shade from the lightest pale brown to the deepest black.

The ivory must be first prepared by soaking it in a strong solution of soap or of ammonia, and then rinsing. In the meantime we prepare a normal ink by dissolving nitrate of silver in ten times its weight of water. The solution is divided into ten equal parts. One is left as it is, the second is diluted with its own volume of water, the third with twice its own volume of water, and so on, so that the last is diluted with nine times its volume. The weaker the solution the paler it will write on the prepared ivory, ranging from a deep black to a very light grey. By judiciously using these inks very tasteful drawings can be executed on ivory, either with brush or pen. They are indelible, and may contain all the ten shades together. If the drawing is to acquire a warm brown-gold colour the ivory is laid in a 1 per cent. solution of the double chloride of gold and sodium. As soon as the desired colour has appeared, the ivory is removed, rinsed, and immediately put into a 10 per cent. solution of hyposulphite of soda.

INK FOR WRITING AND DRAWING ON WOOD.

By skilful treatment pale wood may be adorned with drawings which produce the effect of inlaid work at a distance. The first thing to be done is to prepare the wood by painting it over repeatedly with a boiling solution of gelatine and then with the following mordant :—

Alum	10
Hydrochloric acid	10
Tin salt	2
Water	50

This is applied several times by means of a sponge. It partly serves as a basis for the ink, and partly prevents it from smudging by ensuring its penetration. The following inks are then used, each for the colour named :—

Black : Anacardium ink, painted over with ammonia when dry.
Brown : Solution of potassium permanganate.
Blue : Decoction of logwood.
Red : Decoction of redwood or ammoniacal cochineal ink.
Yellow : Decoction of Persian berries, or solution of picric acid.

XXXI.

SYMPATHETIC INKS.

These have no particular practical value, and are simply chemical playthings.

They are inks which can be made to change, to appear, or disappear. Some of them are one-fluid inks, and others are two-fluid inks—one fluid being used for writing, the other for developing.

YELLOW SYMPATHETIC INKS.

A.

Dissolve copper in hydrochloric acid containing a little nitric, and dilute the solution till writing with it ceases to be visible. On heating the paper the letters appear, of a yellow colour, and disappear again on cooling.

B.

Dissolve antimony in hydrochloric acid containing a little nitric, and write with the solution. If the dry writing is painted over with decoction of galls the writing becomes visible, of a yellow colour.

SYMPATHETIC GOLD INK.

If paper is written on with a not too dilute solution of the double chloride of gold and sodium, the writing appears permanently on treatment with a 10 per cent. solution of oxalic acid. By ironing the paper a fine metallic lustre can be given to the characters.

RED SYMPATHETIC INK.

This is a two-fluid ink. We write on paper with a very dilute solution of the double chloride of sodium and gold, and when the paper is dry we develop the hitherto invisible characters by sponging them over with a solution of tin salt, when Cassian purple is formed. If the paper is first prepared with tin salt the purple will appear at once. In a similar manner all two-fluid sympathetic inks can be used to produce a writing visible from the first.

DISAPPEARING PURPLE INK.

Write with a very dilute solution of iron in aqua regia, and shut up the paper with a watch glass containing sulphocyanide of potassium and a little sulphuric acid. The writing soon becomes visible, of a blood-red colour, but if held over ammonia will disappear again completely.

GREEN SYMPATHETIC INK.

A one-fluid ink is made of a mixture of cobaltous and nickelous nitrate. The characters are scarcely visible when dry, but on heating they appear of a beautiful green, which disappears again on cooling. By varying the proportions of the two salts different shades of green can be obtained.

TWO-FLUID GREEN SYMPATHETIC INK.

Write with a solution of chlorate of sodium, and when the writing is dry go over the paper with a sponge wet with solution of sulphate of copper. The writing will at once appear permanently, and of a lively green.

BLUE SYMPATHETIC INK.

Many cobalt salts form crystals which are red at ordinary temperatures, but turn to a full blue on heating. Hence any soluble cobalt salt can be used as a sympathetic ink. Those most used are the chloride and the nitrate. The characters are almost invisible at ordinary temperatures, but appear of a distinct dark blue when heated, again to disappear on cooling.

Paracelsus used the first green ink we described to draw the leaves of the trees in a landscape, the rest of the drawing being executed with ordinary pigments. The drawing had therefore the effect of a winter landscape when it was cold, and of a summer one when it was warmed.

INK WITH COBALT SULPHOCYANIDE.

This salt is extremely sensitive to changes of temperature. It gives a pale-red writing, which with a very small rise of temperature turns blue. Cobalt sulphocyanide is prepared by adding an alcoholic solution of potassium cyanide to a solution of cobaltous sulphate as long as any potassium sulphate precipitates. The filtrate is a solution of cobalt sulphocyanide and is evaporated at a very gentle heat. Writing with it turns blue even when laid in the palm of the hand.

BROWN SYMPATHETIC INK.

Bromide of potassium	2
Sulphate of copper	2
Water	40

The cold characters are scarcely visible, but turn brown on heating.

OXAL-MOLYBDIC INK.

Boil up a concentrated solution of oxalic acid, and add to it as much molybdic acid as it will dissolve. Preserve the solution in black bottles. The characters written with it are at first invisible, but exposed to the sun they turn dark blue, and, when heated, black.

XXXII.

STAMPING INKS.

These are made in various colours, and their manufacture has become an important branch of our industry since the introduction of self-inking stamps.

A good stamping ink must give a clean impression, and must not dry quickly on the stamp, so as to fill the engraving on it and make the impression indistinct. This is of especial importance with india-rubber stamps, as such stamps cannot be cleaned with a brush, which would destroy the sharp outlines of the letters and make the stamp useless.

Ordinary printers' ink has been much recommended as a stamping ink, and is most excellent for the purpose, except for one thing. It gives a sharp, black impression which dries very quickly on the object stamped, but the ink dries almost as fast on the stamp. This may be remedied, however, by dilution with one-tenth to one-sixth of its volume of filtered linseed oil. Too much of the oil must, however, not be added, for it will not only make the ink too thin and pale, but will cause the impression to be surrounded with a transparent, greasy border.

BLACK STAMPING INK.

Finest lampblack	10
Gum	4
Glycerine	4
Water	3

Dissolve the gum in the water, add the glycerine, and rub the mixture up intimately with the lampblack. The glycerine, which is thick but not greasy, absorbs moisture from the air, and so keeps the ink liquid. For very minutely engraved stamps the proportion of black is increased, to make the ink rather thicker. This excellent ink will not run, and gives very sharp impressions.

COLOURED STAMPING INKS.

These are obtained by replacing the lampblack in the last recipe by other pigments, according to the colour desired, such as chrome-yellow, red lead, ochre, green cinnabar, green ultramarine, indigo, ultramarine, Prussian blue, red ochre, umber, etc.

ANILINE STAMPING INKS.

Very beautiful stamping inks can be made with the coal-tar colours, but some skill is required in doing so. The manufacture is simple enough if the dyes are used in the solid form, for they have merely to be rubbed up to a uniform mass with glycerine and mucilage. If, however, they are to be used in solution, it must be a concentrated solution in the strongest spirit. To this solution glycerine is first added, and the gum is put last, and very gradually. It is also a good plan to replace from a quarter to a third of the gum by sugar.

SOLUBLE STAMPING INKS.

Since the discovery of aniline dyes soluble in water the manufacture of excellent stamping inks has become very simple with their aid. The best to use is water-soluble blue. This is made into a syrup with glycerine. This syrup is applied with a brush to a smooth, soft pad, and rubbed in uniformly with a wooden spatula. A single application to a small pad of about 8 square inches area is enough to enable a rubber stamp to produce hundreds of impressions. The composition of the ink depends on whether it is to be placed on a pad or is to be filled into a soft inking stamp. In the first case it must be thick, so that enough may adhere to the stamp to give a good impression. In the latter case, where the ink has to pass through a filter to the stamp from a reservoir, it must be more fluid, so that it will pass through fast enough to allow the stamp to be quickly used many times.

INDELIBLE STAMPING INK.

Many textile manufacturers desire to so mark their goods that they can be washed, bleached, and dyed without affecting the marking.

One body only is known which resists all chemical reagents entirely, namely carbon. Hence an indelible stamping ink must contain that pigment. The best is ordinary printing ink diluted with one-quarter of its volume of good boiled linseed oil, which makes it penetrate deeply into the fabric and become absolutely indelible. All known bleaching agents leave it quite unchanged. It can, it is true, be hidden by dyeing the fabric, but then if the dye is destroyed with chlorine water or very dilute aqua regia, the marking shows up with perfect distinctness.

XXXIII.

LAUNDRY OR WASHING BLUE.

It is well known that the last rinsing water is mixed with a little blue to neutralise the yellow tinge of the linen and make it a pure white. Many blues are put on the market for this purpose, such as smalts, Prussian blue, sulpho-indigotic acid and indigo-carmine, both in a solid state and as solutions.

It is easy to see that solutions of colouring matter are preferable to solid powders, as they can reach the interior of the fibre, while the powders can only adhere mechanically to the outer surface.

A.—Insoluble Laundry Blue.

Smalts.

Smalts or eschel is a blue glass. It is made by fusing cobalt ores with carbonate of potash and quartz. The glass is ground and levigated with the greatest care. Smalts is thus obtained in several different degrees of fineness and shade of colour.

When smalts is used as a laundry blue it must be carefully mixed uniformly with the starch, which makes it adhere to the garment. There is a powdered washing blue on the market which is an intimate mixture of smalts and starch. When boiled with water it is used in the laundry.

Prussian Blue.

This has already been spoken of several times in this book. It is dark blue with a coppery shade, and the darker sorts are called Paris blue.

If we make our own Prussian blue and leave the wet precipitate for some hours in strong nitric acid, we shall get a product equal to the best Paris blue.

Prussian blue, like smalts, can only be used in combination with starch or gum. It is a very intense colour, so that care must be taken that it does not make the linen look blue instead of white.

A great drawback to the use of Prussian blue as a washing blue consists in the fact that linen on which it has been frequently used gradually assumes a yellow tinge, owing to the action of the washing soda and soap in the Prussian blue and the slow formation of brownish-yellow oxide of iron on the fabric

B.—Soluble Laundry Blue.

Soluble Prussian Blue.

This is prepared for laundry purposes exactly as for ink making. It can be poured into the water in which the linen is rinsed, and need not be mixed with starch or gum.

Although the soluble Prussian blue has the same drawback as that just mentioned as attaching to the ordinary pigment, it has it to a much smaller extent, as the oxalic acid in which the blue is dissolved has also a solvent action on the oxide of iron.

It may here be mentioned that iron-moulded linen can be made perfectly white again by twenty-four hours' immersion in a one-tenth per cent. solution of oxalic acid in distilled water.

Indigo Laundry Blue.

These are the most to be recommended of all washing blues, as they injure the washing in no way, are all freely soluble in water, and adhere very uniformly to the linen. They are used either as sulpho-indigotic acid, which is only employed in solution, or as indigo-carmine, which may be used as a powder, as a paste, or in solution.

Sulpho-indigotic Acid.

This is easily made by thoroughly drying powdered indigo, and then stirring it up with twice its weight of fuming sulphuric acid. The mass, which gets very hot, is well stirred with a stout glass rod, and then left to stand for twelve hours. The whole is then put into a funnel plugged with asbestos. The solution of sulpho-indigotic then drains through. It will be so strong as to look quite black. The insoluble residue on the filter should be rinsed with water, and the rinsings allowed to mingle with the rest of the filtrate. The washed residue is again dried, and serves for the production of more sulpho-indigotic acid with a fresh lot of ingredients. It is of great importance that the indigo should in each operation be in excess of the sulphuric acid, so that none of that acid can be present in the solution of the sulpho-indigotic acid. Such an excess would have a most destructive effect upon the garments. The solution of sulpho-indigotic acid may be bought concentrated under the name of indigo washing blue essence, or diluted, as indigo washing blue. A few drops of the essence are sufficient for a large washing tub of water.

Indigo-carmine.

The preparation of this substance has been already described. We have, therefore, only to say a few words about the various forms in which it comes upon the market.

The paste form, although highly concentrated, is not favoured by the laundry trade, as it is so difficult to avoid taking too much of it, and so making the linen blue. The solution is sold in different degrees of concentration, as indigo-carmine essence and indigo-carmine washing blue. The essence is made by adding to the paste just enough water to make a solution. It looks quite black, except in very thin layers indeed.

Solid Indigo-carmine Laundry Blue Tablets.

Indigo-carmine is triturated with sufficient potato flour to make a thick paste which is rendered homogeneous by beating it with a block of wood and mixing on a stone slab, and is then pressed into moulds similar to those used in making water-colour tablets. The cakes are detached by tapping the moulds, and are placed in a warm room to dry, being turned over repeatedly and left until they have acquired a surface gloss and no longer colour the fingers when touched. For use, the tablets are placed in water, in which they fall to pieces, producing a blue solution with a deposit of starch. They may also be boiled in water, in which case the starch thickens, the resulting dark blue paste being easily distributed in water.

THE END.

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cane-sugars and syrups is optically inactive, but the statement seems to have been disproved by Meissl. Besides, in raw beet-sugars and syrups, raffinose, a very strong dextro-rotatory sugar, is found vitiating the readings for cane-sugar. The correction of the original polarization in such cases is most generally made by the method of inversion proposed by Clerget. The direct polarization is taken in the usual way, and a part of the solution remaining from the one hundred cubic centimetres prepared for this test is put into a 50-cubic-centimetre flask, which has also a 55-cubic-centimetre mark on the neck. Fifty cubic centimetres having been taken, five cubic centimetres of concentrated hydrochloric acid is added, and the whole heated on a water-bath to 70° C. for some ten minutes. This suffices to completely invert the cane-sugar present, while the original invert sugar is unacted on. The flask is then cooled, and part of the liquid is filled into a 220-millimetre tube, closed by glass plates at both ends and provided with a tubulure in the side so that a thermometer may hang suspended in the liquid when the observation is made. The reading will generally be much reduced from the original dextro-rotatory reading, and may even be some degrees to the left. If, then, S represent the sum or difference of polariscope readings before and after inversion (difference if both are to the right, sum if the second reading is to the left), T the temperature of the inverted solution when polarized, and R the correct percentage sought, $R = \frac{200\ S}{285 - T}$. Clerget has also prepared an elaborate set of tables which make the use of the formula unnecessary. (See also under molasses, p. 178.)

(*B*) *Chemical Methods.*—The only chemical method for the determination of cane-sugar ever resorted to is the inversion of the cane-sugar, neutralizing with sodium carbonate, and determination of the reducing sugar so obtained by the method to be described under the next head. The inversion takes place in definite proportions, so that nineteen parts of sucrose produce twenty parts of the invert sugar. When invert sugar is also present in the solution of which the cane-sugar is to be determined by inversion, the former is first estimated as a separate operation, and then a portion of the original solution is inverted, and the total invert sugar, including that formed from the cane-sugar, is determined.

2. DETERMINATION OF GLUCOSE, OR INVERT SUGAR.—The oldest method is that based on Trommer's reaction as applied to sugar analysis by Barreswill and Fehling. This depends upon the fact that an alkaline solution of copper oxide containing a fixed organic acid, as tartaric, is reduced with the separation out of insoluble cuprous oxide by dextrose, or invert sugar, while cane-sugar has no effect. The composition of a standard Fehling's solution, as it is called, is thus given,* 34,639 grammes crystallized copper sulphate are dissolved in water and brought to 500 cubic centimetres; 173 grammes Rochelle salt and 50 grammes sodium hydroxide are also dissolved in water and brought to

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500 cubic centimetres. Equal volumes of these solutions are mixed when required for use and constitute the correct Fehling's solution. The ready-prepared Fehling's solution changes in the course of some days in effective power even when kept in a cool place and in the dark. Ten cubic centimetres of the Fehling's solution given above correspond to .05 gramme dextrose, or invert sugar, or .0475 gramme cane-sugar made active by inversion. For technical determinations merely the work with the solution can be volumetric; for more exact scientific purposes it must be gravimetric, weighing the copper as metal or as cupric oxide. In carrying out the volumetric test, the sugar solution in which glucose is to be determined is placed in a burette. If dark, it may be previously cleared with a small quantity of bone-black, or if it be some of the solution prepared for polarization, it is prepared without lead solution, an aliquot portion taken out for this glucose determination, and the remainder treated with a measured quantity of the lead solution, for which allowance is made. Any lead in this glucose solution must be eliminated thoroughly. This is best done with sulphurous acid, the change of strength in the liquid being noted. Ten cubic centimetres of the mixed Fehling's solution are now measured into a porcelain dish, diluted with twenty or thirty cubic centimetres of water and brought quickly to boiling, when the sugar solution is run in two cubic centimetres at a time, boiling between each addition. When the blue color has nearly disappeared the sugar solution should be added, in small amount but still rapidly. The end of the reaction is reached when a few drops of the supernatant liquid filtered into a mixture of acetic acid and dilute potassium ferrocyanide give no brown color.

In carrying out the gravimetric method the Fehling's solution remains in excess, while the precipitated cuprous oxide is carefully filtered off and further treated. The procedure is as follows: Sixty cubic centimetres of the mixed Fehling's solution and thirty cubic centimetres of water are boiled up in a beaker glass, twenty-five cubic centimetres of the dextrose solution of approximately one per cent. strength added, and the mixture again boiled. It is then filtered with the aid of a filter-pump upon a Soxhlet filter (asbestos layer in a tared funnel of narrow cylinder shape), quickly washed with hot water, and then with alcohol and ether, and dried. The asbestos filter, with the cuprous oxide, is now heated with a small flame, while a current of hydrogen is passed into the funnel, so that the precipitate is reduced to metallic copper. It is allowed to cool in the current of hydrogen, placed for a few minutes over sulphuric acid, and then weighed. A table has been constructed by Allihn which gives in milligrammes the dextrose corresponding to the weight of copper found.

Other methods for the determination of dextrose are those of Defren, who determines the copper as cupric oxide (Leach, Food Inspection, 2d ed., p. 593); of Munson and Walker, who weigh the copper as cuprous oxide (*Ibid.*, p. 598); and of Soldaini, who uses a solution of basic carbonate of copper dissolved in potassium bicarbonate. This last reagent in that it is more sensitive to glucose and is much less affected by cane-sugar even after prolonged boiling.*

3. Analysis of Commercial Raw Sugars.—Raw sugars contain, besides the cane-sugar, invert sugar, moisture, mineral salts, organic non-sugar, and insoluble matter. Raw beet-sugars contain, in addition to the sucrose and glucose just mentioned, small quantities of raffinose, a variety of sugar found in the beet juice and present in all the products from it.

The cane-sugar present is partly crystallized and partly uncrystallizable. Both are, of course, counted together in the polarization figures, but only the first is capable of extraction in the refining process. The method of estimating the crystallized cane-sugar for itself will be described later on. The polarization methods have already been described. In raw sugars containing much invert sugar, such as those from the cane, the double polarization (before and after inversion) is alone to be relied upon.

The methods for glucose have also been described.

The determination of moisture is made by taking five grammes of the sample and drying it spread out on a weighed watch-crystal in an air-bath not over 100° C. until it ceases to lose weight. As sugars containing much glucose cannot stand the heat without some alteration, in their case a lower temperature (about 70° C.) is used. For very syrupy sugars and melados it becomes necessary to dry with the addition of a weighed amount of clean sand. Drying in a vacuum is also practised in many cases, as the operation is shortened and less risk of alteration exists.

The mineral salts are determined as ash. The following analyses give the average composition of raw cane- and beet-sugar ash according to Monier:

	Cane-sugar.	Beet-sugar.
Potassium (and sodium) carbonate	16.5	82.2
Calcium carbonate	49.0	6.7
Potassium (and sodium) sulphate	16.0	
Sodium chloride	9.0	
		11.1
Silica and alumina	9.5	None.
	100.0	100.0

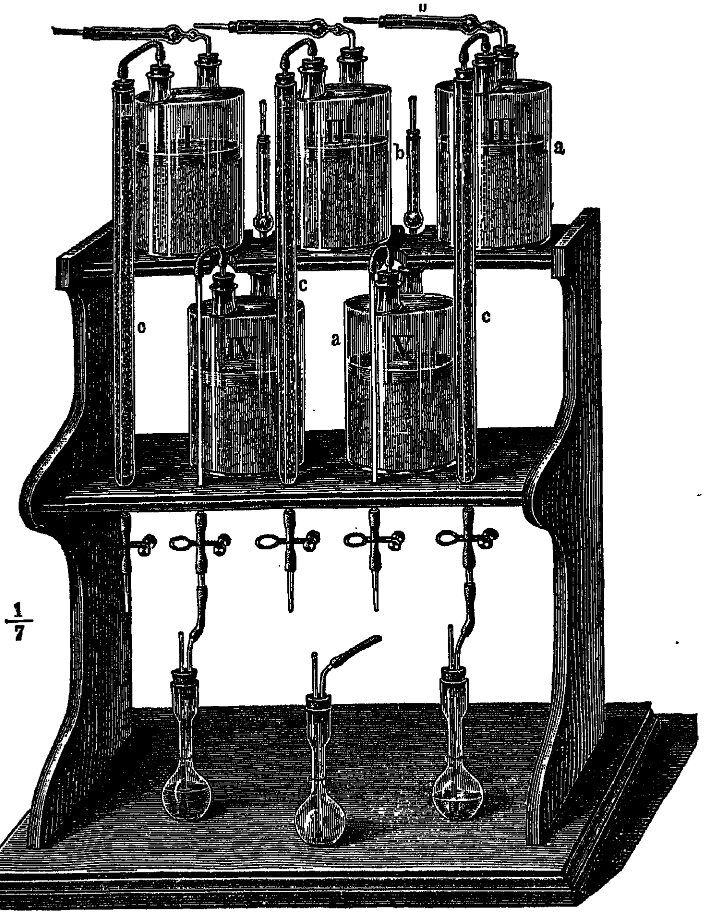
Owing to this decided difference it is much easier to get the ash of cane-sugars completely burned and in weighable condition than that of beet-sugars, which contain so much of the deliquescent and alkaline carbonates. To obviate this difficulty, Scheibler proposes to treat the sugar with sulphuric acid before igniting it, by which means the ash obtained contains the bases as non-volatile, difficultly fusible and non-deliquescent sulphates instead of as carbonates. A deduction of one-tenth of the weight of the sulphated ash must be made in this case for the increase due to the sulphuric acid. The soluble and insoluble ash are often distinguished in addition to total ash. In ordinary commercial analyses of sugars, the sum of the cane-sugar, glucose, ash, and water is subtracted from one hundred, and the difference called organic or undetermined matters. This would include both the soluble organic impurities and the insoluble impurities, such as fibre and particles of cane. Two processes have been proposed for determining the soluble organic impurities separately: Walkoff's method of precipitation with tannin, and the basic acetate of lead method. Neither method is in very general use.

As before stated, the full analysis of a raw sugar will not give any exact measure of its refining value,—that is, of the amount of crystallized cane-sugar that can be extracted from it. The so-called method of coefficients adopted in France, whereby five times the ash, plus once or twice the glucose percentage subtracted from the cane-sugar percentage, is taken to represent the crystallized cane-sugar obtainable, is not much to be depended upon. The true refining value, or *rendement,* of a raw sugar can, however, be determined by a special procedure first proposed by Payen and afterwards improved by Scheibler. The process depends upon the fact that if raw sugars be treated with a saturated alcoholic solution of cane-sugar acidified with acetic acid, the coloring matter and other impurities, together with the syrup and other uncrystallizable constituents, are removed, while the crystallized sugar remains unchanged. The sugary alcoholic liquids are then displaced by absolute alcohol. Fig. 52 shows the arrangement of vessels. The bottle I contains eighty-five per cent. alcohol, to which fifty cubic centimetres of acetic acid is added per litre, and the mixture allowed to stand in contact with an excess of powdered white sugar for a day, being shaken at intervals; bottle II, alcohol of ninety-two per cent. saturated as the other, but without acetic acid; bottle III, alcohol of ninety-six per cent., also saturated with sugar; and bottle IV, a mixture of two-thirds absolute alcohol and one-third ether. Of the sugars to be examined, weights are taken corresponding to the polariscope used, placed in the upright tubes, washed with the successive solutions, and dried by the aid of a filter-pump ready for use in the polariscope test. In carrying out the process, the alcohol and ether mixture is first run in that it may take up any moisture and throw out the sugar that such moisture may have dissolved, then successively down to No. I, which is the effective washing solution. This is then displaced by Nos. II, III, and IV in succession. The method is thoroughly reliable, but great care must be taken to keep the alcoholic solutions just saturated with sugar through all changes of temperature.

4. Analyses of Molasses and Syrups.—The composition of both the cane-sugar and the beet-sugar molasses have already been given (see p. 169), and it was seen that they differed notably. Both still contain considerable quantities of sucrose, but for different reasons. With the cane-sugar molasses because of the invert sugar, with the beet-sugar molasses because of the melassigenic salts. In either case the polariscope reading for sucrose must be corrected by inversion. The glucose is determined as described under raw sugars. The water is determined by weighing

until constant. Drying in a partial vacuum also facilitates the drying off of the moisture. The ash is determined as with raw sugars, sulphuric acid being added, and the bases weighed as sulphates instead of as carbonates, the proper correction being made. The organic non-sugar is simply taken by difference as with raw sugars. The determination of raffinose in raw beet-sugars, and particularly in beet-molasses, has attracted much attention in recent years. Creydt* has suggested a way for determining it in the presence of cane-sugar in connection with the method of inversion. He finds that while cane-sugar polarizing 100° to the right before inversion polarizes 32° to the left after inversion, a change of 132°, raffinose changes from 100° to 50.7° only, a change of 49.3°. He proposes two formulas: $A = z + 1.57\ R$, and $c = 1.322 + 1.57\ R \times .493$, in which A is the direct polarization, c the polarization after inversion, z the percentage of cane-sugar and R that of raffinose.

FIG. 52.



From these formulas, A and c being known, z and R can be found. The reading after inversion must be taken uniformly at 20° C.

5. ANALYSES OF SUGAR-CANES AND SUGAR-BEETS AND RAW JUICES THEREFROM.—The very different physical characters of the sugar-cane and the sugar-beet, the one a bamboo-like shell enclosing a woody pith, and the other a soft root easily brought into pulpy consistency, make the work upon them quite different. In the case of the cane, the samples to be analyzed are weighed and then pressed between rolls, moistened with hot water and again pressed, and this repeated several times. The exhausted stalk, or "bagasse," is usually not further examined, but in the juice the sucrose, glucose, ash, and organic non-sugar are determined as before described. In all analyses of raw cane juices the percentage of total solids is determined by the Brix saccharometer or "spindle." The form of hydrometer in most general use is known as the Balling or Brix, and its readings indicate directly the percentage of impure sugar or solid matter dissolved. Sets of tables also allow of the conversion of the Brix scale into direct specific gravity figures. (See Appendix, p. 570.) With the aid of the specific gravity determination it is possible to make a rapid analysis of raw juice without weighing. The method adopted by Crampton,* one of the chemists of the United States Bureau of Agriculture, for this analysis is to measure out a certain volume of the juice, add lead solution, make up to another definite volume, polarize, and apply the correction for specific gravity to the reading obtained. A set of tables for this correction and the factor needed in the glucose determination are given by Crampton.

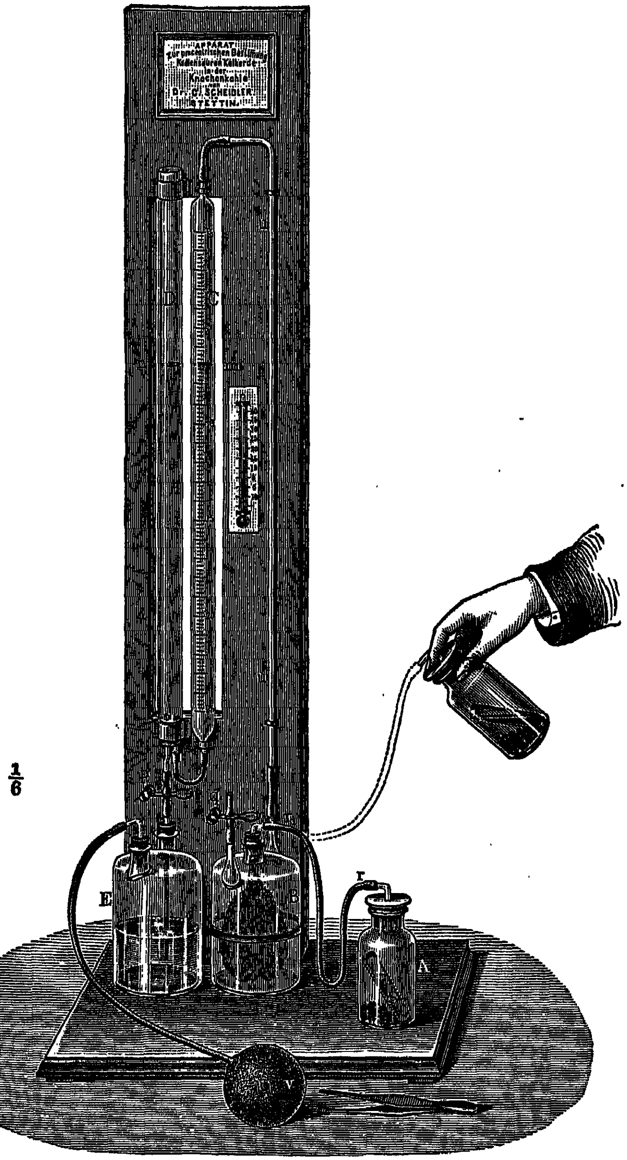
In the examination of sugar-beets, the system of pressing and moistening with hot water can be followed for the extraction of the juice, but the method proposed by Scheibler of extracting the sugar from a weighed quantity of the pulp by the aid of alcohol is much better. This is accomplished by the aid of a Soxhlet or other extractor (see p. 86) connected with an upright condenser. After complete extraction and cooling the necessary amount of lead solution is added, and the liquid brought up to the mark with absolute alcohol and then polarized. Degener has described a still simpler form of extraction, originally suggested by Rapp, in which the pulp remains in the alcoholic solution until after it is cleared with the lead solution and brought to the mark, when it is filtered and polarized. A correction must in this case be applied to the reading on account of the volume occupied by the pulp in the measured liquid.

The amount of dry residue, or "marc," of the beet can be determined in the Scheibler extraction method at the same time by taking the exhausted residue, drying it in a current of air, and weighing it. The moisture and ash of the beet are determined as with raw sugars. The organic non-sugar is gotten by difference or by one of the methods mentioned under raw sugars.

6. ANALYSES OF SIDE-PRODUCTS.—(a) *Of Bone-Black.*—Careful anal-

yses of both fresh char and that which is in use are needed to allow of the proper control in filtration. The most important determinations are those of water, carbonate of lime, carbon, and specific gravity, as upon the changes in these depend in the main its efficiency. The water is determined by drying for several hours at 140° C. The sample should not be powdered. The carbon is determined by treating a weighed quantity of the char with pure hydrochloric acid, with the aid of heat, on a water-bath until the soluble portions have been dissolved, diluting and filtering upon a weighed quantitative filter. After thorough washing with hot water, the filter and contents are dried at 100°, placed between watch-glasses and weighed, again heated and weighed as long any loss of weight is shown. The filter and carbon are then transferred to a weighed crucible and ignited. The insoluble residue, taken from the previous weight, minus the weight of the filter, gives the amount of carbon. The estimation of carbonate of lime in case the char is used with cane-sugar or juices is of much less importance than when the char is used with beet-sugars or juices. In the former case, the percentage decreases at first, and then remains nearly stationary, in the repeated use of the char, while in the latter case it would increase steadily, because of the more thorough liming and carbonatation to which the beet juices are subjected, were it not for the treatment with hydrochloric acid in the revivifying of the char. (See p. 165.) To allow of the proper judgment in this use of hydrochloric acid, it becomes necessary in beet-sugar working to determine carefully the amount of carbonate of lime taken up by the char in using before starting the revivification. It is almost universally done at present by the aid of the Scheibler apparatus, shown in Fig. 53. The normal quantity of pulverized char (1.702 grammes) is placed in *A*, and the tube *S* filled with acid to the mark is carefully placed in the bottle. *E* is then filled with water, and the operator, by means of the compression-bulb, forces the liquid into *D* and *C*, which connect at the base, until it reaches a little above the zero-point in *C*, when it is allowed to flow out by opening the pinchcock at *p* until the level in *C* is at zero. The stopper now being placed in *A*, a connection with *B* is made by the tube *r*. If the level of the liquid in *D* and *C* be then unequal, the equality may be restored by opening the cock *q* for a few seconds, and which for the rest of the operation remains closed. The vessel *A* is now held, as shown in the cut, so that the acid may come in contact with the char, and the bottle gently shaken to cause the acid to mix thoroughly with the assay. The pressure of the gas evolved distends the rubber bag in *B* and depresses the column of water in *C*. The stopcock *p* is now opened to allow the water in *D* to flow out sufficiently rapidly to keep the level in *C* and *D* as near the same as possible during the progress of the determination. When all the gas has been given off and the level of the liquid in *C* becomes stationary, *p* is closed, after bringing the water in *D* to the same level as that in *C*, and the volume and temperature read off. A set of tables accompanying the instrument bonate of lime in the char, any excess, as shown in this determination, can have its equivalent in hydrochloric acid of known strength calculated, and thus the acid treatment in the revivifying process can be made accurate.

FIG. 53.



In determining specific gravity, both apparent and real specific gravity (the latter after boiling the char with distilled water to displace (*b*) *Of Scums, Press-cakes, and Sucrates.*—In the case of the scums and press-cakes obtained in the manufacture of raw sugars, their chief value is in the lime salts they contain, which, notably in the case of beet-sugars, adapt them for use as fertilizing materials. They, however, contain such amounts of sugar, either mechanically held, or, where the carbonatation process has been used, as sucrates, as make it necessary to determine regularly the sucrose in them. In the case of the thin scums from cane-sugar working, the determination can be made exactly as with an impure juice before described. In the case of the heavier press-cake from beet-sugar working, resulting from carbonatation, the procedure is different. Here the sucrate of lime is to be decomposed if possible without decomposing the large amount of accompanying carbonate of lime. This is done by careful addition of acetic acid, controlling the reaction with phenol-phthaleïn. For details of this process, first proposed by Sidersky, see Frühling and Schultz, "Anleitung zür Zucker Untersuchungen," 3d ed., p. 171.

Sucrates, resulting from the working of molasses for sugar by either of the lime or strontium processes (see p. 162), are analyzed by a somewhat similar procedure, using strong acetic acid to set the sugar free from its combination with the lime or strontia and phenol-phthaleïn as an indicator. The excess of acid is afterwards neutralized, lead solution added, the solution brought to strength, and polarized. (Ibid., p. 155.)

V. Bibliography and Statistics.

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STATISTICS.

1. Sugar Production of the United States.—The U. S. Census of 1910 gives the production as well as importations of sugar for 1909 as compared with the figures for the three previous decades:

A. Sugar from Cane in 1909.

Louisiana	325,500 short tons.
Texas	8,600 short tons.
	334,100 short tons.

B. Sugar from Beets in 1909.

	Granulated sugar (tons).	Raw sugar (tons).	Molasses (gallons).
California	126,600	200	2,135,800
Colorado	147,000	1,600	7,669,200
Michigan	103,900	600	5,016,700
Wisconsin	13,000	.....	832,400
All other States	106,300	2,500	5,158,700
Total	496,800	4,900	20,812,800

C. Comparison of Production and Imports.

	Production (in tons).			Imports (in tons).		
	Cane.	Beet.	Total.	Non-contiguous U. S.	Other countries.	Total.
1909	334,100	501,700	835,800	927,800	1,959,300	2,887,100
1899	161,300	81,700	243,000	313,400	1,695,600	2,009,000
1889	150,600	2,500	153,100	280,600	1,186,400	1,467,000
1879	89,400	1,400	90,800	139,200	775,400	914,610

. PRODUCTION, IMPORTATION, AND CONSUMPTION FOR THE UNITED ES IN 1910.—The Bureau of Statistics reports for the year ending e 30, 1910, as follows:

	1910 (tons).	1909 (tons).
Production of sugar from cane (in tons)	362,500	414,500
Production of sugar from beet (in tons)	512,500	483,500
Total production in United States	887,500	898,500
Hawaii	555,500	511,500
Porto Rico	284,500	244,000
Philippines	88,000	42,000
Total from U. S. dependencies	928,000	797,500
Total from U. S. and dependencies	1,815,500	1,695,500
Importation from Cuba	1,755,000	....
Importation from Dutch Indies	157,500	....
Total imports	1,959,000	2,053,800

onsumption for 1910, 7550 million pounds = 82 pounds per capita.

3. SUGAR-BEETS WORKED AND BEET-SUGAR PRODUCED IN EUROPE.

	Sugar-beets worked (tons).		Beet-sugar produced (tons).	
	1910–11.	1909–10.	1910–11.	1909–10.
Germany	15,275,380	12,904,795	2,424,840	2,027,272
Austria-Hungary	9,981,400	8,166,100	1,529,800	1,245,608
France	5,383,000	6,246,850	703,330	803,006
Belgium	1,932,000	1,777,600	271,800	248,403
Holland	1,523,000	1,330,000	221,400	194,822
Russia	13,080,400	6,837,498	2,085,200	1,123,594
Sweden	1,088,300	897,000	167,160	127,000
Denmark	750,000	500,000	105,000	65,000
Italy	1,500,000	970,000	170,000	118,900
Spain	490,000	667,000	60,000	83,000
Rumania	275,000	208,000	35,000	30,775
Servia	75,000	66,000	10,000	8,630
Bulgaria	35,000	20,000	4,200	2,435
Switzerland	25,000	25,000	3,500	3,500
	51,413,480	40,415,843	7,791,330	6,081,945

CHAPTER V.

THE INDUSTRIES OF STARCH AND ITS ALTERATION PRODUCTS.

I. Raw Materials.

Starch is one of the most important, as well as most widely occurring, productions of the vegetable kingdom. It constitutes, either when extracted from vegetable raw materials, or more generally in admixture with the other plant constituents, the staple article of food for the great bulk of the human race. It is only necessary to call attention to the fact that the principal cereal grains used throughout the world for food contain starch as their chief ingredient, and that the tubers of many plants and the stems and roots of some trees also yield starch in great abundance.

The most complete enumeration and classification of starches is that of Muter as amplified by Allen[*] and Blyth,[†] by which they are divided into five groups on the basis of their physical and microscopical differences, as follows:

I. *The potato group* includes such oval or ovate starches as give a play of colors when examined by polarized light and a selenite plate and having the hilum and concentric rings clearly visible. It includes *tout les mois,* or canna arrow-root, potato starch, maranta, or St. Vincent arrow-root, Natal arrow-root, and curcuma arrow-root.

II. *The leguminous starches* comprise such round or oval starches as give little or no color with polarized light, have concentric rings all but invisible, though becoming apparent in many cases on treating the starch with chromic acid, while the hilum is well marked and cracked, or stellate. It includes the starches of the bean, pea, and lentil.

III. *The wheat group* comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes the starches of wheat, barley, rye, chestnut, and acorn, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, etc.

IV. *The sago group* comprises those starches of which all the granules are truncated at one end. It includes sago, tapioca, and arum, together with the starch from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.

V. *The rice group.* In this group all the starches are angular or polygonal in form. It includes oats, rice, buckwheat, maize, dari, pepper, as well as ipecacuanha.

In addition to the differences in form and marking mentioned above,

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[*] Com. Org. Anal., 2d ed., vol. i, p. 335.

starch-granules differ in size according to their different sources, so under the microscope they can be distinguished by the measure- .t of the average diameter of the granule. This ranges, according to marsch, from .01 to .815 millimetre, or from .0004 to .0079 inch.

For practical purposes we may now speak of two classes only of these ch-containing materials,—vix., the cereals and the plants in which starch is extracted from tubers, roots, or stems, such as potatoes on one hand; and the West Indian starch preparations, like arrow-root,), and tapioca, on the other. As before stated, starch is the chief :edient in the cereals, but not at all the only one. The composition he more important cereals is thus given by Bell:*

CONSTITUENTS.	Wheat. Winter sown.	Wheat. Spring sown.	Long-eared barley.	English oats.	Maize.	Rye.	Carolina rice (without husk).
. . . .	1.48	1.56	1.03	5.14	3.58	1.43	0.19
'ch	63.71	65.86	63.51	49.78	64.66	61.87	77.66
ar (as sucrose)	2.57	2.24	1.34	2.36	1.94	4.30	0.88
umen (insoluble in alcohol)	10.70	7.19	8.18	10.62	9.67	9.78	7.94
'ogenous matter (soluble in alcohol) .	4.83	4.40	3.28	4.05	4.60	5.09	1.40
ulose	3.03	2.93	7.28	13.53	1.86	3.23	Traces.
ıeral matter	1.60	1.74	2.32	2.66	1.35	1.85	0.28
sture	12.08	14.08	13.06	11.86	12.34	12.45	12.15
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The chemical formula of starch is $(C_6H_{10}O_5)_n$. According to Tollens, firmed by Mylius, it is $C_{24}H_{40}O_{20}$; according to Brown soluble starch $_{120}H_{200}O_{100}$, while for the ordinary variety he proposes $C_{180}H_{300}O_{150}$. ;eli stated that by subjecting the starch-granules to the slow action ıaliva, salt solutions, and dilute acids two substances could be shown ıe present, *granulose*, which dissolved, and *cellulose* (or, as it has been ed, *farinose*), which remained. Arthur Meyer considers that there ınly a single substance originally present, and that the cellulose, or ınose, which remains is a decomposition product of the starch.

Air-dried starch always retains from eighteen to twenty per cent. of ·er. It is soluble in cold water, alcohol, ether, ethereal and fatty oils. en it is heated with twelve to fifteen times its bulk of water to 55° C., ıegins to show signs of change, swelling up, and at a temperature from 70° to 80° C. (or even below 70° C. with some pure starches) granules burst and it becomes a uniform translucent mass, known 'starch-paste,'' which is not, however, a solution, as the water can be zen out of it. Boiled with water for a long time it goes into solution, part dissolving in fifty parts of water. The action of heat upon 'ch is to change it gradually into *dextrine*, which is soluble in cold ;er.

One of the best known of the reactions of starch is the formation of a e color with iodine. This has been carefully studied by L. W. Anws (*Jour. Amer. Chem. Society*, 1902, p. 865), who considers it to be a dissociable addition compound of iodine with starch molecules. He finds that clear starch solutions made at a temperature of about 150° take up in the cold an amount of iodine corresponding to the formula $(C_6H_{10}O_5)_{12}I$, while starch heated with excess of iodine to 100° for a short time takes up an amount of iodine corresponding to the formula $(C_6H_{10}O_5)_{12}I_2$. The blue coloration is constantly availed of to note the presence or gradual disappearance or alteration of starch in many technical processes.

The action of dilute acids upon starch brings about the change known as "hydrolysis," and there is produced *dextrine*, $C_{12}H_{20}O_{10}$, and *dextrose*, $C_6H_{12}O_6$, the latter eventually as sole product. Many ferments, like saliva, the pancreatic ferment, and especially the diastase of malt, produce in starch a somewhat similar change and yield *maltose*, $C_{12}H_{22}O_{11}$, and a number of intermediate products between this and starch. A great deal of investigation has been devoted to these intermediate products, and as yet no absolute agreement has been reached on the subject. The following is the series of products obtained in this hydrolysis of starch as stated by Tollens:*

Starch		gives a blue iodine reaction.
Soluble starch (amylodextrine)		gives a blue iodine reaction.
Dextrines	erythrodextrine	gives a violet and red iodine reaction.
	achroödextrine	gives no iodine reaction.
	maltodextrine	gives no iodine reaction.
Maltrose		reduces Fehling's solution, but not Barfoed's reagent.
Dextrose		reduces Fehling's solution, and also Barfoed's reagent.

Other chemists notably increase the list of these intermediate products. The existence of erythrodextrine as a distinct compound is doubted by some investigators, who consider it to be merely a mixture of achroö- or maltodextrine with a little soluble starch, such a mixture giving a violet reaction with iodine. By over-treatment with acids unfermentable carbohydrates, of a character differing from any of the products named, appear to form. The name *gallisin* has been given to a compound of this kind, and the formula $C_{12}H_{24}O_{10}$ ascribed to it. For a description of the conditions of its formation see later (p. 197).

Strong nitric acid in the cold acts upon starch, producing nitro derivatives, such as mono-, di-, and tetra-nitro starch, analogous to the nitrocelluloses. Alkalies and alkaline earths form combinations with starch, the barium and calcium compounds being insoluble, of which advantage is taken in the Asboth method for determination of starch. (See p. 199.)

II. Processes of Manufacture.

1. Extraction and Purifying of the Starch.—Of the various starch-containing materials before enumerated, only a limited number are actually utilized for the extraction of the starch in a pure condition,—

viz., maize, wheat, rice, potatoes, and arrow-root. In the United States by far the greater amount is obtained from maize, or Indian corn, a limited amount only being extracted from wheat. In Europe, on the Continent, potatoes serve as the chief starch-producing material, some also being extracted from wheat and some from rice, while in the West Indies arrow-root starch is manufactured at St. Vincent and elsewhere.

In the manufacture of corn starch, after winnowing or cleansing the corn by powerful fans, it is placed in large wooden steeping-vats, holding several thousand bushels of corn, and is covered with warm water at about 140° F., to which is frequently added sulphur dioxide, making a solution of 1° B. sulphurous acid. After twelve hours this water is run off and the germ is separated after a crushing of the softened corn. While the germ is afterwards worked for the corn oil contained, the starchy portion is ground again and passes on to the separator tables, where it is continuously washed. These separator tables are inclined sieves of silk bolting-cloth, which are kept in constant motion and are sprayed with jets of water. The starch passes through the bolting-cloth with water as a milky fluid, while the coarser cellular tissue, or husk, of the corn is left behind. This residue is pressed to remove water, and sold as cattle food. The water from the shakers holding the starch in suspension is run into wooden vats, where the starch settles, and the water is drawn off and discarded. The starch is next thoroughly agitated with fresh water, to which a caustic soda solution of 7° to 8° Baumé has been added, until the milky liquid has changed to a greenish-yellow color. The object in adding the alkali is to dissolve and remove the gluten and other albuminoids, oil, etc. After sufficient agitation and treatment with alkali, the separated starch and glutinous matter is allowed to deposit, the supernatant solution of gluten, oil, etc., is allowed to run to waste, and the impure starch washed and agitated with water. It is allowed to stand at rest for fifteen to twenty minutes to permit insoluble gluten to subside, when the top one of a series of plugs arranged in the side of the vat is withdrawn, and the starch suspended in water allowed to flow by means of a gutter into subsiding-vats placed below; then the next lower plug is drawn, and so on until the last plug has been drawn. The plugs are replaced and the vats again filled with water, and the operation repeated as before. This operation, called the siphoning process, is generally repeated three times, and the three runnings of starch are collected in three separate vats, forming the three grades of starch of the factory. These three grades of factory starch are again agitated with water, sieved through bolting-cloth, and run finally as purified starch into wooden "settlers." After it has been compacted sufficiently, which is effected in boxes with perforated bottoms, it is cut into blocks and dried upon an absorbent support of plaster of Paris while heated in a current of warm air. In drying out thoroughly, any remaining impurities come to the surface with the escaping moisture and form a yellowish crust. When this is removed, the interior is found to be perfectly white. The results on a bushel of fifty-six pounds of corn are thus stated by Archbold:*

Starch recovered	28.000	pounds.
Dry refuse for cattle food	13.700	"
Bran (in cleansing process)	0.728	"
Moisture of the corn	5.626	"
Loss (albuminoids, oil, etc.)	7.946	"
	56.000	"

Besides this very complete treatment known as the "alkali process," much of the cheaper grade of starch is purified by the use of sulphurous acid alone without the use of any alkali, and this product is known as "acid process" starch.

In either case the removal of the germ as a preliminary step is now practised, as from this is obtained the valuable maize oil together with oil cake and ground husk for cattle food. The starch is moreover obtained in a higher state of purity and the process considerably shortened, lessening the danger of fermentation or souring while being treated.

In manufacturing starch from wheat two quite different processes are followed, according as the gluten is to be obtained as a side-product or not. In the process generally known as the "sour," or fermentation, process, the gluten is wasted. In this process the wheat is steeped in tanks until thoroughly softened, then crushed in roller-mills, and placed for fermentation in large oaken cisterns. The temperature is here maintained at about 20° C., and the operation lasts some fourteen days, the mass being well stirred during its continuance. The sugar of the wheat and a part of the starch are converted into glucose, which undergoes alcoholic fermentation, and passes by oxidation into the acetous fermentation also, acetic, propionic, and lactic acids being formed. These rapidly attack and dissolve the gluten, liberating the starch-granules. The impure liquor is drawn off from the starch mass, and the latter is washed, either in hempen sacks while being trodden under foot or in drums with perforated sides. After repeated washings and settlings and renewed sieving through fine hair sieves the starch is sufficiently purified. Wheat starch is also obtained from wheat flour without fermentation by what is known as Martin's process, in which a stiff dough is made of the flour. This is then washed in a fine sieve under a jet of water till all the starch has escaped as a milky fluid. This leaves the gluten, of which about twenty-five per cent. of the weight of the flour is gotten suitable for use in the manufacture of macaroni, or to be used instead of albumen or casein in calico-printing.

In the manufacture of potato starch, the potatoes are washed and then pulped by a grating or rasping machine. The grated mass, made into a paste with water, then goes at once into the sieving machine, where it is rubbed by revolving brushes against the wire or hair sides of the

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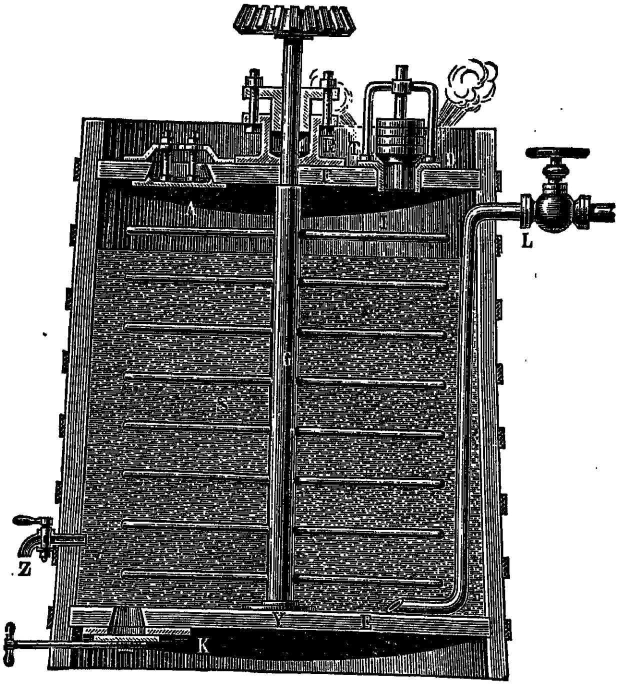
* Journ. Soc. Chem. Ind., 1887, p. 83

tating cylinder, while a current of water is continuously washing out e fine starch from the pulp. The sifted and washed starch deposits large tanks, where it is repeatedly washed by agitation and settling th fresh waters. It is then spread out on absorbent slabs to dry, or ied in drying chambers or kilns heated by steam coils.

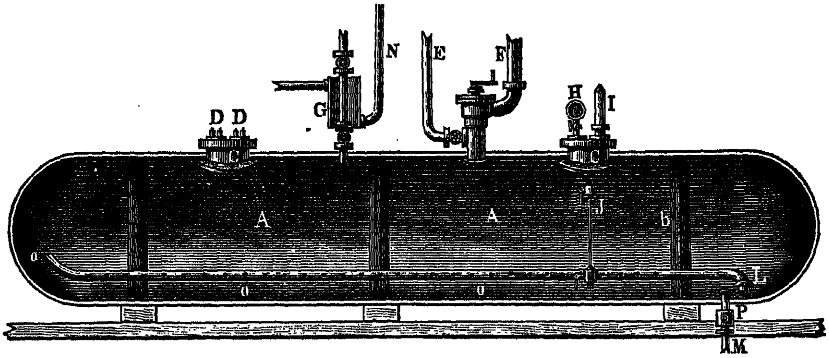
2. MANUFACTURE OF GLUCOSE, OR GRAPE-SUGAR.—As stated on a pre- ling page, the action of dilute acids converts starch into dextrine, ıltose, and dextrose, the last of which becomes by continued action the e product. As it is also the most important product of this action of ds, we shall take it up first. The purified starch obtained as described the preceding section, while yet moist, is taken for the treatment with

FIG. 54.



ı. The "conversion" can be accomplished in either open or closed erters, although the former have been practically entirely super- l by the pressure or closed converters. These converters are large, ;ht vessels of iron or copper lined with sheet lead to prevent the ac- of the dilute acids. Sulphuric acid is generally employed in the con- on if a solid grape-sugar is to be made, or hydrochloric acid prefer- when glucose syrup is the product to be manufactured. Both oxalic and hydrofluoric acid have been used in France as the agents for nversion. The quantity of the acid employed varies with the object manufacturer. For the production of "glucose," a liquid product contains much dextrine, a smaller quantity is used than when is much more complete. The proportion varies from one-half pound oil of vitriol to one and a quarter pounds per hundred pounds of starch. When the open converter is used, a few inches of water is introduced and the acid added, or half the acid may be added to the starch mixture. The acid water is brought to a boil, and the starch, previously mixed with water to a gravity of from 18° to 21° Baumé, is slowly pumped in, keeping the liquid constantly boiling. When all the starch has been introduced, the whole is boiled until the iodine test ceases to give a blue color and shows a dark cherry color. The boiling is usually continued for about four hours. The closed converters may be made from strong wooden vats or may be of copper; they are provided with safety-valves, and are made of sufficient strength to stand a pressure of six atmospheres. Fig. 54 shows the form first introduced in this country by T. A. Hoffmann, while Fig. 55 shows the form proposed by Maubré in London. In this case the starch is mixed with water to a gravity of from 11° to 16° Baumé. This with the acid is introduced into the converter, and the whole is heated under a pressure of from forty-five to seventy-five pounds per square inch. The time required for the conversion is much shorter than in the open converters. The use of open and closed converters successively is often resorted to. The starch and water of a gravity of 15° or 16° Baumé is first boiled in the open converter for from one to two hours, then transferred to the closed converter and boiled under a pressure of from forty-five to seventy-five pounds per square inch. The time of this boiling varies from ten minutes to half an hour.

FIG. 55.



When the starch has been sufficiently converted, according to the product desired, the liquor is run into the neutralizing-vats. Here a sufficient quantity of marble-dust is added to completely neutralize the sulphuric acid (or when hydrochloric acid has been used, a solution of caustic soda). A little fine bone-black is generally added at the same time. The liquor having a gravity of 12° to 18° Baumé, and known as "light liquor," is next filtered through bag filters of cotton cloth or filter-presses. In act as a bleaching agent. It is then filtered through bone-black, by ich it is decolorized and at the same time freed from various soluble ɔurities. Concentration is then effected in the vacuum-pan at a tem- :ature of about 140° F. until it has a gravity of from 28° to 30° umé, when it is called "heavy liquor." A second bag or filter-press ration is now resorted to in many factories to remove the sulphate lime, which separates out at this degree of concentration. It is then ered a second time through bone-black to secure complete decoloriza- n and purification. The final concentration is effected by boiling the uor in the vacuum-pan until it reaches 40° to 42° Baumé. That ɔduct in which the conversion has been least complete remains liquid, d is called "glucose" in the trade; that which is ready to solidify is own as "grape-sugar." Dr. Arno Behr has patented a process for taining the solid grape-sugar in pure crystals. While it is still liquid ɜre is added to it a small quantity of crystallized anhydrous dextrose. ıe mixture is filled into moulds, and in about three days it is found be a solid mass of crystals of anhydrous dextrose. The blocks are ɜn placed in a centrifugal machine to throw out the still liquid syrup, d the anhydrous dextrose remains as a crystalline mass.

3. Manufacture of Levulose.—From invert sugar (mixture of ual molecules of dextrose and levulose) levulose is now obtained as a mmercial product by taking advantage of the insolubility of its cal- ım compound. According to Schering's patent inverted molasses is ed, which has been inverted with the aid of hydrochloric acid. After e inversion is completed the solution is diluted to one-sixth strength th water, cooled to 0° C., and the levulose precipitated as the insoluble lcium levulosate. The precipitate is separated, washed with ice water, ained or centrifugated thoroughly and decomposed at a temperature ıt exceeding 50° with carbon dioxide under pressure. By centrifu- .ting the lime precipitate, a syrup of thirty per cent. levulose strength obtained. This is then acidified with a weak acid and further con- ntrated.

This manufactured levulose is used extensively in the manufacture confectionery, as it prevents the crystallizing of the cane-sugar used ıd so prevents the gradual change of clear transparent sugar products the opaque condition. It is also used in the manufacture of marma- des, jellies, and sugared fruits, for the treatment of wines, particularly veet wines and champagnes. It is also used in medicine in the case of abetes, where ordinary sugar is forbidden to be used in sweetening ods, and as the basis of infant foods.

4. Manufacture of Maltose.—By the action of the diastase of malt ɔon starch is formed mainly maltose. Dilute sulphuric acid will con- ɜrt this by prolonged boiling into dextrose, but diastase alone will not convert it. The manufacture of maltose on a large scale as a prepara- ɔn for use in beer-brewing to simplify the preparation of a suitable ort has been attempted by several. Dubrunfaut and Cuisinier patented process in 1883 for preparing maltose either as syrup or crystallized.

is warmed with two to three parts of water, digested for several hours at 30° C., and afterwards filter-pressed to obtain an "infusion" of malt. One part of starch-flour is then suspended in two to twelve parts of water, and five to ten per cent. of infusion added, the whole gradually warmed to 80° C., then heated under a pressure of one and a half atmospheres for thirty minutes, quickly cooled to 48° C., and treated with five to twenty per cent. of infusion and hydrochloric acid (from six to twenty-five cubic centimetres of acid per one hundred litres). After one hour the mass is filtered through filter-paper fastened upon linen cloth. The solution is allowed to stand at 48° C. for twelve to fifteen hours, then concentrated to 28° B., filtered, again concentrated to 38° B., filtered through animal charcoal, and allowed to crystallize. A sample of the syrup made from corn-starch by the Brussels Maltose Company working under this patent was analyzed by Märcker,* and found to contain 19.8 per cent. water, 78.7 per cent. maltose, 1.5 per cent. non-sugar, and no dextrine. The process is, however, said to have failed as yet of commercial success. Saare,† who has recently investigated it, shows that the complete conversion into maltose only takes place with weak mashes, and he concludes from his results that the process is not suitable for German distilleries under the present conditions. O'Sullivan and Valentin‡ have also patented a process for producing from starch, or starch-yielding substances, preferably from rice, a compound solid body, which the inventors term "dextrine-maltose," consisting of the same proportional quantities of dextrine and maltose as are ordinarily obtained from malt by a properly-conducted mashing process, and which it is intended should replace a portion of the malt used in brewing. For details, see original article. Perfectly pure maltose can be obtained by Herzfeld's process of repeatedly extracting with alcohol from the syrupy product of the action of malt upon starch. The alcohol precipitates the dextrine, but dissolves the maltose, which can then be obtained in crystalline condition.

5. SOLUBLE STARCH.—In recent years considerable attention has been given to preparing products that will either gelatinize in the cold and yield solutions with cementitious value or dissolve completely in hot water. The starch under the influence of acids, alkalies or of different oxidizing agents will be changed in substance without the starch granules losing their outward appearance.

Soluble starch is widely utilized as a substitute for dextrin, casein, gelatin, gums and glue, and specially as a basis of sizing preparations.

One of the earlier methods was to heat starch dried at 80°–90° with glacial acetic acid. The product of this treatment can be washed with cold water without loss and is soluble in boiling water without gelatinizing.

Volatile organic acids, like formic and acetic acids, are advantageously used, as they can be distilled off after the reaction and no neu-

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* Jahresber. der Chem. Tech., 1886, p. 613.

† Dingler, Polytech. Journ., 266, p. 418

lization of the acid is required. One per cent. of such acid acting five to six hours at 115° C. suffices to effect the change.

Starch so prepared with acid is uniformly soluble in hot water, while uble starch prepared with alkalies gelatinizes with cold water. To oid the production of the alkali salts remaining in the product, am- nia has been used. The starch is treated with water containing two r cent. of ammonia and the product is dried in thin layers to volatilize e ammonia. The soluble starch so obtained forms a voluminous powder latinizing with cold water.

Chlorine, persulphates, and perborates have also been used.

6. MANUFACTURE OF DEXTRINE.—This may be effected by acting upon arch with heat alone, by the action of dilute acids and heat, or by the tion of diastase. The first and second of these methods are followed preparing the solid product. In the manufacture by heat alone the mits of temperature are 212° to 250° C., although Payen says that 200° 210° C. produces the most perfectly soluble dextrine. The starch is eated in revolving drums, which are frequently double-jacketed, and ontain oil in the outer space in order to insure uniform heating. After he moisture is given off, the loss of weight in roasting is small, two undred and twenty pounds of starch giving one hundred and seventy-ix pounds of finished dextrine.

In the manufacture by the aid of acids the starch is mixed with dilute nitric or hydrochloric acid so as to form a damp powder. This is exposed to a temperature of 100° to 120° C. until the transformation is complete, which can be determined by applying the iodine test from time to time. The process must be arrested promptly when the starch is all changed, or the dextrine will pass rapidly into glucose. Oxalic acid is also sometimes employed in the manufacture of dextrine.

7. MANUFACTURE OF SUGAR-COLORING (*Caramel, or Zucker-couleur*).—Very considerable quantities of an artificial coloring material for use in coloring beer, rum, cognac, and high wines are made on the Continent of Europe from starch. For the manufacture of rum and cognac coloring, starch is treated with dilute sulphuric acid, as before described for the manufacture of dextrose and dextrine mixtures, but the heating is continued until all the dextrine has been changed into dextrose, as determined by taking a sample from time to time and testing it with an excess of ninety-six per cent. alcohol. When no longer any turbidity from separated dextrine shows, the reaction is considered as finished. The sulphuric acid is then neutralized with carbonate of lime, and after sufficient standing the clear liquor is run off from the precipitated sulphate of lime. It is now concentrated to 36° B. and filtered. The hot filtrate is then run into a vessel provided with mechanical agitation and heated to boiling, when crystallized soda salt (three kilos. of soda to one hundred kilos. of sugar solution) is added in small portions at a time. The contents of the kettle froth and must be continuously stirred. White and inflammable vapors are given off and the color deepens. The heat is now gradually lessened to prevent car-

should taste bitter. The contents of the kettle are then cooled somewhat by adding hot water. When the production of the color is completed, the contents of the kettle are extracted with water, filtered to remove carbonized particles, and then tested as to quality. The coloring is made in several grades or depths of color, which are also differently soluble, the one in seventy-five per cent. alcohol and the other in eighty per cent. alcohol. For beer- or wine-coloring it is not necessary to be so careful to use a glucose freed perfectly from dextrine, and, instead of soda, ammonium carbonate is taken. The product is soluble in water, but not so readily in alcohol.

III. Products.

1. STARCH.—The properties and action of reagents upon starch have already been noted in speaking of it as a raw material. It is only necessary to subjoin a few analyses of commercial starches in order to show the character of that usually obtainable. Those of potato and wheat starch are by J. Wolff, as quoted in "Wagner's Chemical Technology," and those of corn starch are by Dr. Archbold, as given by him in the "Journal of the Society of Chemical Industry," 1887, p. 188.

PERCENTAGE COMPOSITION.	Potato starch. (Wolff.)	Wheat starch, I. (Wolff.)	Wheat starch, II. (Wolff.)	Corn starch, I. (Archbold.)	Corn starch, II. (Archbold.)	Corn starch, III. (Archbold.)
Starch	83.59	83.91	79.63	98.50	92.88	90.33
Gluten	. . .	0.10	1.84	. . .	2.38	4.25
Cellulose	0.50	1.44	3.77	. . .		
Ash	0.53	0.03	0.55	0.30	0.60	0.65
Water	15.38	14.52	14.20	1.20	4.14	4.77
Total	100.00	100.00	100.00	100.00	100.00	100.00

2. GLUCOSE AND GRAPE-SUGAR.—Starch-sugar appears in commerce in a great variety of grades and under a similar variety of names. As already said, in the United States the name glucose is in general applied to the liquid products, while that of grape-sugar is given to the solid products. In France, where large quantities of similar products are manufactured, the liquid product is known as "sirop cristal" and the solid product "glucose massé." The following analyses show the composition of the commercial products as now manufactured by the Corn Products Co.*

	Corn syrup.	70 sugar.	80 sugar.	Anhydrous sugar.
	per cent.	per cent.	per cent.	per cent.
Water	19.0	19.7	11.2	4.0
Dextrose	38.5	70.2	79.9	94.6
Dextrine	42.0	9.3	8.0	0.7
Ash	0.5	0.8	0.9	0.7

3. MALTOSE.—Maltose forms fine white crystalline needles aggregating ı warty groups, which have a faint sweetish taste. It is soluble in water nd methyl and ethyl alcohol, but more difficultly in the last than dex-:ose. Its formula is $C_{12}H_{22}O_{11}$, and it crystallizes with one molecule of ater, which it loses slowly at 100° C. in a vacuum. Its specific rotatory ower is, according to Meissl, $(S)_d = 140.375 - .01837\ P - .095\ T$, here P equals the percentage strength of the solution and T the temerature. A ten per cent. solution at 20° C. would then be 138.3°. 'Sullivan takes it as 139.2° for a ten per cent. solution. Its reducing ower with Fehling's solution is frequently stated to be two-thirds that f dextrose, but Brown and Heron as well as O'Sullivan make it more ıactly sixty-two per cent. of that shown by dextrose. It has no action, owever, upon Barfoed's reagent (see p. 200), which is reduced by dex-:ose. Maltose is said to be directly and completely fermentable without revious change into dextrose, but more slowly than this latter, so that a mixture of maltose and dextrose be fermented with yeast, the whole f the dextrose disappears before the former sugar is acted upon.

4. DEXTRINE.—Pure dextrine is a white amorphous solid. It is taste-ss, odorless, and non-volatile. It is completely soluble in cold water, ıt the commercial varieties usually leave from twelve to twenty per ınt. or even more of starch and other insoluble residue when dissolved. eated with dilute acids it yields maltose and ultimately dextrose. It is ıfermentable if free from sugar. It has no reducing power on Fehling's ılution. Probably what is called dextrine is a mixture of products ɔtained in the breaking down of the complex starch-molecules. Some ıvestigators claim to have obtained sixteen distinct modifications or arieties of dextrine in this way. We have before (see p. 187) alluded amylodextrine, erythrodextrine, achroödextrine, and maltodextrine. Commercial dextrine, or "British gum," gives a brown coloration ith iodine, and probably consists largely of erythrodextrine. The fol-wing analyses by R. Forster give an idea of the composition of the dex-ines usually obtainable:

PERCENTAGE COMPOSITION.	First quality dextrose.	Dark-burned starch.	Brown dextrine.	Gommeline.	Old dextrine.	Light-burned starch.
extrine	72.45	70.43	63.60	59.71	49.78	5.34
ugar	8.77	1.92	7.67	5.76	1.42	0.24
nsoluble	13.14	19.97	14.51	20.64	30.80	86.47
Vater	5.64	7.68	14.22	13.89	18.00	7.95
	100.00	100.00	100.00	100.00	100.00	100.00

Dextrine is used as a substitute for natural gums, especially for gum abic. It is thus used in calico-printing and in the mordanting and inting of colors upon most other classes of textile goods, for mucilage, r glazing cards and paper, as warp-dressing, and in the manufacture beer. It forms the crust on bread by the change of the starch of the ur in baking, and is present in most products from starch or starch

5. UNFERMENTABLE CARBOHYDRATES (*Gallisin*).—The presence of unfermentable carbohydrate in starch-sugar was long since pointed o by O'Sullivan. The compound which has been specially studied is know as gallisin, and is prepared by fermenting a twenty per cent. solution starch-sugar with yeast at 18° or 20° C. for five or six days. Th resultant liquid was filtered, evaporated to a syrup at 100° C., and shak with a large excess of absolute alcohol. The treatment with alcohol w repeated several times until the unaltered sugar and other impuriti were removed, the syrup being converted into a yellowish crumblin mess, which, by pounding in a mortar with a mixture of equal parts alcohol and ether, was obtained as a gray powder. After purifying wi animal charcoal and drying over sulphuric acid, the gallisin was obtaine as a white amorphous extremely hygroscopic powder. Its taste is at fir sweet, but afterwards becomes insipid. It is easily decomposable by hea even at 100° C. It is readily soluble in water, nearly insoluble in abs lute alcohol, and but slighly more soluble in methy alcohol, in whic respect it differs from dextrose. Gallisin is stated to have the compos tion $C_{12}H_{24}O_{10}$. Its concentrated aqueous solution is distinctly acid litmus and a sparingly soluble barium compound may be obtained ther from by adding alcoholic baryta. It reduces nitrate of silver on heatin especially on addition of ammonia, reduces bichromate and permanganate, and precipitates hot Fehling's solution. Its cupric oxide reducing power (dextrose = 100) is stated to be 45.6°. Gallisin is dextro rotatory, the value for S_d being stated to be 80.1° in twenty-seven pe cent., 82.3° in ten per cent., and 84.9° in 1.6 per cent. solutions. B heating with dilute sulphuric acid for some hours gallisin yields a larg proportion of dextrose, but its complete conversion has not so far bee effected.

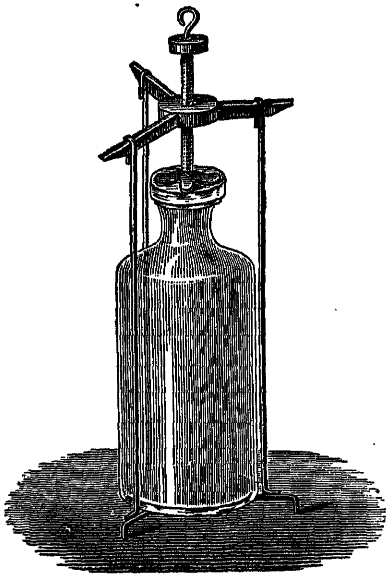
It is doubtful whether "gallisin" as hitherto obtained is really definite compound, but the possibility of isolating a reducing or opticall active body from the liquid left after fermenting solutions of many speci mens of sugar-starch cannot be ignored in considering the compositio of commercial glucose.

IV. Analytical Tests and Methods.

1. FOR STARCH.—The usual method for the determination of starc is to invert by the action of dilute acid, and then determine the dextros produced by the aid of Fehling's solution. In this case one hundre parts of dextrose are taken as indicating ninety of starch. It has bee found, however, that the change to dextrose by the aid of dilute sulphuri acid is not complete, that other non-reducing bodies are formed, an that but ninety-five per cent. of the starch is converted into dextrose The hydrolysis is more completely effected by the aid of hydrochlori acid, as carried out in Sachsse's method. 2.5 to 3 grammes of dry starc (or so much of the starch-containing substance as would correspond t

d heated on the water-bath with inverted condenser for three hours. ärcker states that heating for three hours with this amount of hydroloric acid does not give more than ninety-six to ninety-seven per cent. the starch as sugar, as some of the latter is destroyed. He recomends using fifteen cubic centimetres of acid and heating for two hours.) he contents of the flask are then nearly neutralized with sodium hyoxide, filled to the mark, and the dextrose determined by Fehling's lution. If other carbohydrates or cellulose are present, which would also converted into dextrose by hydrochloric acid, the starch must be eviously brought into the soluble form, which may be done by heating with water to 130° C. in a pressure-flask like that of Lintner, shown in Fig. 56. Or the starch may be hydrolyzed in part by infusion of malt or diastase at 62.5° C., filtered from cellulose, etc., and then treated with hydrochloric acid for complete hydrolysis as above. In this latter case, the process of Reinke* is the simplest. Three grammes of the sample as finely powdered as possible are heated to boiling with fifty cubic centimetres of water, cooled at 62.5° C., and hydrolyzed for an hour at this temperature with .05 gramme of diastase. This is prepared according to Lintner's procedure, by making an alcoholic twenty per cent. extract (1:3) of raw malt, adding to the filtrate two volumes of ninety-six per cent. alcohol, separation of the precipitated iastase, washing with alcohol and ether, and drying in a desiccator. The mixture is then cooled, diluted with water to two hundred and fifty cubic entimetres, and filtered. Of the filtrate, two hundred cubic centimetres are taken and hydrolyzed, as before described, with fifteen cubic centimetres of hydrochloric acid of 1.125 specific gravity for two and a half hours, when the solution is neutralized and the dextrose determined.

Fig. 56.



A more elaborate course of treatment, following in the main the same lines as the procedure of Reinke just described, but stopping with the action of the diastase, has been published by O'Sullivan, and is given at length by Allen.† In this case the filtered liquid, assumed to contain nothing but maltose and dextrine, is made up to one hundred cubic centimetres, and the density determined. It is then tested with Fehling's solution for the maltose, and the dextrine deduced from the rotatory power of the solution. The maltose found, divided by 1.055, gives the corresponding weight of starch, which, added to the dextrine found, gives the total number of grammes of starch represented by one hundred cubic centimetres of the solution.

The method for the determination of starch in cereals most generally used in Germany at present is that of Märcker.* Three grammes of substance are placed in a small beaker (preferably of metal), which is placed as one of several in a Soxhlet pressure-boiler, or the test is carried out in the Lintner pressure-flask, figured on the preceding page, and heated to the temperature of boiling water. It is then cooled to 60° to 65° C., five cubic centimetres of thin malt infusion are added, and it is digested at this temperature for some twenty minutes. It is then made faintly acid (one cubic centimetre of tartaric acid suffices) and heated under a pressure of three to four atmospheres. It is then cooled down and an additional five cubic centimetres of malt infusion added, with which it is digested an half-hour. The solution is then brought up to one hundred cubic centimetres, filtered, and determined with Fehling's solution, either by titration or by weighing the reduced copper.

Of other methods proposed for starch determinations it is only necessary to notice the Asboth method, proposed in 1887. It depends on the fact that starch forms a compound with baryta-water, $C_{24}H_{40}O_{20}BaO$, containing 19.1 per cent. of BaO, which is insoluble in forty-five per cent. alcohol. The baryta-water is used in excess, and the free alkaline earth determined by titration with decinormal hydrochloric acid. Numerous experimenters have taken exception to the method that the results were variable, and that starch combined with varying amounts of barium oxide. To these objections the author made a reply later,† and claims that the presence of fat in the cereals interferes with the accuracy of the determination, and that if the fat be previously extracted by ether, the determinations in the fat-free residue are accurate and concordant. J. Napier Spence, in the "Journal of the Society of Chemical Industry," for 1888, p. 77, has also come to the defence of the Asboth method and shown the conditions under which it yields accurate results.

2. Glucose, or Dextrose.—For the determination of dextrose alone the Fehling's solution affords the most accurate means. For its use, see analysis of raw sugars, p. 174. In the absence of any other optically active body its examination with the polariscope will also suffice. For mixtures like commercial glucose, which contains dextrose, maltose, and dextrine, see later.

3. Maltose.—This variety of sugar, as before stated, has optical activity and reducing power on Fehling's solution. It can, however, be distinguished from dextrose by its failure to reduce Barfoed's solution, which is reduced by dextrose and invert sugar. This reagent is made by dissolving one part of neutral copper acetate in fifteen parts of water, to two hundred cubic centimetres of which five cubic centimetres of thirty-eight per cent. acetic acid is added. Boiled for several minutes with maltose solution it shows no reduction.

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* [illegible]

4. DEXTRINE.—Pure dextrine differs from dextrose and maltose in owing no reducing power with either Fehling's solution or with app's mercuric cyanide solution. It can, indeed, be freed from admixre with dextrose and maltose by heating with an excess of an alkaline ution of mercuric cyanide, which oxidizes these two varieties of sugar, wing the dextrine unaffected. (See Wiley's method below.)

5. COMMERCIAL GLUCOSE AND SIMILAR MIXTURES DERIVED FROM ARCH.—As commercial glucose is likely to be a mixture of the three npounds, dextrose, maltose, and dextrine, its analysis and the deternation of the several constituents becomes a frequently-recurring oblem. Three methods have been proposed. The first, by Allen,* uires the determination of moisture and ash in the sample, which, btracted from 100, leaves the total organic solids, O. The apparent ecific rotatory power, S, and the cupric oxide reducing power (in terms dextrose reduction = 100), K, are now determined. Then, if m be e maltose, g the dextrose-glucose, and d the dextrine, Allen deternes the respective percentages by the use of the formulas $m = S-\frac{52.7\ K+198\ (O-K)}{100}\Big)\div .313$, $g = K - .62\ m$, and $d = O-(g+m.)$ e author states that the presence of gallisin or other unfermentable gar may vitiate the values of K and S, as observed, and so make the ults inaccurate.

The second method is that of Wiley,† which is based upon the theory t boiling with an alkaline solution of mercuric cyanide will destroy e optical activity of maltose and dextrose, leaving that of dextrine changed. The cupric oxide reducing power of the sample is ascerned in the usual way by Fehling's solution. The specific rotatory wer is determined by polarizing a ten per cent. solution (previously ated to boiling) in the ordinary manner. Ten cubic centimetres of s solution used for polarizing are then treated with an excess of an aline solution of mercuric cyanide, and the mixture boiled for two three minutes. It is then cooled and slightly acidulated with hydrooric acid, which destroys the reddish-brown color possessed by the aline liquid. The solution is then diluted to fifty cubic centimetres, d the rotation observed in a tube four decimetres in length. e angular rotation observed will be due simply to the dextrine, percentage of which may then be calculated by the formula $\frac{\text{rotation} \times 1000 \times \text{cubic centimetres of solution polarized}}{3 \times \text{length of tube in centimetres} \times \text{weight of the sample taken}} =$ per- tage of dextrine. The percentages of dextrose and maltose may be luced from the reducing power of the sample, or from the difference in ecific rotatory power before (S) and after (s) the treatment with alkae mercuric cyanide. Thus, $K = 1.00\,g + .62\,m$, $S = .527\,g + 139.2\,m$ $1.98\,d$ and $s = 1.98\,d$, whence $m = \frac{S - s - .527\,K}{1.06526}$. g can now be nd from the first of the three equations, and then d in the second.

Wiley's process was employed by the Committee of the National Academy of Science in their investigation of commercial glucose from corn starch. It is, however, based upon several assumptions that have not been specifically proven, and especially in the presence of any considerable quantity of maltose are its results open to doubt. (See Allen, "Commercial Organic Analysis," 3d ed., vol. i, p. 369, foot-note.)

The third method of estimating the constituents in commercial glucose is due to C. Graham, and is probably more exact than either of those before mentioned. Dissolve five grammes of the sample in a small quantity of hot water and add the solution drop by drop to one litre of nearly absolute alcohol. Dextrine is precipitated, and on standing becomes attached to the sides of the beaker, while maltose, gallisin, and dextrose are soluble in the large quantity of alcohol employed. If the solution be then decanted from the precipitate, the dextrine in the latter can be ascertained by drying and weighing, or by dissolving it in a definite quantity of water and observing the solution, density, and rotation. The alcohol is distilled off from the solution of the sugars and the residual liquid divided into aliquot portions, in one of which the gallisin may be determined after fermentation with yeast, while others are employed for the observation of the specific rotation and reducing power, which data give the means of calculating the proportions of maltose and dextrose in the sample.

V. Bibliography and Statistics.

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STATISTICS.

1. Production of Starch in the United States and Germany.—O. Saare in 1896 gave the following summary of the production in these chief producing countries:

	United States. Hundred kilos.	Germany. Hundred kilos.
Potato starch	120,000 — 180,000	2,000,000 — 3,000,000
Corn starch	2,000,000 — 3,000,000	25,000 — 50,000
Wheat starch	150,000 — 200,000	50,000 — 100,000
Rice starch	....	200,000 — 250,000
	2,270,000 — 3,380,000	2,275,000 — 3,400,000

2. Production of Grape-sugar (Starch-sugar), Glucose, Dextrine, etc.—The same authority gives the following figures for the products from starch:

	United States. Hundred kilos.	Germany. Hundred kilos.
Grape-sugar and glucose syrup	2,500,000 — 3,000,000	350,000 — 400,000
Sugar-color (caramel)	....	30,000 — 40,000
Dextrine	20,000 — 50,000	150,000 — 180,000
	2,520,000 — 3,050,000	530,000 — 620,000

3. Production of Starch in the United States (Census of 1905):

	1900.	1905.
Corn starch produced (lbs.)	247,051,744	150,520,009
Value	$6,133,001	$4,702,309
Potato starch produced (lbs.)	33,941,826	27,709,400
Value	$1,129,129	$924,476
Cassava and wheat starch (lbs.)	16,809,569	17,845,121
Value	$775,835	$1,124,612
Total starch (lbs.)	297,803,139	196,074,530
Value	$8,037,965	$6,751,397

4. Corn Products.—The corn crop of the United States in 1908 is said to have been 2,643,000,000 bushels, valued at $1,615,000,000. Of this, ninety per cent. is used as food and ten per cent. is used in the industries and for export.

Two per cent., or 50,000,000 bushels, is used in the starch and glucose industry.

Four per cent., or 100,000,000 bushels, is used in the fermentation and milling industry.

Four per cent., or 100,000,000 bushels, is exported.

(T. B. Wagner, Jour. Soc. Chem. Ind., 1909, p. 343.)

5. Exportations of Starch, Glucose, and Grape-sugar from the United States.

	1908.	1909.	1910.
Starch (lbs.)	48,125,851	33,228,278	51,535,570
Value	$1,042,054	$780,155	$1,274,773
Glucose (lbs.)	98,608,192	92,652,409	112,730,639
Value	$1,898,652	$1,138,406	$2,623,131
Grape-sugar (lbs.)	31,078,642	19,572,095	37,098,449

CHAPTER VI.

FERMENTATION INDUSTRIES.

A. NATURE AND VARIETIES OF FERMENTATION.

Under the term fermentation are included certain methods of decomposition of organic compounds which presuppose the presence of definite substances called "ferments," which do not, however, apparently take part in the chemical reactions but act after the manner of the inorganic catalytic agents. Their presence in relatively small amount and the existence of conditions of temperature, etc., favorable to them, suffice to bring about the decomposition of large quantities of the fermentable material.

The ferments which seem to determine the decomposition may be either soluble unorganized ferments or insoluble organized ferments, which are minute vegetable growths. The decompositions which are brought about by organized ferments differ quite notably in their results from those which can be induced by mere chemical reagents. Thus, the decomposition of sugar into alcohol and carbon dioxide, as it is brought about by the activity of the yeast-cell, cannot be brought about by purely chemical treatment. On the other hand, the action of the unorganized ferments is much more analogous to that induced by chemical reagents. Thus, the hydrolytic action of diastase on starch can also be perfectly imitated by treating with dilute acids. Buchner has, however, recently shown that the liquid expressed from fresh yeast cells after triturating them can produce all the changes attributed to the cells themselves, and that it owes its activity to an enzyme called zymase, which is produced by the cells.

With regard to the chemical nature of the enzymes, or soluble ferments, we only know that they belong to the class of proteids. A recent analysis of diastase by Lintner may be taken as typical of the class: carbon, 46.66 per cent.; hydrogen, 7.35 per cent.; nitrogen, 10.42 per cent.; sulphur, 1.12 per cent.; and oxygen, 34.45 per cent.

While soluble in water and glycerol they are insoluble in alcohol, and are precipitated from aqueous solutions on addition of lead acetate. Their activity is destroyed by heating, that of diastase at 75° C., and all by boiling with water. Their activity is not destroyed by the presence of antiseptics, which arrest the action of the organized ferments. Thus, chloroform, thymol, and salicylic acid will all arrest the activity of the organized growth but not interfere with that of the soluble ferments. Sodium fluoride in one per cent. solution is said to check entirely the growth of the organized ferments, but is without action on those which

Foremost among the soluble ferments is *diastase*. This is the ferment formed from the albuminoids of the cereals during the process of germination. It is especially developed in the malting process as applied to barley. Its chief function is the saccharification of the starch of the grain, changing it into dextrine, maltose, and dextrose.

The amount of starch that a given quantity of diastase can convert cannot be stated with absolute certainty, as it varies with the conditions of its preparation, the strength of the infusion, and other points. Its progress can, of course, be controlled by the iodine reaction, as stated under starch. Commercial extracts of malt are infusions of malted barley, which contains the products of the inversion of the starch. The solid extracts obtained by evaporation of these infusions in vacuo at low temperatures should be readily soluble, and should show that they still contain active diastatic ferment by being able to convert their own weight of starch within a short time.

Invertase.—Invertase is capable of converting cane sugar or sucrose into invert sugar. This rather resistant enzyme may be readily extracted from the yeast by various means. From yeast cells which have been killed with chloroform it may be extracted with water, and is precipitated from a water solution by the addition of alcohol. This white precipitate is readily dissolved in water and possesses the property of inverting cane sugar or sucrose quantitatively. Invertase is an important enzyme in the fermentation of molasses or any other substance containing sucrose. Invertase acts only in a slightly acid solution. The best temperature for its action is about 55° C.; it is slowly destroyed at about 65° C., and immediately at 95° C.

Zymase.—This enzyme in reality forms a class by itself, in that it possesses the property of converting monosaccharid sugars into alcohol and carbon dioxide. The presence in solution of the enzyme which Buchner named zymase, and which is the cause of alcoholic fermentation, overthrows to a great extent the older theories which regarded the actual cause of the transformation of sugar into alcohol and carbon dioxide as a vital process dependent upon the actual life activities of the yeast cell itself.

The organized ferments or vegetable growths may be divided into three classes: first, mould-growths; second, yeast-plants, or the different species and varieties of *Saccharomyces;* and, third, bacteria, belonging to the two genera *Schizomycetes* and *Schizophycetes*. The most important fermentations from an industrial point of view are the alcoholic, which is brought about mainly* by the presence of ferments of the second class, and the acetic and lactic, which are brought about by ferments of the third class. Upon the alcoholic fermentation depend three important groups of industries,—viz., the manufacture of malt liquors, the manufacture of wines, and the manufacture of ardent spirits, or distilled liquors. Upon the acetic fermentation depends the manufac-

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* Buchner (1897) has shown clearly that there is present in the yeast-cells, even when dead, a soluble ferment or enzyme capable of developing the alcoholic [illegible]tion.

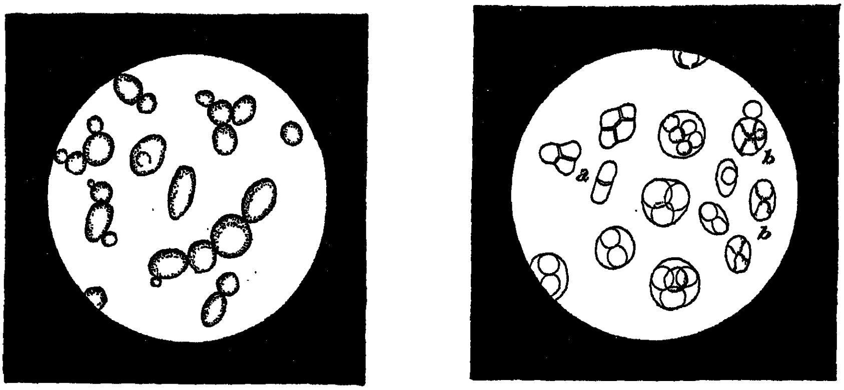
ture of different varieties of vinegar, and upon the lactic fermentation the manufacture of cheese and other milk products.

The alcoholic fermentation is always meant when we use the word fermentation in the narrower sense, as with reference to the change which starch and saccharine bodies most generally undergo. In this fermentation, the action of the yeast-plant seems to differ according to the variety of sugar presented to it. Dextrose is most immediately acted upon, the main reaction being $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, although, as Pasteur first showed, side-products like glycerine and succinic acid are also formed, and in practice only about ninety-five per cent. of the dextrose is decomposed by the main reaction. Cane-sugar is not immediately fermentable. If it has been previously exposed to the action of dilute acids, it is changed into invert sugar, which then acts like dextrose. The yeast-plant can effect the same change itself. Invertin (or invertase, as it is also termed) is a soluble ferment existent in yeast. It has the property of rapidly and completely effecting the transformation of cane-sugar into invert sugar, but is without sensible action on dextrose, levulose, maltose, or milk-sugar. Towards dextrine its action is not so certainly negative.

The conditions of the activity of the yeast-plant have been studied by many chemists, but notably by Pasteur. It has been found that if an abundance of air is supplied the plant grows and multiplies but fermentation proceeds very slowly, when the supply of air is limited, the fermentation proceeds more rapidly while the growth of the cells is largely arrested, and that in the absence of air the fermentation proceeds with greatest rapidity, although the plant-cells do not grow any longer, but gradually disintegrate and die. Pasteur's dictum, that "fermentation is the consequence of life without air," is no longer taken as strictly accurate, as with the cessation of the growth and extension of the yeast-plant (which is dependent upon air like the life of any other plant), although its fermentation activity then becomes greatest, it begins at the same time a decay which leaves it after a time dead and inactive.

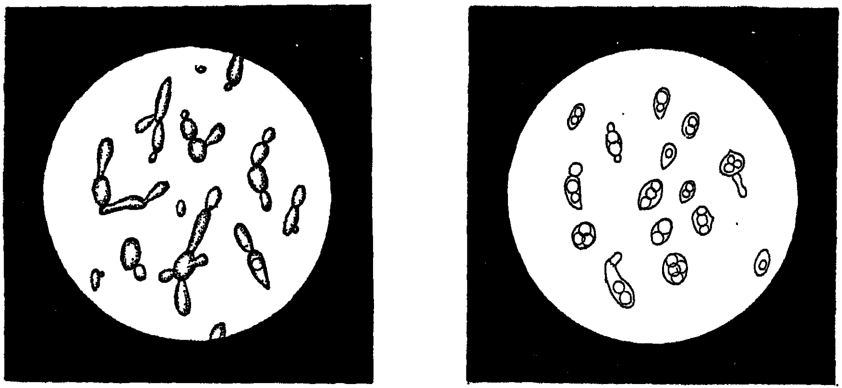
The genus *Saccharomyces* has already been alluded to as the active agent in the alcoholic fermentation. The species *Saccharomyces cerevisiæ* is generally known as the special beer ferment and the *Saccharomyces ellipsoideus* as the wine ferment. Moreover, of the *Saccharomyces cerevisiæ*, two well-marked varieties have been recognized. The one is the most active at the ordinary temperature (16° to 20° C.), and carries through its fermentative work in from three to four days; the other works at a lower temperature (6° to 8° C.) and the fermentation is much slower. The first, placed in a saccharine liquid, is carried by the carbon dioxide which it liberates to the surface of the liquid, where it continues its activity; it is therefore known as a surface or top yeast. The second, on the contrary, is not carried up, and rests during its entire activity on the bottom of the fermenting vessel, and is hence called a bottom yeast. Two quite distinct methods of beer-brewing are practised (see p. 212), depending upon the use of the one or the other of these varieties

Fig. 57.



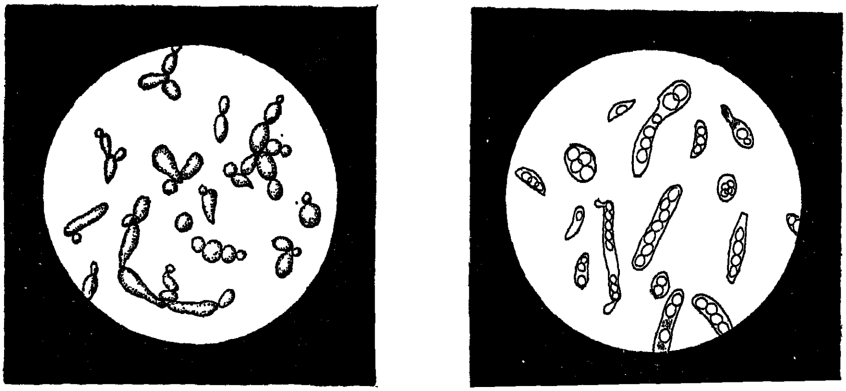
Saccharomyces cerevisiæ.
(After Hansen.)

Saccharomyces cerevisiæ. Ascospores.
(After Hansen.)



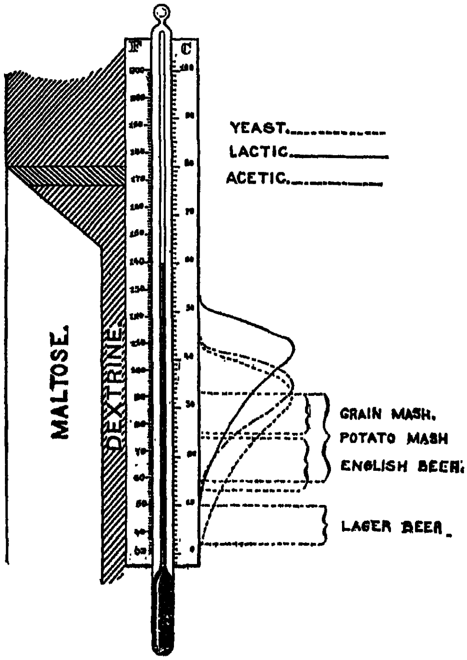
Saccharomyces ellipsoideus.
(After Hansen.)

Saccharomyces ellipsoideus. Ascospores.
(After Hanson.)



yeast is used exclusively or a bottom yeast exclusively, the results are not always uniform. These anomalies are now made clear through the researches of E. Ch. Hansen, of Copenhagen, who has applied the methods of pure cultivation introduced by bacteriologists to the study of the yeast-plant. He has found that if a single yeast-cell of one of the better varieties of *Saccharomyces* be cultivated with the precautions needed to exclude what is called "wild yeast" (germs present in the air, notably in the summer months), absolutely uniform results can be gotten in brewing. Beginning in 1883, he has developed the study, and it has now been accepted by most of the leading authorities on fermentation. He first decribed six species: *Saccharomyces cerevisiæ* I., *Saccharomyces Pastorianus* I., II., and III., *Saccharomyces ellipsoideus* I. and II., of which the second, fourth, and sixth cause bitterness and turbidity (so-called "diseases" in beer). He has since* increased the list of varieties of ferments studied to forty, including both top and bottom yeasts, ferments similar to yeast but not belonging to the genus *Saccharomyces,* and forms of mould-growh. He divides the representatives of each genus into two groups according as they secrete invertin or not.

FIG. 58.



Fresh yeast resembles a dirty yellowish-gray sediment of unpleasant odor and acid reaction, made up of an immense number of vegetable cells. Three of the pure culture varieties of yeast-plant as obtained by Hansen are shown in the illustration Fig. 57, together with the special appearance of the ascospores of the same. Of these the *Saccharomyces* *erevisiæ* and *Saccharomyces Pastorianus* are beer ferments, while the *'accharomyces ellipsoideus* is the wine ferment. For many purposes bread-baking, use in distilleries, etc.), the ferment is prepared as com-ıressed yeast in cakes, generally with the addition of potato starch.

The special conditions of the alcoholic fermentation are: first, an queous solution of sugar of the strength of one part sugar to four to ən parts water; second, the presence of a yeast ferment. If this is not dded already developed and active, or if the fermentation is to be pontaneous,—that is, brought about by spores from the air,—the condi-.ons for the development of these spores must also be present. There ıust be proteïn compounds and phosphates of the alkalies and alkali ırths. Thirdly, the temperature must remain within the limits 5° to 0° C., or, more generally, from 9° to 25° C. Above 30° C. the alcoholic ərmentation readily passes into the butyric and other decomposition.

The effect of temperature upon the several different ferments is ıown in the graphic illustration of Fig. 58, which represents also the ıfluence of temperature upon the decomposition of starch by diastase. n the right side of the figure, the regularly-dotted line represents the əast curve. A slight fermentation is already induced at a temperature əry little over the melting point of ice. As the temperature rises its ɪtivity increases until the maximum is reached, at about 33° C. (92° .), when it diminishes down to nothing again, and at 50° C. (122° F.) thereabouts it is killed. The activity of the acetic ferment is repre-nted at the same time by the irregularly-dotted line, and that of the lactic rment by the uniform black line.

B. MALT LIQUORS AND THE INDUSTRIES CONNECTED THEREWITH.

I. Raw Materials.

1. MALT.—Malt is prepared by steeping barley or other grain in ıter, and allowing it to germinate in order to change the character of e albuminoids and develop the ferment diastase, which then begins to t upon the starch, the germination and change being stopped at a rtain stage by heating in a kiln. The composition of the unmalted .rley was given among other cereals on p. 186. The changes which it .dergoes in composition by the process of malting will be seen by com-ring this with the two analyses of pale malt following, which are by Sullivan:

	No. I.	No. II.
.rch	44.15	45.13
ıer carbohydrates (of which sixty to seventy per cent. consist of ermentable sugar), inulin and similar bodies soluble in cold water	21.23	19.39
lular matter	11.57	10.09
;	1.65	1.96
ıuminoids soluble in water	6.71	5.31
ıuminoids insoluble in water	6.38	8.49
ı	2.60	1.92
ter	5.83	7.47

O'Sullivan states that malt contains no ready-formed dextrine, but that it does contain from sixteen to twenty per cent. of fermentable sugars, of which about one-half is probably maltose, and due to the transformation of starch in the malting process, while the remainder exists ready formed in the barley, and is not identical with the sugar produced in the malting.

Besides the diastase, a second soluble ferment is formed during the malting process, the so-called peptase, which in the mash process changes the proteids of the malt into peptones and parapeptones, which give nutritive value to the beer.

A high percentage of starch in the barley to be used for brewing is desirable in order that when malted it may yield a large amount of "extractive matter." According to Lintner and Aubry,* a good malt should yield at least seventy-one per cent. of extract reckoned on the weight of dry substance. This determination of the value of a sample of malt is one of the most necessary of analytical tests for the malster or brewer. (See p. 219.)

Well-malted barley is always yellow or amber-colored, shading to brown. On breaking the grain, the interior should be of a pure white color and floury appearance, except when the drying has been intentionally carried so far as to partially caramelize the sugar.

Malted wheat, corn, and rice are at times used as partial substitutes for the barley malt, as well as potato starch and starch-sugar. The use of patented maltose and maltose-dextrine preparations has already been referred to. (See p. 193.)

2. Hops.—Hops are the female unfructified blossoms (catkins) of the hop-plant (*Humulus lupulus*). Under the thin membranous scales of the strobile or catkin is an abundance of a yellowish resinous powder, consisting of minute sessile grains, to which the name *lupulin* has been given. The active principles of the hops, contained mainly, but not exclusively, in the lupulin, are: First, the ethereal oil, which is present to the amount of .3 per cent. in the air-dried hops. This is yellowish, of strong odor and of burning taste. It consists of a hydrocarbon, C_5H_8, and an oxygenized oil, $C_{10}H_{18}O_2$, which by atmospheric oxidation becomes valerianic acid, $C_5H_{10}O_2$, to which old hops owe their odor. Second, the lupulin also contains a resinous bitter principle, which is easily soluble in alcohol, but difficultly soluble in water, and extremely bitter. This is supposed to be an oxidation product of lupulinic acid, which can be gotten in white crystals, speedily becoming resinous. Both the acid and its oxidation products seem to be held dissolved in the ethereal oil. Hops also contain tannic acid of a variety allied to moritannic acid and turning iron salts green. Analyses of two well-known Bohemian varieties of hops are given.†

The blossoms are produced in August, and the strobiles are fit for gathering from the beginning of September to the middle of October, according to the weather. The prompt drying of the fresh-picked hops

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is necessary in order that they may be safely baled. This drying takes place by the aid of hot air in a so-called hop-kiln at a temperature of about 40° C., the hops being repeatedly turned with a light wooden shovel as they lie spread out upon a false or perforated floor. When dry they are pressed by hydraulic presses into compact bales. Hops are also often treated with sulphurous acid gas from burning sulphur to preserve them, although this sulphuring is oftener used with old hops for the purpose of brightening them in color and improving their appearance.

PERCENTAGE COMPOSITION.	Water.	Ethereal oil.	Soluble in alcohol.	Of which is resin.	Residue from alcohol soluble in water.		Tannic acid in aqueous extracts.	Ash free from CO_2.	Carbon dioxide in 100 of ash.	Sand.
					Organic.	Ash.				
From Saatz	9.90	0.13	20.12	14.57	11.24	5.42	2.52	10.01	8.71	0.91
From Auscha	10.61	0.17	20.97	15.14	10.51	5.10	3.18	7.87	9.51	0.81

A number of bitter principles have been mentioned as used at times as substitutes for hops in beer-brewing, although it is doubtful if such substitution is much practised. Among these substitutes have been noted quassia, gentian, picrotoxin, the bitter principle of *Cocculus Indicus,* colchicum, wormwood, and picric acid.

3. WATER.—The water used in malting and brewing must be adapted for the purpose in order to get good results. A pure and soft water or a moderately hard calcareous water will do, but it is indispensable that the water be perfectly free from organic impurities. Continental brewers use soft waters most generally in brewing beers, while English brewers prefer gypsum waters for their ales which are specially designed to keep. This is shown in the character of the water of Burton-on-Trent, which contains notable quantities of calcium and magnesium sulphates, calcium carbonate, and sodium chloride.

II. Processes of Manufacture.

1. MALTING OF THE GRAIN.—Although malt has been described as a raw material of the brewing industry, the preparation of it from the raw grain is a process so closely connected with the success of brewing that it must be described, and especially, too, because it is often combined under the same direction as the brewing process. The process of changing barley into malt is to be divided into four stages: the steeping, the couching, the flooring, and the kiln-drying. The first three of these stages have to do with the germination or development of the acrospire, or plumule, which as it develops brings about great changes in the chemical constitution of the grain, developing from the albuminoid matter the diastase, which in turn begins to act upon the starch, forming from it maltose and dextrine. At the same time during the germination atmospheric oxidation is going on at the

grain, water and carbon dioxide being steadily given off. When t development of the diastase is supposed to have reached the right poi which can only be judged of by the growth of the acrospire, or germ, t fourth stage of the process is reached, and the germ must be killed heat, which is done in the kiln-drying.

The first process of steeping is to give the grain sufficient moisture allow germination to begin. For that purpose it is put into large ir or cemented vats. These are half filled with water and the grain add with constant stirring. The sound grains sink shortly under the wat and the dead or imperfect grains float and can be removed. The wat soon takes color and odor, and must be replaced by fresh water. The du tion of the steeping is usually forty-eight to seventy-two hours, depen ing upon the temperature, and in winter-time or with older barley m last considerably longer. The end of the treatment may be told by noti the character of the grain. It has swollen and become nearly sufficient soft to allow of being pierced with a needle and yet exuding no jui It has gained from forty to fifty per cent. in weight and increased fro twenty to twenty-four per cent. in bulk. To offset this gain due to wat absorption, it has lost from one to two per cent. of its substance, part carried off in the steep water and partly given off as gas. The water then run off, and after draining it is turned upon the couching-floo where it remains at first in heaps of from fifteen to twenty-four inch in depth. Here it soon begins to heat up, and a rise in temperature from 7° to 10° takes place. It also begins to "sweat," and gives off a abundance of carbon dioxide, and an agreeable cucumber-like odor recognizable. The germination is now under way and the rootlets sho out. The "couching" stage lasts from twenty-four to thirty-six hour and during that time the grain must be turned several times. Th heated barley must now be spread on the floor in shallow layers so as t check somewhat the rate of growth of the germ, and must be turne from four to six times a day as the growth proceeds. The depth of th layer is at the same time reduced from fifteen to four or five inche During this time the germinating grain must have an abundance o air. The process lasts from seven to ten or even twelve days, accordin to the season of the year, and its termination is decided by the length o the germ, which must be about two-thirds that of the grain. The los in weight during the germinating process, according to Lintner, is te per cent. of the weight of the grain. The loss comes mainly upo the starch, which has in part been changed into maltose and dextrin but has mostly been oxidized to water and to carbon dioxide. To mor efficiently remove the carbon dioxide which would interfere with th germinating process and to prevent too strong a heating, the pneumati process of malting has been proposed by Galland. In this process th steeped barley is placed on a perforated floor in thick layers, and regulated current of moist, well-cooled air is kept passing through i This process is now replacing the other quite largely. Still anothe form of mechanical malti nation must now be stopped promptly, lest it go too far at the expense of the starch of the grain, and this is best effected by heat. The germinating grain may, however, be simply dried thoroughly in the air and the rootlets removed by mechanical means. This constitutes air-dried malt, which is used for some purposes. Most generally it is dried in a kiln at a considerably higher temperature. This must be gradually applied, as if, while the raw malt were full of moisture, it were to be heated strongly, the starch would be gelatinized and the grain made tough, hard, and glassy. It is therefore heated first to about 90° F., and this is gradually raised to 150° F., or even in some cases to 180° F. A light gradual heat produces a "pale" malt, a stronger heat "yellow" or "pale amber," and then "amber" and "brown" malt. The kiln may have two floors, on the upper and cooler of which the moist malt loses its water and then passes on to the lower and hotter floor, where it is heated to the higher limit requisite for developing its empyreumatic odor and flavor, or the heating may all be effected on a single floor, in which case more time is needed for the several stages of heating. Black malt used for coloring is heated in revolving coffee-roasters, and most of the sugar is caramelized.

2. Preparation of the Wort.—The malt after being cleansed and crushed (not ground fine) is ready for use in what is known as the mashing process. This is designed not merely to extract the maltose and dextrine of the malt, but mainly to allow the diastase of the malt to act upon the starch, changing it into maltose and dextrine and the peptase to form peptones from the proteids. It must therefore be carried out under such conditions of temperature and dilution as have been found to be most favorable for effecting these purposes. We have already seen (p. 207) that the action of diastase is most effective at about 62.5° C. (144.5° F.), and therefore at a temperature not much above this is the infusion most successfully made. At a temperature of over 75° C. its power is destroyed. Two quite distinct processes for mashing are at present followed: the infusion, or thin mash, and the decoction, or thick mash, process. The first is used in England and France, the second in Bavaria, Bohemia, and the principal brewing centres of the Continent. Both are used in this country. In the infusion process, water at 60° to 70° C. is run into the mash-tub, a vessel provided with false bottom and mechanical agitation, the crushed malt added and tirred in, and then additional hotter water, so that a temperature of 70° C. (158° F.) is gradually attained. This is maintained for some ime with constant agitation of the liquid, so that the diastase may have ime to act upon the starch. The completion of this action is determined by taking a few drops of the wort from time to time and testing with iodine solution, which finally produces no color on mixing. The lear infusion is now run off from under the false bottom of the tub o the copper boilers, and the malt again covered with hot water and mashed for one-half to one hour longer at 70° C. or somewhat higher

from this third mash is not always added to that of the first and second mashes, but is used to mash a fresh quantity of malt.

In the Bavarian thick-mash process, the malt is put in the mash-tub with some cold water, and then by the addition of boiling water is brought to 35° C. A third of the softened malt is then taken out and brought gradually to boiling with water in the copper. After one-half to three-quarters of an hour's boiling, the half of this is then returned to the mash-tub and thoroughly agitated with what remained there. The temperature of the mash-tub is thereby brought to about 50° C. A second portion of the thick mash is again taken out and boiled in the copper for three-quarters to one hour, when the greater part is returned to the mash-tub and thoroughly mixed, bringing up the temperature here to 65° C. The thinner part of the mash, or clear wort, is now run off and boiled in the copper for fifteen minutes and returned, whereby the temperature of the mash-tub is brought to 75° C. This is now left at rest for an hour to an hour and a half, and then the wort is run off to the copper. The malt is washed by the sparger, and so the saccharine liquor adhering displaced. The whole process is easily understood by reference to Fig. 59, in which *A* is the mash-tub and *C* the copper for boiling up the successive portions taken from *A*.

It is obvious that in the thick-mash process that portion of the diastase contained in the material which is taken out and boiled is destroyed, but the boiling thoroughly disintegrates the malt and converts its starch into a paste. When this is returned to the mash-tub, it is very rapidly acted upon by the remaining diastase, of which there is quite sufficient, and changed into maltose and dextrine. By the thick-mash process, the sugar formation is held in check and the amount of extract increased.

In the mash process the diastase acts upon the starch of the malt, changing it into maltose and dextrine. The ratio of these products to each other changes according to the temperature used in the mashing. Moreover, as dextrine is not fermented in the main fermentation and only partially in the after-fermentation, some of it remaining in the finished beer, this matter of temperature of mashing is obviously of importance for the character of the beer.

According to Märker and Schultze, at temperatures up to 65° C. the reaction takes place as follows:

$$4C_6H_{10}O_5 + 2H_2O = C_{18}H_{34}O_{17} + C_6H_{10}O_5;$$

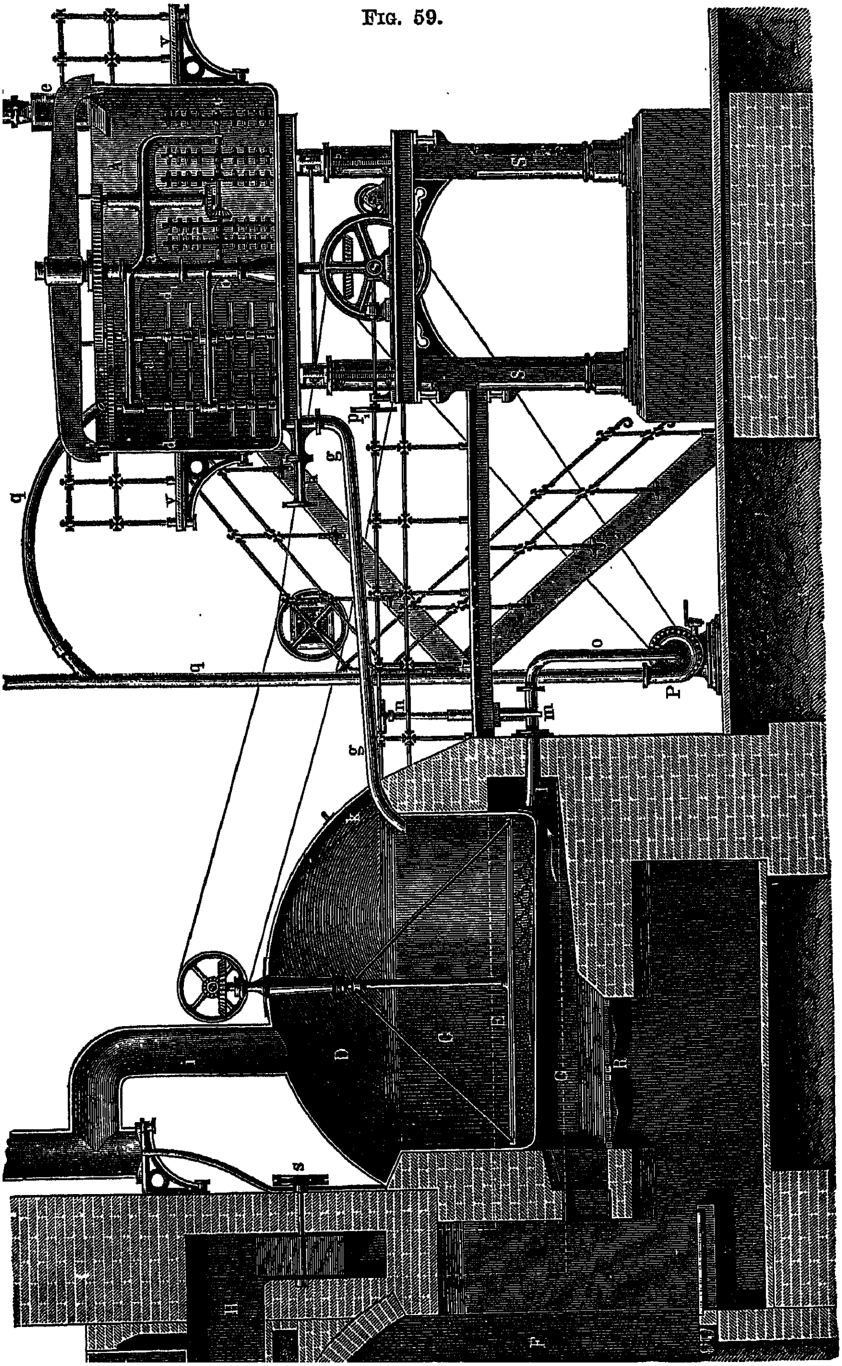
that is, four molecules of starch react with two molecules of water to form three molecules of fermentable sugar (maltose) and one molecule of dextrine. On the other hand, at temperatures over 65° C. the reaction becomes—

$$6C_6H_{10}O_5 + 2H_2O = C_{18}H_{34}O_{17} + 3C_6H_{10}O_5;$$

that is, six molecules of starch react with two molecules of water to form one molecule of maltose and three molecules of dextrine.

The results of practice, at all events, show that in the infusion process, which takes place at low temperatures, beers of lower extract per-

FIG. 59.



process is that it is difficult to avoid here a larger formation of lacti acid, due to the more prolonged action of the water upon the malt, whic is at just the temperature (about 50° C.) favorable for the formation c lactic acid. At the temperature of the infusion process the nitrogenou compounds are also less completely decomposed than in the decoctio process, so that a beer obtained by the former process furnishes a mor nutritious ground for the growth of bacterial ferments than the latter.

As the amount of diastase in the malt is sufficiently large to sacch rify considerably more starch than that contained in the malt itsel at times unmalted grain and starch-containing cereals are added. Th end to be attained is not only the saving of the cost of a portion of th malt, but to obtain a beer richer in extract and therefore of better kee ing quality.

These malt substitutes are generally cereals rich in starch, such corn and rice. At times unmalted barley, rye, oats, and even potato have also been used. Care must be taken that the saccharification these cases of the use of corn and rice is made as complete as possibl and hence it must not be overlooked that the starch of both corn an rice requires a higher temperature (71° C.) for its complete changin into fermentable sugar. The corn or rice before use should be shelle deprived of the germ, and crushed, so as to facilitate the liberation of i starch. The amount of malt substitute thus used should not in any ca exceed thirty per cent. of the weight of the malt. In some countries, in Bavaria, the use of malt substitutes is strictly prohibited by law.

The character of the wort is to be controlled by the use of the Ba ling saccharometer (see p. 179), as the specific gravity of aqueous ma extract corresponds to that of cane-sugar solutions of the same pe centage strength.

3. Boiling and Cooling.—The wort is drained off from the ma residue, or "draff," and run into the copper boiler, where it is boile while the hops are added at once in amount varying from one to thr (or more in the case of India ales) parts to the hundred of malt, lig beers taking the least amount, lager beers next, and heavy export bee the largest amount. If the amount of hops is to be calculated after t wort has been formed, 0.25 to 0.30 kilos. may be taken to the hectolit of wort of 10 to 12 per cent., 0.40 to 0.60 kilos. to the hectolitre of wo of 12 to 15 per cent., and 0.70 to 0.80 kilos. to the hectolitre of strong worts.

The boiling accomplishes several desirable changes in the wort: fir the unhydrolized protein material present separates out, which result facilitated by the action of the tannic acid of the hops, which also thro out any unchanged starch; second, the wort is concentrated; third, t valuable constituents of the hops (hop-bitter and ethereal oil) are tak up by the wort and give to the beer its taste, aroma, and keeping qua ties. The time of boiling varies considerably, requiring to be longer f worts prepared by the infusion process than for those by the decocti process. From one to two hours is generally sufficient where the wo [illegible] concentrated. Too long boiling is injurio

: dry malt, sixty-five to eighty per cent. are taken up as extract in the ort; of one hundred parts of hops, twenty to thirty parts.

The wort is now to be cooled preparatory to the fermentation. This ›oling must be effected as rapidly as possible, so that the lactic fermen- .tion and similar changes may not take place. The cooling is generally fected in very shallow wide tanks, which are placed where a good rculation of air can be assured. From these tanks the still warm wort often run through a circuit of pipes cooled by ice-water flowing around ıem, or is run in thin streams (known as a "beer fall") over a series : pipes through which cold water or chilled brine from the refriger- :ing apparatus circulates. Such an arrangement has now come into ɜneral use in large breweries provided with artificial refrigeration. Of ›urse, in such a method of cooling the wort is exposed for a consider- ɔle time to impure air containing spores, which, getting into the liquid, .ay afterwards affect the fermentation. In all cases where Hansen's ure yeast is to be employed the wort must be cooled in vessels to which ıly sterilized air has access. For an arrangement of this kind, see 7agner's "Chemical Technology," 13th ed., p. 911. It is thus cooled ɔwn to the point needed for the beginning of the fermentation. This ɔint depends upon the character of the fermentation, whether with top ɜast or bottom yeast; for the latter it must be some 8° to 10° C. below ıat needed for the former. The cooled wort is now allowed to deposit sediment of coagulated albuminoids, particles of hops, etc., which were ıspended in it when the cooling began. This sediment is gathered and ressed and the liquid added to the rest of the wort.

4. Fermentation of the Wort.—The wort may either be left to ɔontaneous fermentation depending upon the spores of yeast ferments, hich are always present in the air of a brewery, or it is started into ɜrmentation by the addition of yeast. The former method is followed ı Belgium, but in the great majority of cases elsewhere fermentation is ıcited by the direct addition of a suitable yeast. As stated before in ıe section on the nature of fermentation (see p. 205), there are two ıdically different methods of carrying out this process in practice; the ırface fermentation and the bottom fermentation. The first of these, ›llowed almost exclusively in England for all malt liquors and in this ›untry for ales, is specially adapted for worts rich in maltose, and .kes place more rapidly, at a higher temperature, and produces more .cohol. As English worts, moreover, are usually prepared by the .fusion method, a considerable quantity of soluble gluten is left in the ɿuor, which on exposure to the air, as in half-empty casks, may start .e acetic fermentation, or souring. The second of these, followed in ermany and Austria and in this country for lager-beer, proceeds more owly; the production of alcohol is restrained by the low temperature, ıd as the fermentation proceeds with freer and more prolonged access : air, the yeast-plants in their growth consume the proteid matter as ›od. Consequently there is less albuminoid matter left to start souring, ıd the beer is a better-keeping beer than those prepared by the more

matter of keeping quality, and may offset the advantage just mentione The fermentation, by whichever method carried out, may be divided in three stages: first, the *main fermentation,* which begins shortly after t addition of the yeast, and is specially characterized by the decompositi of maltose, the formation of new yeast-cells, and the rise of temperatur second, the *after-fermentation,* in which the decomposition of malto still continues, but the formation of yeast-cells has nearly ceased, an the yeast particles suspended in the beer settle out and the beer clear and, third, the *still fermentation,* which follows the completed after-fe mentation, in which maltose is still decomposed and some dextrine changed into maltose by what diastase is present, but the yeast-cells a no longer formed.

The fermenting vessels are great oaken tuns holding fifty to o hundred barrels. The thick froth, or magma, of yeast is added in amou varying from one-half to three-quarters of a litre per one hundred litr of wort of ten to fourteen per cent. It may either be added direct to t whole body of the wort and stirred in, or may be mixed with a small amount of the wort, allowed to stand for four to five hours until fe mentation starts, and then the mixture added to the main body of t wort. In the surface fermentation process, the main fermentation las from four to eight days, during which time the temperature must carefully regulated and held at from 14° to 18° C. The surface is first covered with a white foam which rises and curls and breaks in a variety of forms. The temperature rises from two to four degrees, an care must be taken to control and reduce this, which used to be done b the use of conical cans, or ''swimmers,'' holding ice, floated at the to of the tun, cooling the mass, but the tuns are now cooled just as the fe menting cellars are, by artificial means. The fermentation is not allowe to go to completion at this initial temperature, but the beer is tran ferred for the after or slower fermentation to cooler cellars (of abo 5° C.), where it is put into storage-casks. After sufficient time here, is drawn into casks containing beechwood shavings, to which isingla is sometimes added to clear it, and there is added to it some fresh fe menting beer (''Kräusen ''), in the proportion of one barrel to twent which starts a new fermentation, giving the beer its ''head.'' In t bottom fermentation, the fermenting cellar is kept at 4° to 5° C., an the main fermentation lasts from nine to ten days. The after-ferme tation follows in cellars cooled to 1° to 2° C., and lasts correspondingl longer.

Berlin weiss-beer is brewed from malted wheat to which some malte barley is added, and is fermented at relatively higher temperature (16 to 24° C.). At the end of the main fermentation, which is finished i three days, it is transferred, with the addition of some fresh fermentin beer, to tightly-stopped stone jugs, in which the after-fermentation tak place. In eight to fourteen days it is in condition for drinking. It i of course, effervescing, is somewhat turbid, and has a sour taste fro

rse have keeping qualities imparted to it in its manufacture by special
dition of hops, or otherwise, but most beers can have their keeping
alities improved by direct treatment after they are finished beverages.
is is most legitimately done by the process of "Pasteurizing," which
nsists in heating the beer either already bottled or in casks to a tem-
rature of about 60° C., which apparently kills all ferments which
velop the souring of beer. Less legitimate and forbidden by law in
st countries is the addition of salicylic acid, boric acid, or calcium
sulphite.

III. Products.

The various designations that have been given to malt liquors do not
cessarily imply distinctive differences in the character of the product.
ey represent largely the different usages of different countries and
alities. Thus, in England *Ale* was at one time brewed without hops,
t the term now is applied to a beer brewed by the surface fermentation
ocess, which is practically the only method used in England. *Porter*
s now come to mean a dark malt liquor, made partly from brown or
ack malt, the caramel in which gives it the sweetness and syrupy
pearance, and containing four or five per cent. of alcohol. *Stout* is a
onger porter, with larger amount of dissolved solids, and containing
or seven per cent. of alcohol.

Lager-beer is beer as brewed in Germany by the bottom fermentation
ocess, which process is, moreover, retarded, so that the beer has better
eping qualities. It also has a larger amount of hops used in its pro-
ction. It is brewed in winter for storage and use in summer. *Schenk-*
er is also a bottom fermentation beer, but is designed for use as soon
finished, and the process is somewhat quicker than with lager-beer,
d a smaller amount of hops is used. *Bock-beer* is a stronger lager-
er, made with one-third more malt, and brewed specially in the spring
the year. *Weiss-beer*, as before stated, is made chiefly from malted
eat, and is yet in the after-fermentation. Most other names are from
alities, and represent the characteristic products of those places.

The composition of various English and German beers is given in the
companying table on the authority of Professor Charles Graham.
llen, Commercial Organic Analysis, 2d ed., vol. ii, p. 92.)

	Maltose.	Dextrine.	Albuminoids. (Wanklynized.)	Ash, coloring, etc.	Total solids.	Acetic acid.	Lactic and succinic acid.	Alcohol.	Ratio of solids to alcohol.
rton pale ale	1.75	2.48	0.21	0.55	5.13	0.02	0.14	5.37	1:1.05
rton bitter ale	1.62	2.60	0.16	0.87	5.42	0.01	0.17	5.44	1 : 100
ild X	1.87	1.88	0.20	1.30	5.39	0.04	0.14	4.60	1:0.85
XX	2.88	2.04	0.30	1.48	6.80	0.02	0.10	6.50	1:0.96
otch export, bitter . .	1.62	2.50	0.30	0.70	5.21	0.16	0.09	5.00	1:0.96
blin stout, XX . . .	3.45	3.07	0.26	1.76	8.71	0.01	0.17	5.50	1:0.63
blin stout, XXX . . .	5 35	2.09	0.43	1.40	9.52	0.04	0.25	6.78	1:0.71

The composition of various American beers and ales as analyzed C. A. Crampton, of the United States Department of Agriculture, is al given.*

	Maltose.	Dextrine.	Albuminoids.	Free acids as lactic.	Ash.	Phosphoric acid.	Extract.	Alcohol.	Specific gravity.
Milwaukee lager, bottled	1.10	1.57	0.51	0.057	0.196	0.065	4.18	4.28	1.01
Milwaukee export beer, bottled .	1.06	2.63	0.40	0.057	0.309	0.056	5.40	4.42	1.01
Milwaukee "Bohemian" beer . .	1.82	3.04	0.406	0.071	0.224	0.057	5.88	4.16	1.01
Milwaukee "Bavarian" beer . .	1.75	2.87	0.556	0.074	0.346	0.077	6.26	5.06	1.01
St. Louis export beer	2.14	2.54	0.463	0.067	0.312	0.074	6.15	4 40	1.01
St. Louis pale lager, bottled . . .	2.17	2.75	0.463	0.067	0.312	0.064	4.64	4.28	1.01
St. Louis "Erlanger" beer, bottled	2.51	2.58	0.675	0.046	0.183	0.093	6.82	4.68	1.02
Philadelphia lager, bottled . .	1.46	2.30	0.538	0.086	0.241	0.078	5.22	4.29	1.01
Philadelphia "Budweiss," bottled	2.14	2.57	0.531	0.046	0.265	0.095	5.94	4.52	1.01
Philadelphia ale, bottled	0.59	0.90	0.531	0.232	0.401	0.085	3.46	6.24	1.00
Reading ale, bottled	0.93	1.99	0.731	0.382	0.472	0.077	5.55	6.92	1.01
Reading porter, bottled	2.67	2.88	0.763	0.166	0.412	0.100	8.19	4.89	1.02

IV. Analytical Tests and Methods.

1. For Malt.—The brewing value of a sample of malt is depende upon three factors,—namely, the proportion of soluble or extractive matt it will yield to water; the character of this extractive matter; and t diastatic activity. The extractive matter in malt is usually determin by a miniature mashing process. This is carried out, according to t accepted method of the Institute of Brewing in England, as follows The malt is first crushed uniformly fine; fifty grammes are then weigh out as rapidly as possible (on account of its hygroscopic character), a placed in a weighed beaker with 360 cubic centimetres of distilled wat previously heated to 154° to 155° F. The beaker is covered with watch-crystal and placed in a water-bath so that its contents are kept a temperature of 150° F. for fifty-five minutes. The mash is stirred at i tervals of ten minutes during this time. The temperature is then rais to 150° F. in five minutes, and the whole mash washed into a flask gra uated to four hundred and fifteen cubic centimetres, cooled to 60° made up to the mark at the same temperature, well shaken, and filter through a large ribbed paper. The specific gravity of the filtrate is th determined at once at 60° F. compared with water at that temperatu For most purposes, it is sufficiently accurate to make up the unfiltered wo to four hundred and fifteen cubic centimetres, filter a portion through dry filter and take the density. The draff is here assumed to measu fifteen cubic centimetres, and the tedious washing is dispensed wit The excess of density over that of water (taken at 1000) multiplied 2.078 will give the percentage of dry extract yielded by the malt. Th method is based on the fact that each gramme of malt extract per hu dred cubic centimetres of infusion has been shown by experiment raise the density of the liquor by 3.85 degrees (water = 1000). T

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* United States Department of Agriculture, Bulletin No. 13, Part iii, p. 282.

gure 2.078 is then the fraction $\frac{8}{3.85}$. Instead of ascertaining the ravity of the infusion, the proportion of solid matter may be deter- ined by evaporating a known measure of the wort to dryness in a flat- ottomed dish so that the residue may form a thin film. This is dried 105° C. and weighed. Other methods are those of Metz,* with the se of Schultze's tables, and of Metz as improved by Weiss.

The determination of diastatic power in a sample of malt is also of aportance in valuing it, even if the full diastatic power is not likely to called out in the brewing process, where it is usually in excess of the eed for the production of a beer-wort. The process of Lintner adopted the Institute of Brewing† determines by the aid of Fehling's solution e amount of maltose produced by the action of a cold infusion of the alt upon a measured starch solution. This supposes that the action diastase upon starch in the cold is always uniform and produces the me relative amount of maltose, which is now regarded as a matter of me uncertainty. The method proposed by Dunstan (Allen, 2d ed., ol. ii, p. 278) simply notes the end of the transformation of the starch the absence of color with iodine solution. For it five grammes of ery finely-powdered malt are digested and agitated for one hour with fty cubic centimetres of cold water. The liquid is then strained off d the residue again digested for an hour with fifty cubic centimetres water, and the liquids are then mixed and made up to one hundred ibic centimetres. Five-tenths gramme of starch (dried at 100° C. efore weighing) is gelatinized by boiling with water, and the cold quid diluted to one hundred cubic centimetres. The solution of malt tract is then added to twenty cubic centimetres of this mucilage by stalments of one cubic centimetre, at intervals of half an hour, until ceases to give any color, when a small quantity is tested with a dilute lution of iodine. If less than one cubic centimetre of the solution roduces this effect, more of the mucilage should be added and the peration continued.

To determine the soluble proteids of malt assumed to represent the astase C. Graham proposes to use the Wanklyn albuminoid-ammonia rocess.

2. For Beer-worts.—The determination of the specific gravity of e wort is of importance, as from this may be calculated the total solid atter in the wort. If from the specific gravity of the wort we take 00, and divide the difference by 4,‡ we get the number of grammes solid extract contained in one hundred cubic centimetres of the wort. or the purpose of the brewer special forms of hydrometers have been nstructed, the readings of which are immediately available. Thus, ites's saccharometer gives readings of pounds per barrel (of thirty- gallons),—that is, excess of weight in pounds of a barrel of wort over e same bulk of water. These readings can then be converted into real

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* [illegible]

specific gravity figures by a simple proportion, using the weight barrel of pure water, of this wort with the excess of weight shown by saccharometer reading and the specific gravity of pure water as te The Bates saccharometer readings can be converted into those of Bal or Brix by the following formula: Balling $= \frac{260 \text{ Bates}}{360 + \text{Bates}}$. method of ascertaining the original gravity of beer-worts which] undergone fermentation is described later. (See following page.)

In brewing, the relative proportion of maltose and dextrine in wort is of great importance and is liable to considerable variation, b dependent on the temperature at which the mashing was conducted, length of time occupied in the process, and the diastatic activity of malt employed. The composition of the wort largely influences the sequent fermentation, as a wort containing little dextrine will proc a beer of low density which will clarify readily, but be "thin" apparently much weaker than beer of the same original gravity higher final attenuation. C. Graham estimates the maltose and dext in beer-worts from the cupric oxide reducing power of the solu before and after inversion. (For details of his procedure, see Al vol. ii, p. 274.) West Knight (Analyst, vii, p. 211) has describe very simple and rapid method of approximately determining the trine in beer-worts. Ten cubic centimetres of the wort is treated i small weighed beaker with fifty cubic centimetres of methylated spiri .830 specific gravity. This causes the precipitation of the greater p of the dextrine, which after a few hours collects on the bottom of beaker as a gummy mass, from which the alcoholic liquid can be pou off. The deposit is rinsed with a little more spirit, and the beaker dr in the water-oven and weighed. To the weight obtained an addition .045 gramme is made as a correction for the dextrine retained in sc tion by the spirituous liquid.

3. For Beer.—The *specific gravity* of the beer is a determinat that is necessary as a basis of calculation for the other determinati as to its composition. It should be made after freeing the beer fr carbon dioxide as fully as possible. It can be made with a spec gravity flask, but is most readily and accurately carried out with Westphal specific gravity balance (see Fig. 30), which for this purp is provided with a fourth rider giving the fourth place of decimals.

The amount of *extract* is frequently determined by taking a defin volume of beer of which the specific gravity has been determined, ev orating it to one-third its bulk, and then adding water sufficient to rest it to original bulk. The specific gravity of this liquid is then determin as just described. The percentage of extract can now be found by reference to Schultze's tables for determining the amount of extract specific gravity, or more simply by O'Sullivan's method, in which excess of this specific gravity over 1000 divided by 4 gives the numl ubic centimetres of the beer on a flat watch-crystal in an air-bath at a emperature of from 70° to 75° C. The complete drying of the film requires about twenty-six hours.

The percentage of *alcohol* is best determined by distillation. For this purpose one hundred cubic centimetres of the beer are taken, a few drops of caustic soda added to neutralize the free acid, and the liquid brought up to about one hundred and fifty cubic centimetres. It is then distilled with the aid of a Liebig condenser into a graduated flask until nearly one hundred cubic centimetres have come over. The distillate is now thoroughly mixed, cooled to 15° C., and then brought exactly to the 100-cubic-centimetre mark and again mixed. Its specific gravity is now taken, and from a set of alcohol tables (see Hehner's tables, Appendix, p. 579) the percentage of alcohol by weight of the distillate found. Then as the specific gravity of the original sample is to the specific gravity of the distillate so is the weight per cent. in the distillate to the weight per cent. in the original sample. Indirectly the alcohol percentage can be determined, although not with the same accuracy, by the aid of the data gotten in the determination of extract already narrated. For if the specific gravity of the original sample be divided by the specific gravity of the de-alcoholized solution we get the specific gravity of the alcohol driven off, from which figure the percentage by weight of alcohol can be gotten in the tables. When both the alcohol and the extract percentage of a beer are known, by Balling's method the percentage of *extract in the original wort* can be calculated, and then with the aid of this and the percentage of extract in the beer the "attenuation" or diminution in the gravity of the original wort due to fermentation and alcohol production can be determined. As the weight of alcohol produced is approximately fifty per cent. of the saccharine matter destroyed by the fermentation, we have the formula $2a + e = w$, in which a is the alcohol percentage, e the extract percentage of the beer, and w the percentage strength of the original wort. Then using this figure just obtained $w : 100 :: 2a : x$, in which x will represent the degree of attenuation. More accurately, the actual degree of fermentation (*Wirklicher Vergährungsgrad*) is gotten by the proportion $p : p - n :: 100 : v'$, in which p is the extract in the original wort, n the extract in the beer, and v' the actual fermentation degree; $(p-n)$ is termed the "real attenuation." It is obvious from the two proportions given that in practice $2a$ is often taken as equivalent to $(p - n)$. This is not strictly correct. It is found in the fermentation of beer-worts that 100 parts of extract yield 48.391 parts of alcohol, so that what is termed an "alcohol factor" is necessary to convert one into the other. In England a different procedure is followed. A definite volume of beer is taken and one-half distilled off. This distillate is brought up with water at 60° F. to the original volume and its specific gravity taken. The difference between 1000 and the observed gravity is called the "spirit indication" of the beer. With this can be found, in a table prepared for the Inland Reve-

Then the liquid left in the retort after the distillation is diluted wi water and brought up to the original volume, when its specific gravity carefully taken. This is called the "extract gravity," and this added the degrees of gravity lost gives the "original gravity of the wort."

The *acidity* of beer is partly due to lactic and succinic acids, whi are fixed acids, and partly to acetic acid, which is volatile. The fix acids are usually determined jointly in terms of lactic acid by dissolvi the dry extract of the beer in water and titrating the solution with de normal alkali solution. Baryta-water is preferred by many chemists, the sulphate of baryta which forms carries down much of the colori and allows the end reaction to be better seen. The volatile acid of be is chiefly acetic acid, which is usually determined by subtracting t measure of alkali required to neutralize the extract from that requir by the original beer (after getting rid of the carbonic acid by shaki thoroughly).

The chief *adulterations* of beer are from the use of salicylic acid as preservative and the addition of various bitter principles as substitut for hop-bitters. The salicylic acid may be searched for by concentrati the beer to one-half at a gentle heat and shaking the cooled liquid wi ether, or a mixture of ethylic ether and petroleum-ether. The ethere layer is then separated, evaporated to dryness, and the residue dissolv in warm water. On adding ferric chloride, a violet coloration is pr duced if salicylic acid be present. Other chemists recommend dialyzin when the salicylic acid will readily dialyze into the pure water and ca then be tested. For the detection of the bitter principles used as subs tutes for hops elaborate schemes have been proposed by Enders (give in Allen, 4th ed., vol. i, p. 162) and Dragendorff (Gerichtliche-Chemisc Ausmittelung der Gifte).

C. THE MANUFACTURE OF WINE.

I. Raw Materials.

1. The Grape.—While the name wine is often used to include t products of the spontaneous alcoholic fermentation of any sweet fruit berry, it is usually limited to the product of the fermentation of t grape, which alone is cultivated on an extensive scale throughout t civilized world purely for the manufacture of wine.

The cultivation of the grape-vine and the production of wine ther from dates back to the earliest historic times. Beginning in the Ea and the Mediterranean lands, it extended northward and westward unt at present France is the chief wine-producing country, while German Austria, Spain, and Portugal have all established flourishing wine i dustries indigenous to their soil. In this country, the wine industry mainly established in the States of Ohio, New York, Virginia, and Cal fornia.

The varieties of the vine (estimated to number almost two thousand species, *Vitis vinifera.* In this country four or five wild species have yielded varieties which when cultivated have proven adapted to wine production. Thus *Vitis riparia,* or "frost-grape," has yielded as cultivated varieties the Taylor and the Clinton grapes; the *Vitis æstivalis,* or "summer-grape," has yielded as varieties Norton's Virginia, Cythiana, and Herbemont; the *Vitis Labrusca,* or "Northern fox-grape," has yielded as varieties the Catawba, Isabella, Concord, and Delaware grapes; the *Vitis vulpina* or *rotundifolia,* or "Southern muscadine," has yielded as varieties the black, red, and white Scuppernong. Numerous varieties of the European vine, the *Vitis vinifera,* have also been cultivated successfully in California, among which may be mentioned the Mission, Riesling, Traminer, Rulander, Gutedel, and Zinfandel.

The grapes owe their wine-producing value in the first place to the grape (or invert) sugar which they contain, and in the second place to the free acids, which in the later ripening of the wine are to develop the fragrant ethers, and to the albuminoids, which exert a great influence on the fermentation. The composition of the grape varies of course in different localities and even from year to year in the same locality, but its mean composition is thus stated by König: Grape-sugar, 14.36 per cent.; free acid (tartaric), .79 per cent.; nitrogenous material, .59 per cent.; non-nitrogenous extract, 1.96 per cent.; skins and kernel, 3.60 per cent.; ash, .50 per cent.; and water, 78.17 per cent.

The grapes are taken for wine-making only when they are fully ripe, and in many localities it is even customary to wait until the grape shows a slight appearance of over-ripeness or evidence of wilting, so that the maximum of sweetness may be attained. In some cases the grapes are plucked from the stems, either by hand or by the aid of three-pronged forks, while in other cases the stems are left when they are crushed in order that the tannin so obtained may aid in the clearing of the fermenting juice. This juice is known as "must," and the pressed pulp and skins as the "marc."

2. THE MUST.—This may properly be considered as still a raw material, as its expression from the grapes is purely a mechanical process. This is now generally effected by power-presses of various forms, although at one time largely effected by trampling the grapes under feet. (This method is still followed in the Oporto and the Maderia wine districts.) The first portion of must that runs from the presses is often collected separately, as it is the juice of the ripest and sweetest grapes; that which comes later is richer in acid and in tannin, as it comes partly from unripe grapes and partly from the stems and skins. The amount of must that is obtained usually ranges from sixty to seventy parts in he one hundred of grapes.

The composition of this must is of the greatest importance, as upon t depends the character of the wine that will be produced, whether it hall ferment normally throughout and develop the perfect flavor and aroma desired, or whether it shall be thin and sour and show tendencies owards alteration or "disease." The proportions of its constituents to year, and in grapes grown in the same year under different condition of soil, exposure, etc.

Thus, two different musts of 1868 are given and two musts of th same variety of grape in two succeeding years, the first of which was favorable year and the second an unfavorable year. The analyses ar all by Neubauer.

	Sugar.	Free acid.	Albuminoids.	Ash.	Non-nitrogenous extract.	Water.
Neroberger Riesling, 1868	18.06	0.42	0.22	0.47	4.11	76.72
Steinberger Auslese, 1868	24.24	0.43	0.18	0.45	3.92	70.78
Hattenheimer, 1868, (good year) . . .	23.56	0.46	0.19	0.44	5.43	69.92
Hattenheimer, 1869, (bad year) . . .	16.67	0.79	0.33	0.24	5.17	76.80

The percentage of grape-sugar in the must sinks at times to twelve per cent., and may rise as high as twenty-six to thirty per cent. The ratio between acid and sugar, according to Fresenius, ranges from 1:29 for good varieties of grapes in good years to 1:16 for inferior varieties in medium years. If the ratio falls as low as 1:10, the grapes are unripe and taste acid. This ratio of acid to sugar is now generally taken as the criterion for the quality of the must in any year or special locality.

In bad seasons the free acid is more generally malic than tartaric, which is the normal constituent.

II. Processes of Manufacture.

1. Fermentation.—The fermentation of the must is a spontaneous one following exposure to the air, and due to the spores which drop upon the surface of the must as exposed in the fermenting-tubs. It may be a surface fermentation, taking place at temperatures of 15° to 20° C., as is the practice in Italy, Spain, and the south of France, or a bottom fermentation, taking place in cooler cellars at 5° to 12° C., as is the practice in Germany and with the finer French wines. The first method produces a fiery wine rich in alcohol, but without bouquet or aroma; the second method, lighter wines with delicate bouquet, due to the formation of wine esters. In either case the fermentation can be divided, as was the case with malt liquors, into three stages: the first, or main fermentation, which, according as the surface or the bottom fermentation method is followed, lasts from three to eight days, or from two to four weeks; the second, or still fermentation, which lasts until the following spring; and the third, the storage fermentation, which lasts for several years, until by the gradual development of its bouquet it becomes perfectly ripe.

In the case of red wines, the main fermentation is allowed to take place with the marc added to the must, so that as the alcohol is developed it may dissolve out the coloring matter (œnocyanin) of the skins as well as some of the tannin, which latter is of benefit in effecting a more rapid separation of the protein materials. To prevent this pulpy mass from

'ers are often used in this case to hold it down. In the main fermen-
ion, the casks are usually freely exposed to the air. Many wine ex-
:ts recommend in addition the aeration of the fermenting must or a
ipping of the liquid, so as to induce a fuller and more vigorous fer-
ntation. On the other hand, other authorities consider that this exces-
e exposure to air injures the quality and aroma of the wine, and
:ommend only a partial exposure to the air after the main fermenta-
n has begun. As the main fermentation comes to an end, the yeast
ith more or less tartar, gummy matter, and albuminoids) settles to
; bottom, the liquid clears and is ready to be racked off into casks,
der the name of *young wine* (Jungwein), to undergo the after- or still-
·mentation. If the racking off does not take place promptly with the
ding of the more energetic main fermentation, the young wine, of
ich a considerable surface is exposed to the air, is very apt to start
;o the acetic fermentation. The casks into which it is now put are
pt quite full in order to prevent this undesirable change, slight addi-
ns being made every few days if necessary, and the bungs are set
sely in place. During this after-fermentation there deposits upon
; inner walls of the cask *argols,* or impure acid potassium tartrate
Veinstein), with some yeast and albuminoid matter. This fermenta-
n lasts from three to six months, and then the wine is racked off
ain into smaller casks to undergo the final ripening, in which the
iquet of the wine is especially developed by the formation of esters,
ile it clears more thoroughly from the remaining particles of yeast,
. The duration of this ripening may be two, four, or with rich wines
in eight years or more, when it is considered "bottle-ripe." During
s ripening fungous vegetation is very apt to start, and must be
'ested in order to prevent the spoiling of the wine.

2. Diseases of Wines and Methods of Treating and Improving
em.—The souring of wine, due to the beginning of the acetic fermen-
ion, is one of the commonest of these so-called diseases, especially with
ht wines, poor in alcohol and tannic acid, and hence commoner with
ite than with red wines. It arises from too free an exposure to the
and too high a temperature during fermentation. If just begun it can
cured by the addition of a small quantity of potashes, which form
:assium acetate, or by starting the alcoholic fermentation afresh by
ding a new quantity of sugar. If the souring is very pronounced it
not be cured, and the wine is made into wine-vinegar.

The gumminess or ropiness of wine frequently arises from a prema-
'e filling into bottles, and is due to the beginning of the mucous fer-
ntation of sugar. It takes place in wines poor in tannic acid, and
ice more readily with white than with red wines. It can be cured by
dition of tannic acid, treatment with sulphurous oxide, or starting a
w fermentation by addition of grape-sugar.

The development of a stale or flat taste in the wine is due, according
Pasteur, to the growth of a thread-like ferment. The wine becomes
udy, diminishes in alcohol and increases in acid percentage, it darkens

put into a cask which has been filled with sulphurous oxide fumes, which destroy the ferment.

The turning bitter of red wines is due also, according to Pasteur, to a plant-growth, according to others to the formation of a bitter aldehyde resin. Neubauer has found that the tannic acid and the coloring matter both decrease in percentage in this disease. It can be cured completely by heating the wine to 60° to 64° C., or by starting the fermentation anew by adding fresh quantities of grape-sugar.

The mouldiness of wine is due to the development of a fungoid growth in the form of a white film on the surface of wines poor in alcohol, and always precedes the souring of the wine. It is to be obviated by treatment with sulphur dioxide or more effectual protection of the young wine from the air.

Of the general lines of treatment adopted to prevent the development of these various diseases, we notice first the clarifying with isinglass (finings) or other form of gelatine. This is particularly applied to the sweet and heavy white wines, which often remain turbid and have to be cleared by the coagulating of the albuminoid which is added. With red wines which contain tannic acid, casein or blood albumen is used instead of gelatine. Fine clays are also used, especially in Spain, for this clarifying.

The most important process, however, which is applied for the preservation and protection of wine against diseases is that known as "Pasteurizing." It consists in heating the wine either in casks or in bottles to a temperature of 60° C., and then preserving it without exposure to the air. This temperature is found to be sufficient to kill most of the germs which bring about the diseases before mentioned. A form of cask much used for this "Pasteurizing" process is shown in Fig. 60.

The use of salicylic acid for preserving wines has been extensively tried, but its use here is open to the same objection as before stated in speaking of beer, and it is now forbidden in most countries.

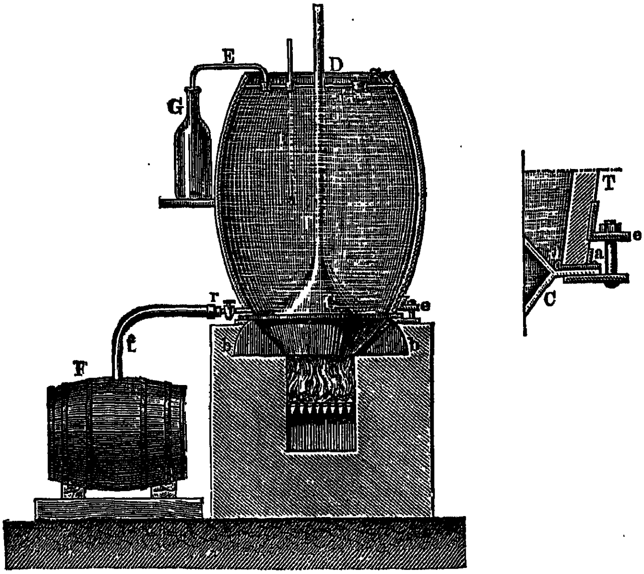
Of the methods of "improving" wines, as it is termed, that known as "plastering" is probably most largely practised, its use for red wines extending to Spain, Portugal, Italy, and the South of France. It consists in adding plaster of Paris (burnt gypsum) either to the unpressed grapes or to the must. The plaster takes up water and so increases the alcoholic strength of the fermenting must, which in turn allows of a greater extraction of the coloring matter from the skin. At the same time the wine is given better keeping qualities as well as deeper color. However, the sulphate of lime changes the soluble potash salts of the wine into insoluble tartrate of lime and soluble acid sulphate of potash, which latter remains dissolved along with some of the gypsum, and undoubtedly has an injurious effect upon the consumers of the wine. The process has hence had to be controlled by law, and in France the sale of wine containing over .2 per cent. of potassium sulphate is prohibited. The ash of pure wine does not exceed .3 per cent., but in the samples of sherry usually met with it reaches .5 per cent., and is almost

Hugonneng recommends adding dicalcium phosphate instead of gypsum. This process, called "phosphotage," is said to have all the good effects obtainable from plastering without increasing, as the latter does, the percentage of sulphuric acid and decreasing that of phosphoric acid.

Chaptalization consists in neutralizing the excess of acidity in the must by the addition of marble-dust, and increasing the saccharine content by the addition of a certain quantity of cane-sugar, which the vintners sometimes replace by starch-sugar. In this process the quantity of the wine is not increased, but it becomes richer in alcohol, poorer in acid, and the bouquet is not injured. It is much used in Burgundy.

Gallization, as proposed by Dr. Gall, has for its object the bringing of the must of a bad year up to the standard found to belong to a good must (he takes as standard 24 per cent. of sugar, .6 per cent. of acid, and 75.4 per cent. of water) by correcting the ratio of acid to sugar. This he does by adding sugar and water in sufficient quantity, and tables have been prepared to indicate the quantity needed according to the acid ratio shown by analysis. In both these processes, starch-sugar ought never to be used as a cheaper substitute for cane-sugar, as commercial starch-sugar will always introduce dextrine, an entirely foreign constituent, into the must.

FIG. 60.



Petiotization is a process which takes its name from Petiot, a proprietor in Burgundy, and is carried out as follows: The marc from which the juice has been separated as usual by pressure is mixed with a solution of sugar and water and the mixture again fermented, the second steeping containing, like the first, notable quantities of bitartrate of pot-being mixed. This process is very largely used in France, and is said to produce wines rich in alcohol, of as good bouquet as the original wine, and of good keeping qualities. It is not allowed to be sold there, however, as *natural* wine.

Scheelization consists in the addition of glycerine to the finished wine so as to improve the sweet taste without injuring its keeping qualities. The limits of the addition of glycerine lie between one and three litres to the hectolitre of wine. If the wine has not fully fermented, however, and if yeast-cells are present, the glycerine may yield propionic acid by decomposition.

3. MANUFACTURE OF EFFERVESCING WINES (*Champagnes*).—For the manufacture of champagne the blue sweet grapes are preferred. They must be pressed promptly after picking in order that the least possible amount of color be taken up by the must. The first pressing only is used for the champagne, and a second pressing of the marc yields a reddish wine, which is differently utilized. The must is first put into vats that impurities may settle and then filled into casks for the main fermentation, which is retarded as much as possible by being carried out in cool cellars. Cognac is also added to the amount of about one per cent., so as to increase the alcohol percentage and thus moderate the fermentation. After the main fermentation is finished the wine is racked off into other casks and left stopped until winter (end of December). It is then fined (or cleared) with isinglass and transferred to other casks, and this operation is repeated in a month's time. Towards the beginning of April it is ready to be transferred to bottles. The wines of different growths are now mixed and the amount of sugar in the wine determined, when a calculated additional quantity is added in the form of "liqueur" (a mixture of alcohol and pure cane-sugar). The bottles which are to receive the champagne must be specially chosen and be sufficiently strong to stand the pressure, which rises later to four to five atmospheres. They must also have sloping sides, so that the sediment may not adhere to the sides in the after-process. The wine after being corked is thoroughly secured by an iron fastening called an *agrafe,* and the bottles are arranged in piles in a horizontal position in the large champagne-vaults, where they remain throughout the summer months. Previous to the wine being prepared for shipment, the bottles are placed in a slanting position, neck downward, in frames, and the incline is gradually increased day by day until the bottle is almost perpendicular. With the sediment thus on the cork it goes into the hands of a workman called a "disgorger," who, holding the bottle still neck downward, proceeds to liberate the cork by slipping off the agrafe, and when the cork is three-fourth parts out he quickly inverts the bottle. The cork is thus forcibly ejected with a loud report by the froth, which carries with it the greater part of the yeast and other solid matters, what remains of these being got rid of by the workman working his finger round the neck of the bottle, whereby they are detached and forced out by the still rising froth. The wine is now dosed again with liqueur, the bottles filled

sweet heavy wines, like sherry, malaga, and port, are characterized high alcohol percentage, ranging from sixteen to twenty or twenty- This they cannot acquire through fermentation alone, as twelve or ;een per cent. seems to be the limit of alcohol developed in a wine by :t fermentation. They have the additional alcohol added to them :tly in order to give them keeping qualities. With some sweet wines alcohol is added to the must before the fermentation in order that fermentation shall be arrested, while a certain amount of sugar ins in the wine unchanged. The quality of wines is often improved lending. Light wines with too little alcohol are mixed with stronger s with the formation of an excellent product with better keeping ities, which can then be transported to long distances without in- . These mixtures can best be made when the wines are new, in r that after mixing they may undergo an insensible fermentation take a character distinctive of the new product.

'he practice of adding flavoring substances totally foreign to the :ituents of the must to new and inferior wines in order that they take the flavor and appearance of older and more valuable wine ilso become very wide-spread. Such practices are of course illegal l countries where laws against adulteration are enforced. Thus, flowers, orris-root, iris, cloves, oil of bitter almonds, and numerous imes, such as oil of orange flowers, of neroli, of petit-grain, and of t, are used, as well as coloring infusions like raspberries and walnuts. heavy wines are the ones most generally imitated. Port is fretly flavored with a mixture of elderberry juice, grape juice, brown :, and crude brandy. Sherry often consists of the cheaper Cape mixed with honey, bitter almonds, and brandy. In Spain and hern France a wine prepared from the vine known as the *Teinturier* ossessing an intense bluish-red color is extensively used for coloring her wines.

ı recent years, because of the deficiency in the wine crop of France o the ravages of the *Phylloxera,* the production of wine from dried ıs or prunes has enormously increased. This product, known as de raisin sec,'' is said to be a very close imitation of natural French ı. Spon * gives the following as the components of such a raisin :

sugar	5 kilos.	Common brandy	12 litres.
s	5 kilos.	River water	95 litres.
on salt	125 grammes.	Gall-nuts (bruised)	20 grammes.
ic acid	200 grammes.	Brewer's yeast (in paste)	200 grammes.

ɔ make this wine of a red color it is necessary only to add to the ingredients two hundred and fifty to three hundred grammes of ɔicked hollyhocks, taking care to keep them at the bottom of the

ıe reports of the United States consular agents show that the manıre of this raisin wine has become an industry of large proporof the development of this artificial wine industry and of the similar one of petiotizing in France is found in the statement of the amounts of cane-sugar used by French wine manufacturers in recent years. In 1885 there was used in France for the manufacture of grape wines 7,933,887 kilos. of cane-sugar; in 1886, 27,856,592 kilos.; for the manufacture of fruit wines in 1885, 24,142 kilos. of sugar; in 1886, for the same purpose, 145,555 kilos. Most of this fruit wine forms the basis of factitious champagne.

III. Products.

The normal constituents of a natural wine agree of course with those contained in the must, except in so far as new compounds have been developed by the fermentation process and previously existing ones have been decomposed or made to separate out.

We may divide the constituents of wine into two classes, volatile and fixed. The volatile matters are as follows: Water (eighty to ninety per cent.); alcohol (five to fifteen per cent.); glycerine (two to eight per cent.); volatile acids, acetic, œnanthic, etc., constituting one-fourth to one-third of the total acidity; aldehyde, compound ethers, together with other fragrant indefinite constituents, which give the wine its flavor and bouquet. The fixed matters are glucose, or grape-sugar, in small quantities in most wines; bitartrate of potash, tartaric, malic, and phosphoric acid, partly free and partly combined with various bases, of which compounds phosphate of lime is the most abundant, constituting fror twenty to sixty per cent. of the weight of the ash, the remainder bein chiefly carbonate of potash, resulting from the calcination of the bitartrate, with a little sulphate and traces of chlorides; coloring matter pectin and analogous gummy matters; tannin, one to two per cent. i red wines and traces only existing in white wines.

No very simple scheme of classification is possible, as the method and products of most countries are not fixed by rule, but vary widel according to the season and market. Still, we may distinguish betwee the red and white, and the sweet and the dry, wines; between the lig and delicately-flavored German and French wines and the more fie but coarser Italian and Swiss wines; between natural wines and tho fortified by addition of alcohol, as port, sherry, and madeira; betwe still wines and effervescing or champagne wines.

Most of these terms have already found their explanation in t description of the processes of manufacture. We may add that a *swe* wine is one in which a notable portion of the original grape-sugar of t must has escaped fermentation, or to which an addition of sugar h been made subsequent to the main fermentation. A *dry* wine, on t contrary, is one in which the sugar, whether originally present or su sequently added, has almost all undergone change in the processes of f mentation. *Champagnes* are wines in which a supplementary ferm tation is purposely developed subsequent to the bottling, where quantities of carbon dioxide gas are developed and held dissolved un

[illegible] the pressure a hi

akers distinguish three grades of effervescence. In *mousseux* the ressure in the bottles amounts to from four to four and a half atmosheres; in *grand mousseux* it reaches five atmospheres; and less than ur atmospheres' pressure constitutes *cremant* (from *la crème,* cream "), a wine which throws up a froth, but does not give off caronic acid violently. Some manufacturers also distinguish a grade *emi-mousseux.*

Of natural and unfortified foreign wines the following analyses rom Elsner * refer to German wines exclusively:

	Specific gravity.	Percentage of alcohol.	Percentage of extract.	Percentage of free acid (as tartaric).	Percentage of ash.	Percentage of phosphoric acid.
Rhine wines, Rüdesheimer . . .	0.9960	9.30	1.97	0.50	0.20	0.020
" " Rauenthaler	0.9960	9.25	2 10	0.54	0.19	0.023
" " Johannisberger . .	0.9958	8.60	2.20	0.52	0.19	0.023
" " Hochheimer	0.9935	8.00	1.50	0.72	0.16	. . .
" " Niersteiner	0.9956	7.54	1.75	0.62	0.18	0.012
Moselle wines, Brauneberger . . .	. . .	. .	2.60	. .	0.18	0.041
" " Pisporter	. . .	. .	2.40	. .	0.15	0.038
" " Zeltinger	. . .	. .	2.40	. .	0.16	0.039
Iessian wines, Bodenheimer . . .	0.9930	7.54	1.25	0.63	0.14	. . .
" " Laubenheimer . .	0.9934	6.83	1.00	0.60	0.10	. . .
" " Liebfrauenmilch .	0.9940	8.00	1.96	0.62	0.20	. . .
'alatinate wines, Deidesheimer .	0.9968	9.60	2.12	0.50	0.18	. . .
" " Oppenheimer .	0.9935	8.87	1.50	0.60	0.16	. . .
" " Wachenheimer.	0.9954	8.65	1.72	0.65	0.17	. . .
'ranconian wines, white	0.9943	6.65	1.20	0.60	. .	0.015
" " red	0.9932	8.00	1.50	0.47	0.20	. . .

The following analyses of French wines are from the official report the Laboratoire Municipal at Paris for 1883: †

	Alcohol by volume.	GRAMMES PER LITRE.						
		Extract at 100° C.	Extract in vacuo.	Ash.	Tartar.	Reducing sugar (as glucose).	Sulphate of potash.	Acidity (in H_2SO_4).
rdeaux wines, St. Estephe, 1878	11.1	22.4	28.3	2.20	1.31	1.50	0.49	2.96
" " Medoc, 1880	10.3	19.0	23.7	2.05	1.42	0.9	0.76	3.96
" " Latour, 1878	9.5	17.0	22.8	2.14	2.07	1.1	0.50	4.06
" " Chateau Margaux, 1878.	10.2	23.6	. .	. .	. .	1.5	0.48	. .
" " Larose, 1877.	11.2	23.0	30.1	2.34	2.44	1.3	0.63	. .
" " (white,) Sauterne, 1880	10.4	16.0	. .	.	. .	3.6	0.53	. .
rgundy wines, Chambertin, 1882	11.5	23.3	29.5	1.77	3.57	1.4	0.55	. .
" " (white,) Chablis, 1878	11.0	16.7	. .	. .	. .	0.6	0.38	. .
wer Burgundy, average of 7 analyses	7.8	20.2	. .	. .	. .	1.2	0.37	. .
per Burgundy, average of 25 analyses	9.1	20.7	. .	. .	. .	1.1	0.48	. .

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* Praxis des Nahrungsmittels Chemiker, 1880, p. 103.

Of sweet and fortified or treated wines the following analyses are given by König: *

	Specific gravity.	Alcohol by weight.	Extract.	Sugar.	Tartaric acid.	Glycerine.	Albuminoids.	Ash.	Phosphoric acid.	Sulphuric acid.
Tokay, 1868	1.0879	9.80	26.36	22.11	0.509	0.212	0.427	0.343	0.050	0.061
Tokay, Ausbruch, 1866	1.0588	10.29	18.34	14.99	0.517	0.234	0.389	0.300	0.074	0.022
Ruster, Ausbruch, 1872	1.0849	8.96	23.64	21.74	0.512	0.162	0.231	0.409	0.057	0.035
Malaga, 1872	1.0691	13.28	21.23	16.57	0.416	0.248	0.217	0.239	0.042	0.026
Muscat wine, 1872	1.0574	10.02	16.91	15.52	0.555	0.298	0.151	0.312	0.036	0.073
Port wine (white), 1860	1.0126	16.28	8.83	4.88	0.538	0.168	0.094	0.208	0.035	0.039
Port wine (red), 1865	1.0125	17.93	8.83	6.42	0.451	0.145	0.200	0.236	0.032	0.019
Marsala (Ingham)	0.9966	16.73	4.94	3.48	0.396	0.298	0.150	0.270	0.024	0.087
Marsala (Woodhouse)	1.0111	15.52	5.45	3.78	0.470	0.457	0.231	0.418	0.024	0.155
Madeira, 1868	1.0018	15.34	5.33	3.39	0.489	0.291	0.144	0.376	0.082	0.081
Sherry, 1870	0.9952	18.66	3.78	1.88	0.438	0.506	0.200	0.483	0.032	0.184
Sherry, Amontillado, 1870	0.9924	16.34	2.68	0.52	0.490	0.560	0.200	0.650	0.038	0.268
Samos wine, 1872	1.0519	10.97	14.46	11.82	0.502	. . .	0.237	0.563	0.058	0.044

Two analyses of champagne and effervescing wine are also given by König: †

	Specific gravity.	Alcohol by weight.	Extract.	Sugar.	Tartaric acid.	Glycerine.	Albuminoids.	Ash.	Phosphoric acid.	Sulphuric acid.
Champagne, Carte Blanche	1.0433	9.51	13.96	11.53	0.581	0.084	0.219	0.184	0.027	0.017
Effervescing Rhine wine	1.0374	9.80	10.88	8.49	0.566	0.062	0.294	0.171	0.034	0.026

Of American wines a large number have been investigated by the United States Bureau of Agriculture. A selection from those analyzed by H. B. Parsons ‡ in 1880 is given:

	Specific gravity.	Alcohol by weight.	Alcohol by volume.	Extract.	Ash.	Glucose.	Total acid as tartaric.	Fixed acids as tartaric.	Volatile acid as acetic.
Dry red wines:									
Concord, Virginia, 1879	0.9953	8.83	11.08	2 10	0.174	Trace.	0.709	0.452	0.206
Clinton, Virginia, 1879	0.9950	9.82	12.31	2.36	0.238	None.	0.784	0.513	0.217
Norton's Virginia, 1879	0.9937	10.21	12.77	2.88	0.298	Trace.	0.772	0.377	0.316
Ives's Seedling, Virginia, 1879	0.9944	8.68	10.82	2.18	0.247	Trace.	0.723	0.512	0.169
Sonoma Red Mission, California, 1879	0.9968	7.99	10.03	2.42	0.428	None.	0.722	0.301	0.337
Sonoma Red Zinfandel, California, 1879	0.9962	7.80	9.78	2.43	0.255	Trace.	0.693	0.391	0.242
Concord Bouquet, New Jersey	0.9928	9.84	12.31	2.18	0.141	0.71	0.741	0.272	0.375

	Specific gravity.	Alcohol by weight.	Alcohol by volume.	Extract.	Ash.	Glucose.	Total acid as tartaric.	Fixed acids as tartaric.	Volatile acid as acetic.
white wines:									
rocton Catawba, New York	0.9890	12 28	15.30	2.09	0.121	. . .	0.542	0.470	0.068
issouri Catawba, Missouri	0.9911	8.88	11.08	1.67	0.129	Trace.	0.772	0.387	0.308
hio Catawba, Ohio	0.9892	10.25	12.77	1.63	0.113	Trace.	0.728	0.424	0.243
ulānder, Virginia, 1880	0.9914	10.46	13.05	1.90	0.199	Trace.	0.545	0.302	0.194
elaware, Virginia, 1880	0.9932	9.35	11.70	1.88	0.255	Trace.	0.562	0.332	0.184
aylor, Virginia, 1880	0.9921	10.37	12.96	1.99	0.185	Trace.	0.732	0.317	0.332
erbemont, Virginia, 1880	0.9928	7.78	9.80	1.60	0.146	None.	0.562	0.302	0.208
ry Muscat, California	0.9928	9.14	11.44	1.82	0.150	Trace.	0.619	0.248	0.289
hite Zinfandel, California	0.9911	9.52	11.26	1.47	0.139	Trace.	0 590	0.227	0.290
iesling, California	0.9918	9.64	12.05	1.72	0.221	Trace.	0.696	0.210	0.389
utedel, California	0.9920	9.36	11.70	1.58	0.196	Trace.	0.726	0.212	0.411
onoma Mission, California, 1879 . . .	0.9935	8.30	10.38	1.67	0.193	Trace.	0.619	0.317	0.242
et wines:									
rocton Port, New York	1.0508	10.00	13.24	17.04	0.139	11.80	0.828	0.600	0.182
eer's Port, New Jersey	1.0213	13.67	17.59	10.69	0.309	7.44	0.705	0.347	0.286
ort, Los Angeles, California	1.0339	12.68	16.52	14.18	0.345	11.39	0.508	0.348	0.128
ew York Sherry	1.0074	13.87	17.59	6.83	0.166	4.84	0.689	0.209	0.323
eer's Sherry, New Jersey	0.9949	17.62	22.09	4.89	0.219	3.33	0.476	0.271	0.164
lifornia Sherry	0.9942	13 42	16.80	3.91	0.198	2.20	0.573	0.232	0.273
arsala, California	1.0052	16.06	20.33	6.42	0.428	3.53	0.626	0.418	0.166
Eclipse" Extra Dry Champagne . .	1.0174	9.26	11.87	7.78	0.149	6.51	0.885	0.295	0.472
old Seal"Champagne, New York .	1.0402	8.26	10.82	13 31	0.110	12.02	0.880	0.447	0.346
ok's "Imperial" Champagne . . .	1.0207	8.41	10.82	8.47	0.130	7.23	0.779	0.470	0.247
eet Catawba, Bass Island, Ohio . .	1 0338	11.68	15.21	14.49	0.152	11.00	0.595	0.296	0.239
eet Catawba, Brocton, New York .	1.0512	10.71	14.18	16.71	0.113	15.22	0.714	0.471	0.194
eet Catawba, Iowa, 1871	1.0101	9.89	12.58	7.23	0.211	4.01	0.668	0.318	0.280
eet Muscatel, California	1.0245	17.33	18.58	31.34	0.371	25.37	0 753	0.421	0.266
lifornia Angelica	1.0440	8.96	11.79	14.41	0.196	12.48	0.489	0.310	0.143
octon Sweet Regina	1.0515	9.71	12.87	16.52	0.101	15.31	0.628	0.465	0.130
eet Delaware, 1879	1.0320	8.73	11.35	12.07	0.118	10.27	0.799	0.355	0.355
uppernong, Sweet, 1878	1.0404	9.06	11.87	14.13	0.132	11.56	0.758	0.323	0.348
uppernong, Dry, 1879	0.9948	10.72	13.43	3.39	0.108	1.31	0.925	0.346	0.468

ide-products.—The first of these is the *marc* of the grapes, sepa- d from the must in the original pressing of the grapes, or left when fermenting must is drained from it. This consists of the stems, s, and stones of the grapes. If the marc instead of being washed with water has been merely pressed, it still contains sufficient must llow of its being used in the manufacture of petiotized wine. Be- s this, the marc serves for a great variety of purposes. It is fer- ted for brandy; it is used with sheet-copper in the manufacture of igris; it is used to start the fermentation in vinegar-making; as e-food; when dried, as fuel or for fertilizing purposes; the tannic is extracted, or it is used direct in producing black colors, and for r minor applications.

he second and more valuable side-product is the deposit formed on ottom and sides of the casks in which the fermentation takes place. on the bottom of the casks is called "lees." It contains from thirty rty per cent. of vegetable matter (from the yeast-cells depositing), remainder being tartrates, sulphates (in plastered wines), alumina, phoric acid, etc. Its composition is greatly altered by "plastering" wine, in which case the tartrate exists chiefly as the neutral calcium ate instead of the acid potassium salt. The crystalline crust that s on the sides of the vessels used for fermentation is called "[illegible]" ranging from forty to seventy per cent. and being always present, chiefly as the acid potassium tartrate. From this crude tartar is prepared, by extraction with boiling water, filtering, and crystallizing, "cream of tartar." This, however, still contains some calcium tartrate mixed with the acid potassium salt, the amount ranging from two to nine per cent.

V. Analytical Tests and Methods.

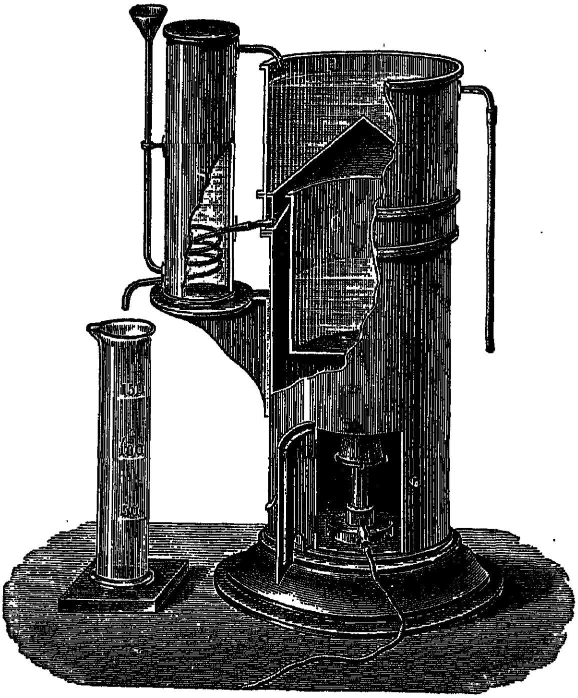
In 1884 the Imperial German Health Office appointed a commission of experts to report upon the best uniform methods for the analysis of wines. The methods agreed upon by that commission are very generally adopted now in Germany, and largely used elsewhere in guiding wine analysts. These official methods have been fully described and explained in a little work entitled "Weinanalyse," by Dr. Max Barth, Leipzig, 1884.

The *specific gravity* of the wine is determined either by the pyknometer (specific gravity bottle) or by the Westphal balance (see p. 87), the readings of which have been compared with those of the specific gravity bottle. In the case of champagnes and effervescing wines, as was the case with beer, the carbonic acid must be got rid of as far as possible before taking the specific gravity readings.

The *alcohol* is determined by the direct distillation, as described on p. 222. Wines that have a tendency to foam have a little tannin (.1 gramme) added. If one hundred cubic centimetres of the sample is taken, sixty cubic centimetres only need be collected, and will contain all the alcohol. This is then diluted to nearly one hundred cubic centimetres, cooled, uniformly mixed, and then brought exactly to the 100-cubic centimetre mark, mixed again, and the specific gravity taken. The form of apparatus best adapted for this determination of alcoholic strength of wines and liquors is shown in Fig. 61. For the rapid determination of the alcoholic strength of wines various forms of apparatus have been devised, such as the vaporimeter of Geissler, in which the vapor-tension of an alcoholic liquid exerted upon a column of mercury is made to indicate its percentage strength in alcohol, the ebullioscope of Tabarie, of Malligand and Vidal, and of Amagat, which depend upon the observation of the boiling-points of a spirituous liquor as determining the amount of alcohol contained. None of these can be said to have scientific accuracy, as wine is not merely a mixture of alcohol and water, but contains other constituents which affect the results in either case.

The *extract* detemination. Here the direct weighing of the residue after evaporation is preferred to the indirect method, fifty cubic centimetres of the wine, measured at 15° C., are to be evaporated on the water-bath in a platinum dish (according to the German wine commission, this dish should be eighty-five millimetres in diameter, twenty millimetres in height, seventy-five cubic centimetres in capacity, and should weigh about twenty grammes), and the ntaining more than .5 per cent. sugar, a smaller quantity must be ;en and suitably diluted, so that the extract shall not weigh more an 1.0 to 1.5 grammes. In this method, the loss of glycerine by evap-ation is trifling. The indirect method for determining the extract is ry like that described under beer (see p. 221) as O'Sullivan's method, cept that with wine we divide the excess of specific gravity observed er 1000 by 4.6 instead of 4, as the solids of wine have a higher solu-n density than those of extract of malt. Or with the specific gravity the de-alcoholized liquid we may get the extract percentage from iger's tables, which are analogous to those of Schultze for malt extracts fore referred to.

FIG. 61.



The *ash* percentage can be obtained by incineration of the evaporated ract above referred to.

To determine the percentage of *glycerine,* one hundred cubic centi-res of the wine are evaporated down to about ten cubic centimetres spacious porcelain dish; some sand and milk of lime are then added the reaction is strongly alkaline and the mixture evaporated almost lryness. The residue is next treated with fifty centimetres of ninety-per cent. alcohol, warmed and stirred on the water-bath, and the ition obtained then passed through a filter. The insoluble matter is hed with successive small portions of hot alcohol a rule suffice, so that the entire filtrate will be from one hundred cubic centimetres to two hundred cubic centimetres. The alcoholic extract is now evaporated to a viscous consistency, and the residue taken up with ten cubic centimetres of absolute alcohol; this solution is mixed with fifteen cubic centimetres of ether in a stoppered flask and the mixture allowed to stand until clear. The clear liquid is decanted or filtered into a light tared glass vessel, carefully evaporated, and the residue dried for one hour in the water-bath. It is then cooled and weighed. In the case of sweet wines (containing more than five per cent. of sugar), only fifty cubic centimetres of the wine are taken for the estimation of the glycerine; sand and lime are added, and the mixture is warmed on the water-bath. After cooling it is treated with one hundred cubic centimetres of ninety-six per cent. alcohol, the precipitate formed allowed to settle, the solution filtered, the insoluble matter washed with spirit, and the alcoholic filtrate treated as above described.

To estimate the *sugar* in wine, Fehling's solution is used, as the sugar should be only glucose. After neutralization of the wine with sodium carbonate, the determination is made (using the separately preserved solutions for Fehling's mixture. See p. 175). Strongly-colored wines must be first decolorized. If the sugar percentage is low, it is done with purified bone-black; if they contain over .5 per cent. of sugar, bone-black cannot be used because of its absorptive power, and basic acetate of lead must be substituted. After filtering, the wine is then treated with sodium carbonate and Fehling's solution. If the polarization indicates the presence of cane-sugar, the solution must be inverted (see p. 174) and then the Fehling's test applied again, and the cane-sugar calculated from the difference in the two readings. The Fehling's test is best carried out gravimetrically, and from the weight of reduced copper the corresponding amount of glucose can be obtained from the tables.

The *polarization,* which is essential in the case of heavy wines to indicate the nature of the sugar contained, is carried out as follows: *With white wines,* to sixty cubic centimetres of the wine are added three cubic centimetres of the basic acetate of lead solution and the precipitate filtered off on a dry filter. To 31.5 of the filtrate is added 1.5 cubic centimetres of a saturated solution of sodium carbonate and the solution again filtered and the polarization tube filled with the filtrate. The dilution of the original wine in this case is 10:11. *With red wines,* sixty cubic centimetres of the wine are treated with six cubic centimetres of the lead solution, and to thirty-three cubic centimetres of the filtrate three cubic centimetres of the saturated sodium carbonate solution added, the solution filtered and polarized. The dilution here is 5:6. This diluted solution is observed in the 220-millimetre tube of the polariscope, and large and accurate instruments are necessary.

The *free acids* (total acid-reacting constituents of the wine) are estimated in twenty-five cubic centimetres of the wine heated to incipient boiling by means of one-tenth normal alkali. Any considerable quantity of carbonic acid to be first removed by shaking. The "free acids" to be

The *volatile acids* are determined by steam distillation and calculated acetic acid ($C_2H_4O_2$).

The quantity of *non-volatile acids* calculated as tartaric is found by tracting the equivalent of the acetic acid in tartaric acid from the e *acids* previously determined.

These three determinations are all that are usually made in wine lyses. If a special qualitative test for free tartaric acid is desired or, case it be shown to be present in appreciable quantity, a quantitative thod for its determination, they can be made by Nessler's method, for ails of which the reader is referred to Barth's "Weinanalyse" before ntioned, or to a summary of its methods in the "Journal of the ciety of Chemical Industry," 1885, p. 553.

The *tannin* may be determined by Neubauer's method with permanate of potash, or approximately by the following procedure: the free ds in ten cubic centimetres of the wine are neutralized with standard ali, after which one cubic centimetre of a forty per cent. solution of ium acetate is added, and finally a ten per cent. solution of ferric oride, drop by drop, and avoiding excess. One drop of this solution ices for the precipitation of every .05 per cent. of tannin.

Salicylic Acid.—To detect this acid, one hundred cubic centimetres the wine are shaken repeatedly with chloroform, the latter is evapted, and the aqueous solution of the residue tested with very dilute ric chloride solution. For the purpose of an approximate quantita- estimation, it is sufficient, on the evaporation of the chloroform, to e recrystallize the residue from chloroform and weigh it.

One of the most important questions that arises in the examination of wines is as to the genuineness of the *coloring matter*, as both vegee and artificial dye colors have been used for years to imitate the ural coloring matter in the manufacture of factitious red wines. Very orate schemes for the recognition of foreign coloring matters, includboth the vegetable coloring matters like dye-woods and color-yielding ries and the large number of the newer coal-tar colors, have been en by Gautier * and by Chas. Girard,† the director of the Laboratoire nicipal in Paris, to which we can only give references. The coloring ters most generally used to imitate the natural pigment of the grapes are fuchsine, cochineal, alderberry, hollyhock, and logwood. Dupré s the coloring matter as follows: Cubes of jelly are prepared by dising one part of gelatine in twenty parts of hot water and pouring solution in moulds to set. These are immersed in the wine under nination for twenty-four hours, then removed, slightly washed, and nined. Pure wine will color the gelatine only very superficially; the ority of other coloring matters (fuchsine, cochineal, logwood, Brazild, litmus, and indigo) penetrate more readily, passing to the very tre of the cube. The double dyeing test of Sostegni and Carpentieri‡ ow very frequently employed. Take one hundred cubic centimetres

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* Wynter Blyth, Foods, Composition and Analysis, p. 464.

† Deuxième Rapport du Laboratoire Municipal, p. 272.

of the wine, acidify with from two to four cubic centimetres of a ten per cent. solution of hydrochloric acid. In this solution immerse a piece of woolen cloth which has been washed in a very dilute solution of boiling potassium hydroxide and then washed in water and boil for from five to ten minutes. Remove the cloth, thoroughly wash it in water and boil in a very dilute hydrochloric acid solution. After washing out the acid dissolve the color in a solution of ammonium hydroxide (1:50). Take the wool out, add a slight excess of hydrochloric acid to the solution, immerse another piece of wool and boil it again. With vegetable coloring matter, such as the wine color, this second dyeing gives practically no color, and there is no danger of mistaking such a color for one of coal-tar origin which dyes the second piece of wool a bright shade. This test will detect minute quantities of fuchsine or aniline red. The fact that pure wine color is not changed or decolorized by nascent hydrogen (zinc and acid), while most of the aniline dyes are decomposed by it, is also used as a test.

D. MANUFACTURE OF DISTILLED LIQUORS, OR ARDENT SPIRITS.

This industry differs radically from the two fermentation industries already described, firstly, in that the effort is made to push the fermentation to the fullest possible limit, so that the maximum quantity of alcohol may be produced, and, secondly, in that this product of fermentation is then distilled, and it may be redistilled in order to get a distillate richer in alcohol than the fermentation product itself can be. The end to be attained may be either the production of an alcoholic beverage as the product of distillation or of raw spirit, which takes name from the material used, as "grain spirit," "potato spirit," "corn spirit," etc. From this raw spirit by the processes of rectification is obtained the "rectified spirit" used as the basis of the manufacture of various alcoholic beverages and as a solvent in various manufacturing processes, and by purification and dehydration the absolute ethyl alcohol of the chemist.

I. Raw Materials.

These may be divided into three classes: First, alcoholic liquids, themselves the product of fermentation,—these require only to be submitted to distillation in order to yield the stronger spirit; second, solid and liquid materials containing some variety of sugar, whether cane-sugar, grape-sugar, or maltose, which are directly or indirectly fermentable; and, third, starch-containing cereals and all materials capable under the influence of diastase or dilute acids of hydrolysis and the production of a fermentable sugar.

1. ALCOHOLIC LIQUIDS (*Wines*).—The distillation of wines is followed for the production of an alcoholic beverage (brandy) which takes to some degree its flavor and bouquet from the wines used in the distillation. While factitious brandies are largely made from grain or potato spirit,

The manufacture of wine brandy has been chiefly carried out in France, and in minor degree in Spain and Portugal. Within recent years California wines have also been used for the manufacture of brandies. The French wines which are used are largely those of the departments Charente and Charente-Inférieure, in the southwest of France, and the product is all known as Cognac brandy.

White wines are said to yield a superior spirit to that obtained from red wines, and older wines better than newer ones. About eight and a half hectolitres of wine are needed to produce one hectolitre of brandy. Because of the ravages of the Phylloxera insect, the manufacture of genuine wine Cognac has decreased enormously in France in recent years, while the manufacture of factitious Cognac has correspondingly increased. Thus we find it officially stated[*] that the production of alcohol from wine in France had decreased from 530,000 hectolitres in 1875 to 14,678 hectolitres in 1883.

The marc of the grapes, as already stated (see p. 234), is also utilized in the manufacture of an inferior grade of brandy, known in France as *eau de vie de marc.* The lees, or sediment, of the wine-casks are also used in this same way. This brandy is not necessarily sold for consumption, but is used to strengthen the alcoholic percentage of wines in which fermentation is to be arrested.

2. Sugar-containing Raw Materials.—The most important sugar-yielding materials cultivated on a large scale, it will be remembered, are the sugar-cane and the sugar-beet. The sugar-canes are not used directly for the production of spirits (except in the case of accidental souring), and the "bagasse," although still containing saccharine juice, is too bulky, and hence is at once burned as fuel, but the molasses obtained on so large a scale in the extraction of raw sugar is a most valuable material for the purpose. Throughout both the West Indies and the East Indies enormous quantities of this molasses are fermented and the resultant product distilled for rum. Even the sugar scums obtained in the defecating and concentrating of the sugar juice are fermented, and produce an inferior grade of rum.

With the sugar-beet, both the beet itself and the beet-molasses are utilized, the former being used in France and the latter in both France and Germany. Sweet fruits, the juice of which is rich in sugar, also serve as raw materials for the spirit industry. Thus peaches, plums, and cherries are much used in different countries for the manufacture of fruit brandy, and the fermented juice of the date-palm in the East Indies and of the plantain in the West Indies both serve for the distillation of an alcoholic beverage.

3. Starch-containing Raw Materials.—This list includes the main sources for the distillation of spirits, as the high percentage of starch in many cereals, ranging from sixty to seventy-seven per cent., the ease with which the starch can be converted into fermentable sugar under the influence of diastase or dilute acids, and the cheapness of these starchy products of nature all combine to make them for most countries the

cheapest and best materials for the spirit industry. In the United States the three cereals used almost exclusively for the manufacture of distilled liquors are corn, rye, and malted barley; in England, barley, both raw and malted, rye, corn, and rice; in Germany the potato is almost the only starchy material used. The composition of the several cereals showing their relative percentage of starch was given on p. 186.

II. Processes of Manufacture.

1. Preparation of the Wort.—In England and the United States, where grain spirit is mainly manufactured, the first process is that of saccharifying the starch of the grain. In the special cases where malted grain alone is used, the mash process somewhat resembles that already described under beer-brewing. Most distillers, however, use mixtures of raw and malted grain, in which the raw largely predominates, being often ten to one or even more, as a very small quantity of diastase can be made to convert a large amount of starch into maltose or fermentable sugar. It is stated, moreover, that the yield of spirit is larger when several kinds of grain are mixed than when one kind is used singly. The mixture of raw and malted grain, properly ground, is put into the mash-tub (see Fig. 59, p. 214) with water at 150° F. and agitated. This first mashing requires from one to four hours, the larger the quantity of raw grain used the longer being the time required for mashing. The temperature of the mixture is kept up to about 145° F. by the successive additions of water at a somewhat higher temperature (190° to 200° F.). The object of the distiller in this is somewhat different from that of the beer-brewer. He wishes to convert the whole of the starch, if possible, into maltose, which is directly fermentable by the action of yeast, while the dextrine is not, so he must mash at not much over 146°, which it will be seen from Fig. 58 (p. 207) is the limit above which the maltose production begins to decrease. When the gelatinization of the starch is complete, the temperature of the mash may go slightly higher. By keeping within this limit of temperature, a minimum of diastase from the small admixture of malt will gradually change not only the starch, but bring about a hydration of the residual dextrine, converting it into maltose. When the wort has acquired its maximum density, as found by the saccharometer, it is drawn off, and fresh water at about 190° F. is run upon the residue in the mash-tub and allowed to infuse with it for one or two hours. This second wort is then added to the first. A third weak wort is often obtained, and used to infuse new lots of grain. The mash is then cooled down promptly to the temperature required for fermentation so that the acetous fermentation may not set in.

It is stated that in this method of open-tub mashing ten per cent. of the starch escapes decomposition, even although the grain may be taken finely ground. Hence a preliminary warming with water to which a little green malt is sometimes added, followed by heating with water under a pressure of several atmospheres, now often precedes the addition of the tarch and dextrine into maltose. This treatment is carried out in so-alled "vacuum cookers."

In Germany potatoes constitute the chief raw material for the spirit aanufacture. They contain from eighteen to twenty per cent. of starch nly, however, while the cereals contain over sixty per cent. The amount f the malt needed for the saccharification of the starch can therefore be orrespondingly reduced. Instead of mashing the ground, rasped, or hipped potatoes in open mash-tubs as was formerly done, they are now irst steamed under a pressure of two to three atmospheres, whereby the tarch-containing cells are thoroughly ruptured and the starch put in ondition to be easily acted upon by the diastase. Among the forms of pparatus based upon this principle may be mentioned those of Hollereund, Bohm, Henze, and Ellenberger. In that of Henze, which has een largely adopted, the potatoes, after steaming under a pressure of everal atmospheres, are so disintegrated that on opening a valve in the ottom of the vessel the pulp is forced out through a grating in a thin tream. This is cooled, mixed with the requisite quantity of malt, and tarted to mashing. In the Hollefreund and in the Bohm cookers, the teaming, disintegrating, and mashing all take place in the same closed essel, the malt being added after the disintegrated mass has been proprly cooled down. Green malt is found to work better in this case than ir malt, and produces more alcohol.

2. Fermentation of the Wort, or Saccharine Liquid.—In the case f mashing, as described above, either with grain or with potatoes, the vort must first be cooled down before adding the yeast and starting the ermentation. The yeast used is a surface yeast, and either fresh rewer's yeast or compressed yeast (previously softened in warm water) nay be used. The procedure is now somewhat different, according as ve have a grain-mash or a potato-mash to deal with. In the former case, ısing a thin wort drained from the exhausted grain, it has been found hat the best results are obtained when the temperature during fermenation rises to about 33° or 34° C. (92° to 94° F.), as shown in Fig. 58 (see p. 207); in the latter case, where the entire mash, solid matter and ll, is fermented, the fermentation begins at a much lower temperature, nd the heat evolved in the fermentation of such a concentrated wort ltimately carries the temperature to the same maximum. In the English lan, considerable lactic acid forms because of the higher temperature, nd this constitutes a sour yeast mash, while in the German plan, because f the low initial temperature of the fermentation, comparatively little actic acid is produced, and when the higher temperatures are reached he mixture already contains so much alcohol that the lactic acid ferment rows with considerable difficulty.

For one thousand litres of grain-mash, eight to ten litres of brewer's east or one-half kilo. of compressed yeast are used; for one hundred itres of potato-mash, one to two litres of brewer's yeast or three-fourths o one kilo. of compressed yeast are needed.

The fermentation is sometimes divided into several stages, th hol formation; the *main* fermentation, in which the maltose is fermented; and the *after*-treatment, in which the dextrine is gradually changed into maltose and this into alcohol.

The time of fermentation varies from three to nine days, but it is carried on until the density of the liquid ceases to lessen or attenuate, which is determined by the saccharometer.

The coefficient of purity of a fermentation is a term used to designate what percentage of the available starchy material in a substance has actually undergone the pure alcoholic fermentation. Thus, the reaction $C_6H_{10}O_5 + H_2O = 2C_2H_6O + 2CO_2$ demands from one kilogramme of starch a percentage of alcohol equal to 71.7 litres, and such a yield from one kilogramme of fermented material would indicate a purity coefficient of one hundred per cent. A percentage yield equal to sixty litres of alcohol from one kilo. of material would give a purity coefficient of 83.7 per cent.

The use of hydrofluoric acid or ammonium fluoride, first proposed by Effront as an antiseptic and indirect aid to the alcoholic fermentation, has become quite important in the spirit industry. The advantages claimed for its use are: first, by preventing the losses due to secondary fermentation, the alcohol yield is increased; second, this yield is especially maintained when raw materials of somewhat inferior quality are used, when without the hydrofluoric acid the yield would be diminished; third, the development of foaming in the fermentation is in large degree prevented.

In France, the juice from inferior beets instead of being worked for the extraction of sugar is often fermented and distilled. The juice is made slightly acid with sulphuric acid to prevent any viscous fermentation, and a small quantity of brewer's yeast is added. The temperature of the fermentation is from 20° to 22° C., and the process is usually complete in from twenty-four to thirty-six hours.

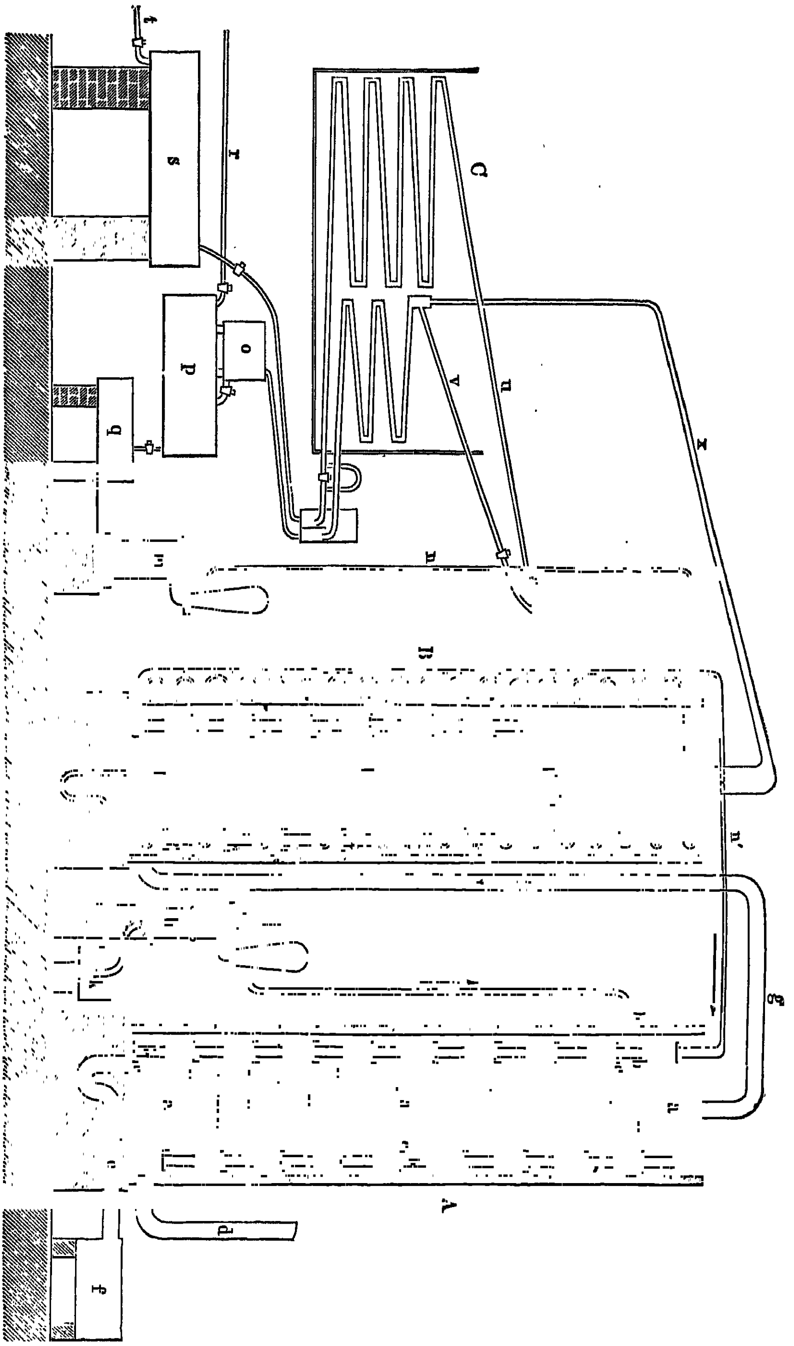
The use of the molasses obtained in the extraction of the raw sugar, whether from the sugar-beet or the sugar-cane, is, however, much more common. In France and Germany, where the beet-sugar molasses is produced in large quantities, the molasses originally marking 40° to 48° Beaumé is diluted to 8° or 10° Beaumé, and sulphuric acid of 66° is added to the amount of 1.5 per cent. of the molasses taken. This neutralizes the bases of the beet-molasses and inverts the cane-sugar present, bringing it into fermentable form. Brewer's yeast is then added, and the fermentation proceeds rapidly. The temperature ranges from 22° C., that usually chosen in France, where more dilute solutions are fermented, to 25° to 30° C. in Germany, where the concentration is usually as much as 12° B. Two hundredweight of molasses at 42° B. will furnish about six gallons of pure spirit.

In the West Indies, notably in Jamaica, the cane-sugar molasses is similarly utilized, but the procedure is somewhat different. In this case the addition of yeast is unnecessary, as the nitrogenous matters present sweet-waters" which accumulate in the extraction of the sugar. se is added some "dunder" (fermented wash, deprived by dis- n of its alcohol and much concentrated by boiling), which acts as rment and starts the action. Molasses is then added in the pro- n of six gallons to every hundred gallons of the fermenting liquid e action allowed to go to completion. One hundred gallons of this re when distilled should yield twenty-five gallons of "low wines" gallon of proof rum for each gallon of molasses employed.

DISTILLATION OF THE FERMENTED MASH, OR ALCOHOLIC LIQUID.— the construction of apparatus for the distilling from the fermented of the alcohol which it contains much skill and ingenuity have been yed, and some of the later forms of stills and rectifying apparatus yed in large distilleries are wonderfully adapted for obtaining in tinuous operation the purest and strongest alcohol from the crude ntation products. We may distinguish some five main classes of ing apparatus, of which the minor varieties are too numerous to be lly enumerated. These classes are: first, simple stills with worm nser heated by direct firing; second, simple stills with closed "wash- er"; third, stills with rectifying "wash-warmer"; fourth, stills "wash-warmer," rectifying and dephlegmator apparatus for inter- nt working; and, fifth, similar forms of construction for continuous ing. The first and simplest of these classes hardly needs any special iption. The stills are usally of copper, flat-bottomed, and often of size, especially in Irish and Scotch whiskey distilleries. It is obvi- hat their use involves a great waste of fuel. Therefore one of the est devices for economizing the heat of distillation consisted in posing between the still and the refrigerating apparatus a "wash- ner," or vessel filled with the liquid ready for distillation. Through vessel the pipe conveying the hot vapors to the refrigerator coil ed, and the vapors partly condensing there heated up the wash, h then went into the still quite hot. Dorn's apparatus, still some- used in smaller establishments in Germany, accomplished the same g, and effected a partial rectification of the distillate by having inter- d between the still and the refrigerator a vessel divided horizontally two compartments by a diaphragm of copper. The upper and er compartment served as a wash-warmer, and through it the tube eying the vapors from the still passed into the lower compartment, re at first the distillate condensed. As the wash becomes warmed up distillate gives off alcoholic vapors, which then pass on and are con- sed in the worm, while the watery portion is allowed to flow back into still by a side-connection. It is obvious that this rectifying on can be increased by the introduction of two or more such vessels veen the still and the final condenser, and so a distillate much richer lcohol be obtained.

Another principle was now brought into play in effecting a fractional densation, that of dephlegmation, or chilling the vapor coming off by

FIG. 62.



r passes on into the rectifier or condenser. Three types of these elaborate apparatus may be briefly referred to: the Pistorius appa- s, used in Germany for the thick potato-mashes of that country, h is intermittent, the Coffey still, used in England and Scotland for thinner worts from grain, and the column apparatus, first introduced avalle and improved by later inventors, which is used in France for lling wines and in Germany to follow up the work of the Pistorius milar apparatus. Both the Coffey still and the column apparatus are inuous in action. In the Pistorius apparatus, two boilers and a -warmer are used for the fresh mash, and are connected so that vapors from the first boiler pass into the second boiler, heating it up in time driving vapor from it, which then passes around the wash- ner and goes through several dephlegmators placed one above the r. In these the watery alcohol is continually being condensed and ing back to the second boiler, while the uncondensed vapor which pes from the top dephlegmator goes finally to the refrigerating ratus. The Pistorius apparatus has been improved upon by Gall, wartz, and Siemens. The Coffey still, illustrated in Fig. 62, consists o columns placed side by side, made of wood and lined with copper. analyzer, *A*, is divided into twelve small compartments by four zontal plates of copper, *a*, perforated with numerous holes and fur- ed with valves opening upwards. Dropping-pipes, *b b*, are also hed to each plate, the upper end of the pipe being an inch or two e the plate and the lower end dipping into a shallow pan, *c*, placed he lower plate. The second column or rectifier, *B*, receives the spirit- vapors passing from the column *A* through the pipe *g*. This column so divided into compartments like *A*, but there are fifteen instead elve. The ten lower diaphragms, *l*, are pierced with small holes and ished with drop-pipes, while the upper five have only one large ing surrounded by a ring to prevent the finished spirit from return- Between each of these compartments passes a bend of a long zigzag , *n n'*, one end of which is attached to the pump *m*, whilst the other discharges the contents of the pipe into the top of the column *A*, dicated by the arrow. The following is the working of the appa- . In the first place, the fermented liquor or wash is pumped up by ump *m* until the zigzag pipe is filled and the wort flows over the artments *a a a*. Steam is then admitted into the compartments of nalyzer by the pipe *d* and heats the wash, which is deprived of all cohol by the time it reaches the bottom of the clyinder and flows off *f* as spent wash. The strong spirituous vapor passes through *g* to ectifier, and at last through the worm *c* of the refrigerator into the ver. The Coffey still is recognized as the best and most economical e for preparing a highly-concentrated spirit in a single operation. specially adapted for preparing from grain-mashes what is called nt spirit," which is almost entirely destitute of flavor, and of a gth ranging from fifty-five to seventy over proof. It is not so well alcoholic distillate of the volatile oils produced in the mash, and the Coffey still separates the alcohol from these as well as other impurities. The forms of apparatus used in France for the distillation of wines are illustrated in that of Cellier-Blumenthal as improved by Derosne, shown in Fig. 63. The alcoholic vapors from *A* pass into *B*, and thence into the rectifying column *C*, which contains a series of perforated metal cups over which wine from the wine-warmer, *E*, is trickling. The vapors thus

FIG. 63.

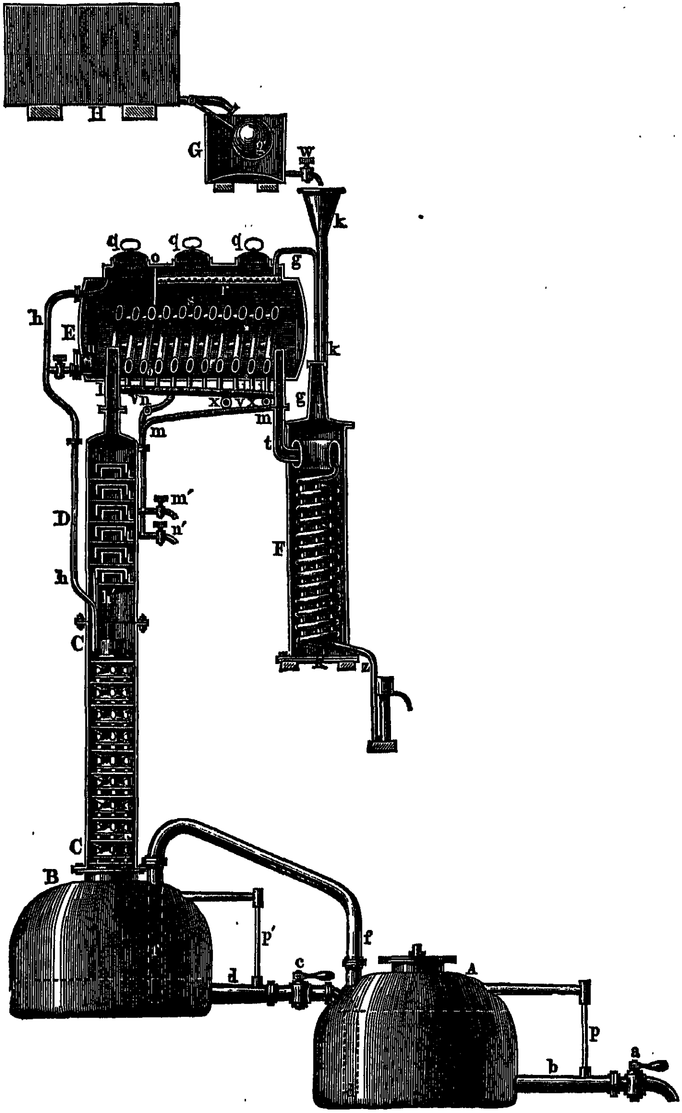


Fig. 64.

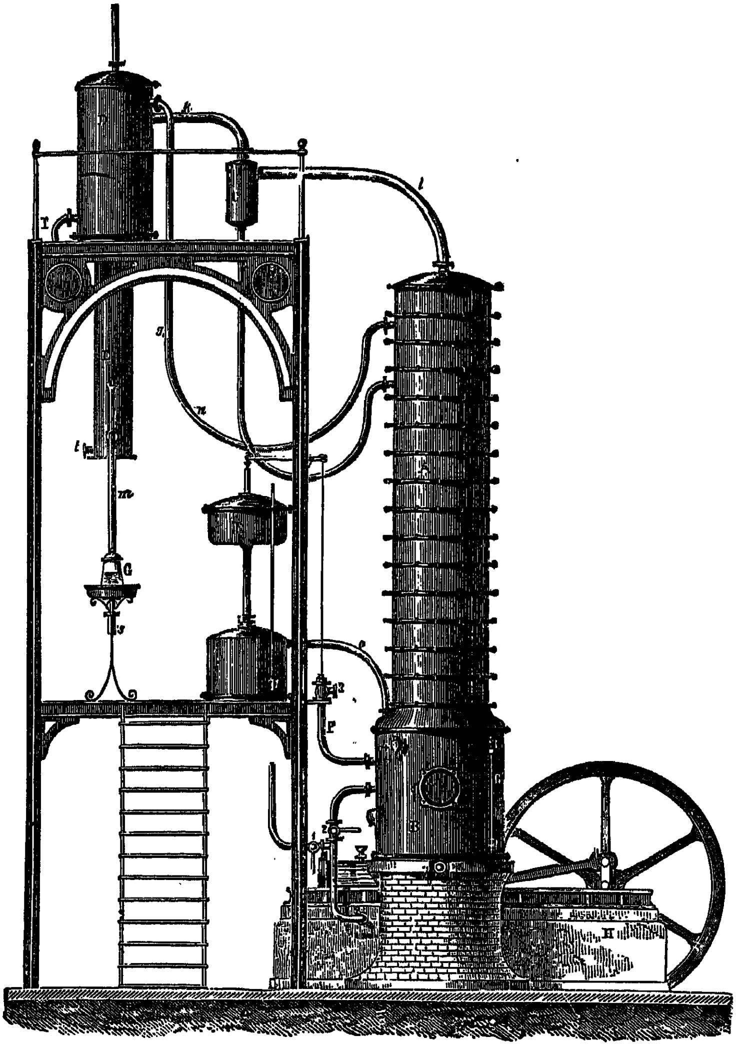


Fig. 65.

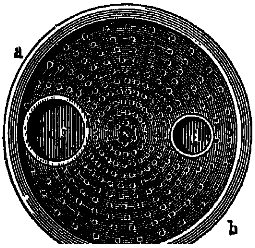
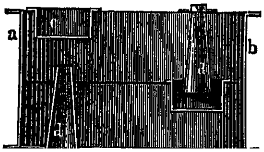


Fig. 66.



condenser, *F*, and so to the collecting vessel. After the operation is we under way the supply of wine can be introduced from *H* through *G*, and *E*, while the de-alcoholized liquid can be run off from the lower sid of *A*.

Another form of still very largely used in France and Belgium, esp cially for thin mashes like molasses and beet-mash, is that of Savall illustrated in Fig. 64. It is a continuous-working apparatus. *B* is tl still proper heated by steam-pipes, *A* is the rectifying column, *C* is fc catching froth, *D* is a warm tube condenser and *E* the cold condense The elements which form the condensing and rectifying parts of tl column *A* are shown in Figs. 65 and 66. The vapors rising pass throug the holes of the perforated plates, on which rests a layer of condense liquid which can only drain down through *d* into the cup *c* placed belo it. From these cups it overflows upon the perforated plate and is agai drained off by the next connecting tube, *d*. The rising vapors are ther fore washed by the liquid upon each perforated plate.

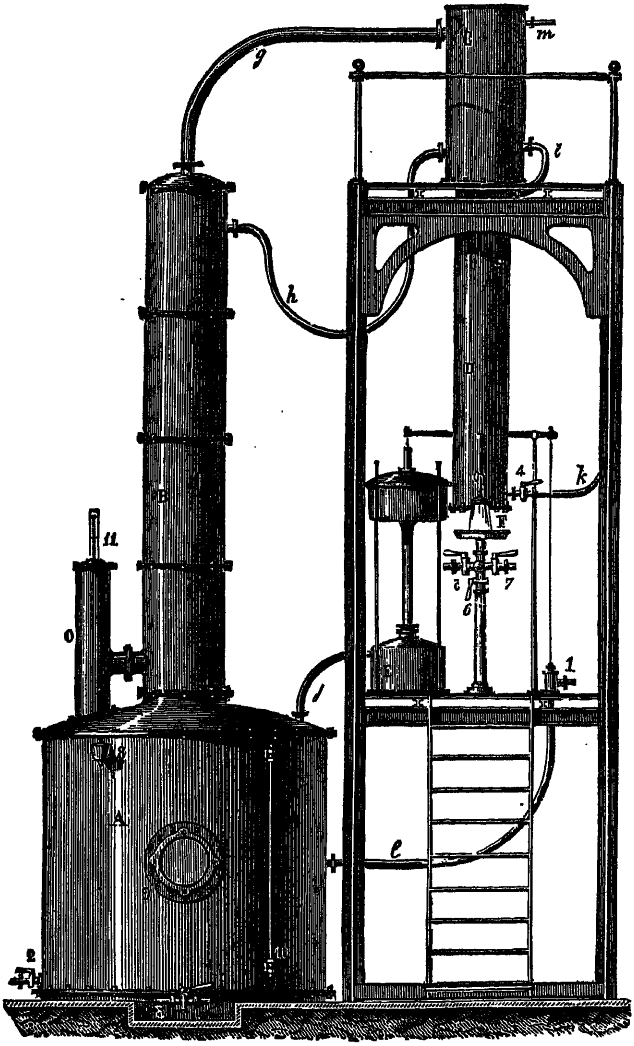
4. RECTIFYING AND PURIFYING OF THE DISTILLED SPIRIT.—Th products from the preliminary distillation from the fermented grain- c potato-mash are not at first sufficiently strong, but must be strengthene by rectifying. In England, the spirits obtained by the first distillatio from grain-mash are generally called *low wines*, and have a specifi gravity of about .975. By rectifying, or *doubling*, a crude milky spiri abounding in oil, at first comes over, followed by clear spirit, which i then caught separately. When the alcoholic strength of the distille liquid has considerably diminished, the remaining weak spirit that distil over, called *faints*, is caught separately and mixed with the low wine preparatory to another distillation. The rectifying is most rapidly an effectually done in the several forms of column apparatus, the best c which will yield a very pure alcohol in one or two operations.

An improved Savalle rectifying colunm as used generally in Frenc and Belgian distilleries is shown in Fig. 67. It consists of a still, heated by closed steam-coils, a rectifying column, *B*, two tubular cor densers, *C* and *D*, from the upper of which any condensed vapors flo back into the rectifying column as "low wines," while the lower cor denser takes the more volatile product and passes it on as high-grad alcohol to the receiving-vessel, *F*.

The purifying of raw spirit, notably that from grain and potatoe from what is called fusel oil (propyl, isobutyl, and amyl alcohols) is als a matter of great importance if the spirit is to be used as the basis of an manufactured liquors. This fusel oil sticks persistently to the alcoholi distillates, and alcohol rectified until it reaches a strength of ninety-fiv or ninety-six per cent. by volume contains fusel oil. Some acetaldehyd also remains dissolved in the alcohol, giving the raw spirit a bitter tast The rectifier's method is to dilute the alcohol with water until it is abou fifty per cent. strength, by which means the fusel oil separates out ir soluble in the dilute spirit, and then to filter through wood charcoa ı petroleum oils, which have the power of absorbing the fusel oil and vithdrawing it from the dilute alcohol.

In this country the storage of the grain spirit in charred oaken cels in warm rooms is extensively practised as a method of improving

FIG. 67.



juality of the spirit. It was supposed that the fusel oil disappeared ng this storage, but Crampton * has shown that it does not and is ly masked by the empyreumatic extractive matter taken up from the l. Esters, however, are formed and the rawness disappears.

. MANUFACTURE OF ALCOHOLIC BEVERAGES FROM RECTIFIED SPIRIT.—

h of the rectified spirit from

connection with the manufacture of wines for fortifying them and in arresting fermentation at any desired stage. The so-called "silent spirit" made in England by the use of the Coffey still from grain-wort is largely utilized in the manufacture of factitious brandies and wines, and the same thing applies to the spirit manufactured in France from beet-roots and beet-root molasses, where it is made to supply the deficiencies in the wine and Cognac production. The composition of many of these factitious or imitation liquors will be spoken of in the next section in enumerating the products of this industry.

III. Products.

1. Rectified and Proof Spirit.—"Rectified spirit" is the name often given to the most concentrated alcohol producible by ordinary distillation. The British Pharmacopœia describes rectified spirit as containing ninety per cent. by volume real alcohol and having a specific gravity of .834. The United States Pharmacopœia under the name "alcohol" simply calls for a spirit containing 94.9 per cent. by volume of real alcohol and having a specific gravity of .816 at 60° F. The "spirit" of the German Pharmacopœia has a specific gravity of .830 to .834, and hence corresponds more nearly to the British "rectified spirit."

"Proof spirit" is a term in constant use in England for the purposes of excise, and its strength was defined by act of Parliament to be such that at 51° F. (10° C.) thirteen volumes shall weigh the same as twelve volumes of distilled water. The "proof spirit" so made will have a specific gravity of .91984 at 15.5° C. (60° F.) and contain, according to Fownes, 49.24 per cent. by weight of alcohol and 50.76 per cent. of water. Spirits weaker than proof are described as U. P. (under proof), stronger than proof as O. P. (over proof); thus, a spirit of fifty U. P. means fifty water and fifty proof spirit, while fifty O. P. means that the alcohol is of such strength that to every one hundred of the spirit fifty of water would have to be added to reduce it to proof strength. Tables are in use which give for alcohol of a given specific gravity at 15.5° C. (60° F.) the corresponding percentage by weight, percentage by volume, and percentage of proof spirit contained. (See Wynter Blyth, Foods, Composition and Analysis, 5th ed., p. 380.)

2. Alcoholic Beverages made by Direct Distillation of the Fermentation Products.—*Arrack.*—Any alcoholic liquor is called "arrack" in the East, but arrack proper is a liquor distilled either from toddy, the fermented juice of the cocoa-nut palm, or from malted rice. The arrack from Goa and Columbo is considered the best, and is made from toddy alone. This latter is gotten by the incision of the palm, and is collected in pots hung to the tree under the cuts. It is then fermented and distilled. In preparing the other variety, as carried out in Batavia and Jamaica, the rice is covered with water and allowed to germinate, dried at a temperature of 59° F., which arrests germination, and then a wort is made from the malted rice in

generally narcotic, very intoxicating, and unwholesome. It is prepared from coarse jaggery sugar, spoilt toddy, refuse rice, etc., and rendered more intoxicating by the addition of hemp leaves, poppy-heads, juice of stramonium, and similar deleterious substances.

Brandy in its purest form (Cognac) is the direct product of the distillation of French wines. Its peculiar flavor and aroma are due to the presence of ethyl pelargonate (œnanthic ether). The better qualities of Cognac are distilled from white wines, the inferior varieties from the dark-red Spanish and Portuguese wines or from the marc or refuse of the wine-press, and called *eau de vie de marc.* A great deal is also entirely factitious, being mixtures of grain spirit and water to which different coloring and aromatic substances have been added. When first distilled, brandy, like other spirituous liquors, is colorless, when it is known as *white brandy,* and continues so if kept in glass- or stone-ware, but if stored in oak casks, as is usually the case, it gradually acquires a yellowish tint from the wood, and it is then termed *pale brandy.* The still deeper color which it frequently possesses is given it by the addition of caramel-color, which was originally designed to simulate the appearance of an old brandy long stored in casks. The coloring matter is also sometimes prepared from catechu and similar astringent and aromatic substances.

Numerous recipes for factitious brandies are furnished for the use of rectifiers in making up imitations of Cognac. Two such recipes are given:

No. 1.—Powdered catechu, 100 grammes; sassafras-wood, 10 grammes; balsam of tolu, 10 grammes; vanilla, 5 grammes; essence of bitter almonds, 1 gramme; well-flavored alcohol (at 85°), 1 litre.

No. 2.—Malt spirit (17 U. P.), 100 gallons; nitrous ether, 2 quarts; ground cassia-buds, 4 ounces; bitter almond meal, 5 ounces; sliced orris-root, 6 ounces; cloves in powder, 1 ounce; capsicum, 1½ ounces; good vinegar, 3 gallons; brandy-coloring, 3 pints; powdered catechu, 2 pounds; full-flavored Jamaica rum, 2 gallons. Mix in an empty Cognac-cask and macerate for a fortnight, with occasional stirring. Produces 106 gallons at 21 or 22 U. P.

Kirschwasser is a spirituous liquor obtained in the Black Forest and in Switzerland by the distillation of cherries. These are picked free from the stalks and only the sound fruit taken. They are crushed for the extraction of the juice, and a portion of the cherry-stones are then separately crushed so as to bruise the kernels and returned to the juice. These bruised kernels impart the almond flavor to the product and give to it a small quantity of prussic acid (.15 gramme per litre in good kirsch and more in inferior kinds). After fermentation the liquor is drawn off and distilled by steam. The kirsch is colorless, of agreeable odor and flavor, which improves by keeping, and equal in strength to the strongest spirit.

Rum is a spirit obtained in the West Indies, notably in Jamaica, Maras carried out in Jamaica has already been described. When new, rum is white and transparent, and has when freshly distilled an unpleasant odor, due to oils contained. These are got rid of by treatment with charcoal and lime. It owes its characteristic flavor to butyric ether, which compound is also prepared artificially on a large scale, and as rum essence is used with "silent spirit" to make a factitious rum. Rum is always colored artificially with caramel-color.

Whiskey is the spirit obtained from the fermented wort of corn, rye, and barley, either raw or malted. In Scotland and Ireland, malted barley, pure or mixed with other grain, is chiefly used; in the preparation of the Bourbon whiskey of Kentucky partially-malted corn and rye are taken, while for the Monongahela whiskey of Western Pennsylvania only rye (with ten per cent. of malt) is used.

The difference between the Irish and the Scotch whiskeys lies mainly in the fact that the latter is distilled from barley malt dried by peat fuel, giving a characteristic smoky flavor to the spirit, while the malt of the Irish whiskey is destitute of this flavor. Both are in general pot-still whiskies, while the product of the Coffey still with less flavor is used for blending. The Irish "poteen" whiskey, however, has the smoky flavor and this is imitated by the addition of one or two drops of creosote to the gallon of spirits.

3. ALCOHOLIC BEVERAGES MADE FROM GRAIN SPIRIT BY DISTILLATION UNDER SPECIAL CONDITIONS.—*Gin* is common grain spirit distilled and aromatized with juniper-berries, either when the "low wines" are concentrated or later, using full-strength spirit. The proportion employed is variable, depending upon the nature of the spirit; usually one kilogramme of berries is enough to flavor one hectolitre of raw grain spirit. The finest gin, known as "Hollands," is made in the distilleries of Schiedam, whence also the name "Schiedam Schnapps." Strassburg turpentine, oil of fennel, coriander and cardamom seeds are frequently substituted either wholly or in part for the juniper-berries, particularly in the English-made gin. The quality and healthfulness of the gin depend largely upon the purity of the spirit used in the distillation, whether raw or rectified.

It is obvious that many factitious brandies belong also in this class, being made by distillation of mixtures of which grain spirit is the basis and not by distillation of wine. These have already been described.

4. LIQUEURS AND CORDIALS.—Liqueurs is the name now given to such spirituous drinks as are obtained by mixing various aromatic substances, such as anise, absinthe, essence of orange-peel, etc., with brandy or alcohol. Most are obtained by steeping in pure brandy or spirit different fruits or aromatic herbs and submitting the resulting liquid to distillation. They are then colored, and are usually sweetened with sugar. The best known of them, absinthe, contains a characteristic ingredient, oil of wormwood, to which its deleterious effects on the nervous system are supposed to be due. At the same time the amount of total essential oils

Among the liqueurs may be enumerated *Absinthe* (consumed chiefly in Paris), *Anisette* (made in the south of France), *Chartreuse* (made by the monks of the Grande Chartreuse Monastery near Grenoble), *Curaçoa* (originally made in Holland of Curaçoa oranges), *Maraschino* (made in Italy of Dalmatian cherries), *Ratafia* (made in France from a great variety of fruits), and *Usquebaugh* (a strong cordial made in Ireland. It furnishes the name from which the word whiskey is derived).

The composition of the several alcoholic liquors enumerated cannot be given in great detail, as their differences depend so largely upon the flavoring and aromatic ethers and essential oils, which are present in very minute quantities. Their general differences in alcoholic strength and the extract and ash of several are, however, given on the authority of König: *

	Alcohol by volume.	Alcohol by weight.		Alcohol by volume.	Alcohol by weight.
Russian Dobry wutky	62.0	54.2	Gin	47.8	40.3
Scotch whiskey . . .	50.3	42.8	Ordinary German schnapps	45.0	37.9
Irish whiskey	49.9	42.3	Rum	49.7	42.2
English whiskey . .	49.4	41.9	French Cognac brandy . .	55.0	47.3
American whiskey . .	60.0	52.2			

And in one hundred cubic centimetres of the following:

	Specific gravity.	Alcohol by volume.	Alcohol by weight.	Extract.	Ash.
Arrack	0.9158	60.5	52.7	0.082	0.024
Cognac	0.8987	69.5	61.7	0.645	0.009
Rum	0.9378	51.4	34.7	1.260	0.059

The composition of some of the well-known liqueurs is also given on the same authority: †

	Specific gravity.	Alcohol by volume.	Alcohol by weight.	Extract.	Cane-sugar.	Other extractions.	Ash.
Absinthe	0.9116	58.93	. .	0.18‡	. .	0.32	. . .
Bonekamp of Maag bitters	0.9426	50.0	42.5	2.05	. .	. .	0.106
Benedictine bitters . . .	1.0709	52.0	44.4	36.00	32.57	3.43	0.043
Ginger	1.0481	47.5	40.2	27.79	25.92	1.87	0.141
Crême de menthe	1.0447	48.0	40.7	28.28	27.63	0.65	0.068
Anisette of Bordeaux . .	1.0847	42.0	35.2	34.82	34 44	0.38	0.040
Curaçoa	1.0300	55.0	47.3	28 60	28.50	0.10	0.040
Kümmel liqueur	1.0830	33.9	28.0	32.02	31.18	0.84	0.058
Peppermint liqueur . . .	1.1429	34.5	28.6	48.25	47.35	0.90	0.068
Swedish punch	1.1030	26.3	21.6	36.61	. .	. .	. . .

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* [illegible]

5. Side-products.—The distiller's residue (Schlempe, vinasse) forms a side-product of considerable value as a cattle food because of its composition. It is especially rich in protein matter, fat, and non-nitrogenous extractive, or carbohydrates. The residues from the beet- and cane-molasses distillation, moreover, yield an ash very rich in potash salts, so that they constitute, especially in France, a very important source of potashes. The constituents of several of these distillery residues in the moist state are here given on the authority of König: *

	Water.	Fat.	Nitrogenous matter.	Non-nitrogenous extract.	Cellulose.	Ash.
Rye-mash residues (ten analyses)	93.48	0.22	1.40	4.05	0.52	0.33
Potato-mash residues (six analyses)	95.10	0.17	1.17	2.17	0.92	0.47
Molassos residues . . .	91.86	. .	2.04	4.56	. .	1.54

Two complete analyses of distillery residues dried by centrifugating and heating in kilns are given on the authority of Rosenbaum: †

Water	11.62	7.83
Ash	6.50	16.40
Crude proteid matter	21.44	23.08
Crude fibre	10.54	8.60
Non-nitrogenous extractives	38.96	40.54
Crude fat	11.44	3.55
	100.00	100.00

Of these constituents the following were assimilable as food:

Albuminoids	17.20	18.50
Carbohydrates	37.40	39.40
Fat	9.10	2.85

IV. Analytical Tests and Methods.

The most important determination in this class of beverages is the *alcoholic strength.* In the case of rectified or proof spirit, a simple specific gravity determination is all that is necessary, and then the percentage strength can be found from the alcohol tables that have been prepared. The determination should be made at 15.5° C. (60° F.), or if at another temperature, a correction in the reading must be made. By multiplying the number of degrees above or below 15° by .4 and adding the product to the percentage given by the table when the temperature is lower than 15°, or deducting it when the temperature is above, we get a correct result. In freshly-distilled and colorless whiskeys and brandies, in which the amount of extract is trifling, the alcoholic percentage can also be determined with sufficient accuracy by the specific gravity method. In such liquors as contain more extractive matter, like rum and the liqueurs and cordials, the alcohol must first be distilled off, and then made up to original volume with distilled water, as described on p. 235.

The detection and determination of *fusel oil,* which is a persistent impurity in potato and grain spirit, is one of the most important tests to be made. To detect it, the greater part of the alcohol is distilled off at as low a temperature as possible, the residual liquid mixed with an equal amount of ether and well shaken. The ethereal layer is then separated and allowed to evaporate spontaneously, when amyl alcohol, if present, will be recognized in the residue by its smell and chemical characters. Petroleum-ether may be advantageously substituted for the ether in this test.

Two quantitative methods are now in use, the Roese method in which the increase in volume of a measured amount of chloroform when shaken with a distillate from the sample in question is compared with that obtained in a blank experiment with fusel-free alcohol, and the Allen-Marquandt method in which the fusel oil extracted with a solvent (preferably carbon tetrachloride) is oxidized by bichromate of potash and sulphuric acid, the volatile acids produced distilled off and titrated with one-tenth normal sodium hydroxide solution. For full working directions for the use of these processes see "Official and Provisional Methods of Analysis," Bulletin No. 107 (Revised) Bureau of Chemistry, Department of Agriculture.

Caramel (burnt sugar) is used for coloring and flavoring spirits, and nay be detected by the Crampton and Simons test. Evaporate fifty cubic centimetres of the sample nearly to dryness on the water-bath, wash nto a fifty cubic centimetre flask, add twenty-five cubic centimetres of bsolute alcohol, cool to a definite temperature and dilute to mark with water. Transfer twenty-five cubic centimetres to an apparatus such as s used in the Roese fusel oil determination, add ether (fifty cubic cenimetres) and shake at intervals for half an hour and allow to settle. After withdrawing the water, the aqueous layer is compared with twentyve cubic centimetres of the solution which have not been treated with ther. The amount of color removed is expressed on the percentage asis.

The Amthor test, as modified by Lasché, is based upon the action f paraldehyde solution upon a sample of the liquor. A permanent turidity after ten minutes indicates caramel.

Tannin is often present in brandy and whiskey, being chiefly extracted rom the casks used in storing. Sometimes, as in factitious brandies, it s purposely added in the form of tincture of oak-bark. It may be etected by the darkening produced on adding ferric chloride to the pirit, and any reaction thus obtained may be confirmed by boiling off he alcohol from another portion of the spirit and adding solution of elatine to the residual liquid, when a precipitate will be produced if

E. BREAD-MAKING.

Bread-making as ordinarily conducted is to be classed as one of the fermentation industries, as the swelling of the dough which must precede the baking is generally accomplished by the aid of the alcoholic fermentation brought about by the addition of "leaven" or yeast. For every kilogramme of bread, on the average, 2.5 grammes of alcohol and 2.7 grammes of carbon dioxide gas are produced. Both are lost in the baking, but the carbon dioxide gas when first generated is caught in the thick and viscid dough and causes it to swell up and become spongy in structure. This not only gives to the bread when baked a porous and cellular structure, but allows the chemical changes to take place throughout its entire substance, whereby it is made more readily digestible.

As the only effective result of the alcoholic fermentation is performed by the carbon dioxide, of course the addition of chemical mixtures liberating carbon dioxide gas in the dough may be made to obviate the necessity of using leaven or yeast, and similarly aerated breads may be made by simply forcing carbon dioxide under pressure into the dough.

A few varieties of bread are made from dough, baked without any aeration either natural or artificial, such as hard crackers, the unleavened bread of the Jews, the Scotch oat-cake, and the corn-cake of the Southern States. These exceptions are of relatively minor importance, and by far the largest amount of bread is prepared by the aid of a fermentation process.

I. Raw Materials.

1. FLOUR.—This may be from either wheat, rye, barley, oats, maize, —Indian corn,—or rice, although wheat flour is used in far the largest amount.

The average composition of the several cereals has already been given. (See page 186.) Wheat flour contains the following substances: starch, dextrine, cellulose, sugar, albumen, gliadin, or gluten, mucin, fibrin, cerealin, fat, mineral matters, and water. The first four are carbohydrates, or non-nitrogenous substances, and they form nearly three-fourths of the entire weight of the flour. The nitrogenous matter consists of at least five principles, three of which, gluten (or gliadin), mucin (or mucedin), and fibrin, constitute the bulk of the material known as crude gluten, which is the substance left when flour is kneaded with water and afterwards washed to remove the starch and any soluble substance. The remaining two nitrogenous principles, albumen and cerealin, are soluble in water, and are carried away with the starch in the process of washing. Crude gluten possesses a peculiar adhesiveness, arising from the presence of gliadin, which is a highly tenacious body, and which is not present in the same form in other cereal flours. It is this adhesive property which gliadin imparts to gluten that renders wheaten flour so well adapted for bread-making purposes.

The vegetable alb

which is also soluble in water. The cerealin is a soluble nitrogenized ferment occurring especially in the husk or bran of wheat and other cereals. It has a powerful fermentative action on starch, rapidly converting it into dextrine and other soluble bodies. The presence of cerealin in bran renders "whole meal" unsuitable for making bread by fermentation with yeast, though it can be used with baking-powders, and "aerated bread" can be made from it. The cerealin acts like malt extract, causing a too rapid conversion of the starch into dextrine and sugar, and hence, although the bran is rich in nitrogenous food constituents and salts like phosphates, it is ordinarily separated from the flour. The difference in the composition of the several parts of the wheat-grain is seen in the following table given by Church: *

	FINE WHITE FLOUR.		COARSE WHEAT BRAN.	
	In 100 parts.	In 1 pound.	In 100 parts.	In 1 pound.
Water	13.0	2 ounces 35 grains.	14.0	2 ounces 105 grains.
Fibrin, etc.	10.5	1 “ 297 “	15.0	2 “ 175 “
Starch, etc.	74.3	11 “ 388 “	44.0	7 “ 17 “
Fat	0.8	0 “ 57 “	4.0	0 “ 280 “
Cellulose	0.7	0 “ 49 “	17.0	2 “ 316 “
Mineral matter	0.7	0 “ 49 “	6.0	0 “ 422 ‘

Of course, milling processes have to be specially adapted to the separation of these quite different parts of the wheat-grain, the white flour free from bran being sought. By the old-fashioned "low-milling" process, or grinding between stones placed very close together and bolting, it was impossible to obtain a flour entirely free from contamination. The advance to "high-milling" with stones far apart, allowing the middlings which were produced to be purified before grinding to flour, was a step which made it possible to make from winter wheat an excellent and pure flour. When, however, spring wheat with its hard and brittle outer coats became important commercially, it was necessary to resort to the roller methods of milling, which, in conjunction with peculiar purifying machinery, would furnish a flour free from all undesirable impurities. This latter process has now almost universally replaced the other in the newer mills.

While most of the other cereals before mentioned may be found occasionally in admixture with wheat flour, very few are used alone as substitutes for it. Rye flour is probably the only one. It makes a dark-colored, heavy and sourish bread, which, however, keeps moist a long time. It is much used in Germany and Northern Europe under the name of "black bread." A more palatable bread may be made from a mixture of two parts wheat flour and one part rye flour. This latter flour contains a slightly larger amount of fat and of mineral matter than wheat flour. It is never so white as wheat flour and the gluten has very little adhesive character. Ritthausen states that the gluten of rye flour consists chiefly of mucin (mucedin) and vegetable casein, and that gliadin is absent entirely.

2. Yeast, or Ferment.—The yeast is at present almost always added, either as brewer's yeast or compressed yeast. In former times (and to a considerable extent still in France) wheat bread was made by the use of *leaven*, which consists of a portion of dough left over from a previous baking, charged with the ferment and in part changed by its action. The leaven is originally gotten by allowing flour and water to start into spontaneous fermentation, the nitrogenous matters becoming soluble and attacking the starch and sugar. The leaven tends, however, to continue its decomposition and to pass from the alcoholic into the lactic fermentation. Hence, if the leaven is in the proper stage of decomposition, it will induce the alcoholic fermentation and generate carbon dioxide gas, raising the dough; if it be, however, in a more advanced state of decomposition, lactic fermentation will be induced and the bread will not rise, but become heavy and sour. In domestic practice, to avoid this latter result, saleratus (bicarbonate of potash or soda) is added to the dough. This neutralizes the lactic acid as fast as formed, and at the same time liberates carbon dioxide gas to inflate the dough. An excess of this salt, however, makes the bread alkaline to the taste and yellow in color.

The black rye bread of Germany is also made with the aid of a leaven known as "sour dough." In this both the alcoholic and the lactic fermentations are in progress, the latter, however, preponderating. Four parts of such sour dough are used for one hundred parts of flour.

The brewer's yeast for bread-raising purposes must be a fresh and vigorous yeast-growth, as its value here depends largely upon the energy of the fermentation set up and the amount of gas given off. Its appearance and characters have been described before. (See p. 207.) Unless of the best quality, compressed yeast is to be preferred because of its reliability. The manufacture of this latter is carried out chiefly in connection with the spirit distilleries. At the time when the fermentation is most energetic, the yeast is skimmed off the surface and conveyed by wooden shoots to steam sieves, by which the husks are eliminated, the strained liquid passing on to the settling cisterns. When settled the surface liquid is drained off and sent for distilling purposes, and the yeasty sediment mixed with starch and put into the filter-presses, which squeeze out all the liquid, leaving a dough-like paste, which, when sufficiently dry, is packed into bags and packets and is ready for distribution. Yeast from its peculiar slimy nature cannot be pressed well, hence the addition of starch, which permits the removal of more of the liquid from the yeast. Absolutely pure yeasts do not keep so well as the same yeasts with an addition of from five to ten per cent. of starch. In high-class yeasts the quantity added is about five or six per cent.; it is often added in quantity beyond this as an adulterant. A good sample of compressed yeast has the following characteristics: It should be only very slightly moist, not sloppy to the touch; the color should be a creamy pples, not like that of cheese; neither should it have an acid taste or dor. Any cheesy odor shows that the yeast is stale and that incipient ecomposition has set in.

3. Baking Powders.—To obviate the necessity of using yeast and raiting until the dough should rise sufficiently under the influence of fer- ıentation, it was early sought to supply the necessary carbon dioxide to he dough by chemical reactions. The earliest proposal was that of iebig to use sodium bicarbonate and hydrochloric acid, which should volve carbon dioxide and leave sodium chloride (common salt) in the ough. Next was proposed sodium bicarbonate and tartaric acid, or acid otassium tartrate (cream of tartar). More generally satisfactory than ither of these was acid calcium phosphate (either alone or with acid ıagnesium phosphate), which with bicarbonate of soda formed Hors- ɔrd's baking-powder. More objectionable was the introduction of alum ith the sodium bicarbonate. Most of these baking-powder mixtures, ıen, have starch or flour added as "filling," and in amount varying om twenty to sixty per cent. Sesquicarbonate of ammonia is also used many of the mixtures, replacing part of the bicarbonate of soda. *elf-raising flours* have these baking-powders already added to the flour such proportions as will insure a spongy dough upon the simple addi- on of water and kneading into loaves.

II. Processes of Manufacture.

1. The Mixing of the Dough and its Fermentation.—The mixing the flour with water is not only for the purpose of bringing into solu- ɔn the dextrine, the sugar, and the soluble albuminoids, and of allowing ese latter as peptones to act upon the insoluble consituents of the flour, ch as the gluten, but also to penetrate and soften the starchy material.

The yeast may be added directly along with the water to some of the ur to prepare a "sponge," from which the whole batch of dough is terwards made, or a "ferment" may be made from the yeast with tatoes, which then is used to prepare the "sponge." In the latter se, potatoes are boiled and mashed with water into a moderately thin uor, to which the yeast is added, and the fermentation is allowed to oceed for some time. In either case, whether the yeast is used direct a potato ferment is first made, it is worked up with a portion of the ur into a slack dough, which constitutes the sponge, and is set to rise a warm place. When the sponge has risen sufficiently the remainder the flour is worked in with sufficient water to which some salt has en added, and the dough is made, kneaded, allowed to stand again to e, and then prepared for baking.

The use of potato ferment is based upon the belief that the yeast-cells strengthened by the soluble nitrogenous matter of the potato, which s as a yeast stimulant and enables a smaller quantity of yeast to drolyze a larger amount of starch. The yeast-cells then act very idly upon the glucose so produced and develop the alcoholic fermen- ion. The albuminoids of the

2. Baking.—For baking, the oven should have a temperature of 400° to 450° F. (200° to 230° C.). Before putting the loaves in, they are often wetted on the surface so as to assist in the prompt formation of a crust that shall prevent the dough from expanding too rapidly. The heat expands the gases throughout the loaf and so swells it and vaporizes a portion of the moisture. The action of the heat and steam soon converts the starch on the surface of the loaf into dextrine and maltose, and these at the high temperature are slighly caramelized, thus giving the crust its brownish color. At the temperature of the interior of the loaf (212° F. or slightly above) the starch-cells will have burst, the coagulable albuminoids will have been coagulated, and their diastatic power entirely destroyed.

Steam is often injected into the oven during the baking. The effect is to produce a glazed surface on the outside of the crust. It not only dextrinizes and glazes the crust, but keeps the interior of the loaf moist by preventing too rapid evaporation. Of course, in perfectly tight ovens the steam resulting from the evaporation of the moisture of the bread is kept in, and soon acts in the same manner though in a lesser degree.

One hundred kilogrammes of flour will yield, according to its quality, from one hundred and twenty-five to one hundred and thirty-five kilos. of bread.

3. Use of Chemicals Foreign to the Bread.—Both alum and sulphate of copper (and notably the former) have been used in baking bread from inferior or unsound flours in order to improve the appearance of the bread. This form of adulteration is rarely practised at present. Much more important in recent years is the practice of bleaching flour with nitrogen peroxide. If not used in excess this promptly whitens the gray or slightly yellowish flour and increases the whiteness of the bread baked from the same. In the Alsop process most generally employed the nitrogen peroxide is formed by a flaming electric discharge which causes nitrogen and oxygen of the air to combine. Other processes use chlorine or bromine or nitrosyl chloride.

Liebig suggested the use of lime-water as a means of retarding too rapid decomposition of the starch during the fermentation of bread-making. The bread made with the proper amount of lime-water is said by Jago * to be more spongy in texture, pleasant in taste, and quite free from sourness. In the bread the lime exists as calcium carbonate, but in such quantities as to be perfectly harmless.

III. Products.

1. Bread.—The nature of the change which the flour undergoes in the bread-baking process has already been indicated in part. The composition of the finished bread can now be noted. A loaf of wheaten bread consists of two parts, the *crumb* and the *crust,* which differ somewhat in both physical and chemical character. The crumb is white in color, more or less vesicular in structure, soft when fresh, and of agreeable

nut-brown color, and nearly destitute of all porous character, is sweeter in taste, because of the greater change of the starch into dextrine and maltose. The chemical differences between well-known forms of bread are shown in the following analyses from the U. S. Bureau of Chemistry, Bulletin 13, Part 9:

	Number of analyses.	Moisture.	Proteids, N x 6.25.	Proteids, N x 5.70.	Ether extract.
Vienna bread	10	38.71	8 87	8.09	1.06
Home-made bread	2	33.02	7.94	7.24	1.95
Graham bread	9	34.80	8.93	8.15	2.03
Rye bread	7	33.42	8.63	7.88	0.66
Miscellaneous bread	9	34.41	7.60	6.93	1.48
Biscuits or crackers	48	7.13	10.34	9.43	8.67
Rolls	11	27.98	8.20	7.48	3.41

	Crude fibre.	Salt.	Ash.	Carbohydrates, excluding fibre.	Calculated calories of combustion.
Vienna bread	0.62	0.57	1.19	53.72	4435
Home-made bread	0.24	0.56	1.05	56.75	4467
Graham bread	1.13	0.69	1.59	53.40	4473
Rye bread	0.62	1.00	1.84	56.21	4338
Miscellaneous bread	0.30	0.49	1.00	56.18	4429
Biscuits or crackers	0.47	0.99	1.57	73.17	4755
Rolls	0.60	0.69	1.31	59.82	4538

The differences between wheat bread made by the usual fermentation process and wheat bread aerated by carbon dioxide under pressure (Dauglish system) are shown also in the following analyses by Dr. Bell:*

CONSTITUENTS OF THE BREAD REDUCED TO DRY STATE.	AERATED BREAD.				HOME-MADE BREAD.			
	Tin loaf.		Cob loaf (Paris bread).		Tin loaf.		Cob loaf (Paris bread).	
	Crumb.	Crust.	Crumb.	Crust.	Crumb.	Crust.	Crumb.	Crust.
Starch, dextrine, cellulose, etc.	78.93	78.96	82.75	82.82	78.12	77.62	82.05	83.42
Maltose	6 40	5.61	4.66	3.94	6.87	6.68	4.85	4.11
Nitrogenous matter, insoluble in alcohol	10.30	11.28	8.58	9.09	11.65	11.17	10.59	8.68
Nitrogenous matter, soluble in alcohol	1.96	1.75	1.80	1.85	1.74	2.00	1.28	2.37
Fat	0.18	0.16	0 13	0.17	0.22	1.22	0.15	0.39
Inorganic matter or ash	2.23	2.24	2.08	2.13	1.40	1.31	1.08	1.03
Percentage of moisture in bread when new	44.09	19.19	41.52	16.48	42.02	22.92	41.98	20.02

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* Analyses and Adulteration of

2. Crackers and Hard Biscuit are made from a dough composed of flour and water, with the addition in special cases of a great variety of sweetening and flavoring ingredients, such as milk, eggs, sugar, butter or lard, spices, and flavoring essences. The dough prepared in large masses is passed between rollers, and from the sheet of dough so obtained by other machines are cut out the various forms desired. Sheets or trays of these dough-forms pass by automatic machinery into and through long ovens at a regulated rate of speed, which can be so controlled as to give them exactly the requisite exposure to the heat needed for baking.

IV. Analytical Tests and Methods

1. For the Flour.—The *moisture* is determined by drying five grammes of the flour in a water-oven until constant weight is obtained.

The *starch* is estimated from the amount of glucose which is produced from it by the action of dilute acid. Two grammes of the flour are boiled in a flask with inverted condenser for several hours with some twenty cubic centimetres of sulphuric acid suitably diluted. When the conversion of the starch is completed the solution is neutralized with soda, made up to definite volume with water, and the glucose determined with Fehling's solution either gravimetrically or volumetrically, as described under glucose. (See p. 175.) After deduction of the sugar found in a previous test to be contained in the sample, the difference is the amount produced from the starch, together with a small quantity from the dextrine and traces of fibre. One hundred parts of glucose correspond to ninety of the starch.

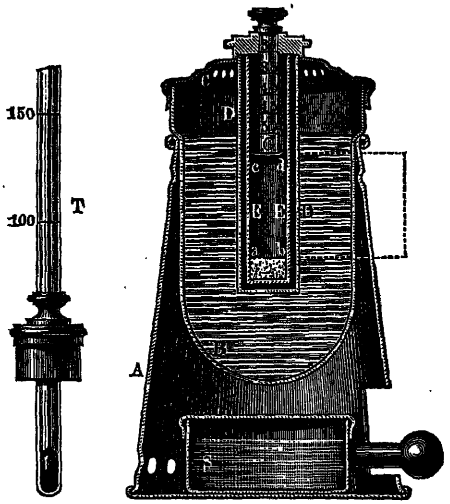
To determine the *cellulose,* a weighed quantity of the flour is boiled with rather dilute sulphuric acid for ten minutes to dissolve the starch. A large quantity of water is then added, and the undissolved part allowed to settle. The residue is thrown upon a filter, well washed with boiling water, and then digested with dilute potash solution to dissolve the albuminous matter. It is then washed upon a tared filter, dried, and weighed. It is now incinerated and the ash determined. This subtracted from the weight of material on the tared filter gives the cellulose or fibre.

To determine the *sugar,* ten grammes of the flour or powdered grain are repeatedly digested in alcohol of seventy per cent. and the filtrate made up to a bulk of three hundred cubic centimetres. This solution is first tested directly for glucose, but generally with negative results. A known portion of the filtrate is then boiled for four minutes with five cubic centimetres of normal sulphuric acid, neutralized with soda and tested with Fehling's solution, and the sugar present reckoned as cane is calculated from the result.

The total *nitrogenous* compounds, and the portions soluble or insoluble in alcohol, are generally determined. The total nitrogen is determined by the Gunning or Kjeldahl method and the nitrogen figure multiplied by 5.70 for wheat flour. For the alcohol soluble proteid ten grammes of the flour are completely exhausted with the total filtrate evaporated to dryness and weighed. A known quantity of this residue is then analyzed for nitrogen by the Kjeldahl or Gunning process, using the same factor 5.70 as before. The flour left after treatment with alcohol is dried, and a weighed portion analyzed for nitrogen and similarly calculated for albuminoids (albumen and fibrin).

The *gluten* is best determined as recommended by Wanklyn and Cooper.* Ten grammes of the flour are mixed on a porcelain plate with four cubic centimetres of water so as to form a compact dough. This is placed in a conical test-glass or measure, fifty cubic centimetres of water added, and the dough manipulated with a spatula so as to free it from starch. The water is decanted off, a fresh quantity added, and the kneading continued until the water remains colorless. The gluten mass is then removed, kneaded in a little ether, and spread out in a thin layer on a platinum dish, where it is dried by the aid of a water-oven until the weight is constant. The crude gluten contains ash equal to about .3 per cent. of the flour and fat equivalent to 1.00 of the flour.

FIG. 68.



An examination of the crude gluten as to its power of distending under the influence of heat is often made as a means of judging of the value of a flour for bread-making. This is done by the aid of the *aleurometer* of Boland, shown in Fig. 68. Some thirty grammes of the flour are kneaded as just described, and seven grammes of he freshly-separated crude gluten obtained is placed in the inner vessel s shown at *a b*. In the mean time, while the gluten is being prepared, he tube *D* is heated by means of an oil-bath until the thermometer *T*, hich is at first sunk in the tube *D*, registers 150° C. The thermometer then withdrawn, and the aleurometer *E*, containing the gluten, put its place. The spirit lamp under the oil-bath is allowed to burn for n minutes longer and then extinguished. The piston *G* is graduated that when pushed down it registers 25°. When the gluten swells and lls the space from *a b* to *c d* it touches the bottom of the piston and is 25°. If it continues to swell the reading may be 30° or 35°, as shown the scale when the piston is pushed up. If the gluten does not indite at least 25° on the aleurometer it may be considered unfit for breadaking. A similar instrument, termed an *aleuroscope*, has been invented Sellnick.

To determine the *fat* of the flour, four grammes are dried and re peatedly digested with ether until exhausted. The filtrates are ev orated in a tared vessel and weighed.

To determine the *ash*, ten grammes of the flour are incinerated i platinum capsule to a white ash, which is then weighed.

Among the adulterations of flour, besides the admixture of ot starchy material of lesser value, which must be looked for with the mic scope (see starches, p. 185), the most frequently occurring is *alum*. I the detection of this, one of the best known tests is based upon the pr erty of alumina of forming a violet- or lavender-colored lake with coloring matter of logwood. Ten grammes of the flour should be mi in a wide beaker with ten cubic centimetres of water, one cubic cen metre of the logwood tincture (five grammes of logwood-chips diges with one hundred cubic centimetres of strong alcohol) and an eq measure of a saturated aqueous solution of ammonium carbonate then added, and the whole mixed together thoroughly. If the flour pure, a pinkish color, gradually fading to a dirty brown, is obtain whereas if alum be present, the pink is changed to a lavender or act blue. As a precaution, it is desirable to set the mixture aside for a f hours or to warm the paste in the water-oven for an hour or two and n whether the blue color remains.

To determine whether flour has been bleached with nitrogen peroxi or not, two tests have been employed. The first is to shake up twen five grammes of the flour in a four-ounce wide-mouthed glass-stopper bottle with gasoline. After the latter has settled, if the flour had be unbleached the gasoline will show distinctly yellow; if bleached, it w remain nearly colorless.

The second test is with the reagents, sulphanilic acid and alpha-nap thylamine chloride solutions, used to detect nitrites in water analys Ten grammes of the flour, one hundred cubic centimetres of distill nitrite-free water, and four cubic centimetres of each of the reagents a shaken up in a wide-mouthed, glass-stoppered bottle. With bleach flour a pink or red tint will be developed. For the quantitative det mination of nitrites in flour, this latter test, known as the Griess-Ilosv reaction, is carried out with special precaution, and the results compar with those obtained from a standard sodium nitrite solution. (S Leach, Food Inspection and Analysis, 2d ed., p. 321).

2. For Bread.—The methods just described under flour are almo all equally applicable to the baked bread. To test bread for adulterati from alum a slightly different procedure is to be followed. To about wineglassful of water in a porcelain capsule five cubic centimetres freshly-prepared tincture of logwood and the same quantity of t carbonate of ammonia solution are added. A piece of the crumb of t bread, say about ten grammes, is then soaked therein for about fi minutes, after which the liquid is poured away and the bread is dri at a gentle heat. If alum be present the bread will acquire a lavend color or more or less approaching dark blue, according to the quantity the alum which has been added; whereas if the

F. THE MANUFACTURE OF VINEGAR.

Under the general heading of fermentation mention was made of the acetic fermentation, which frequently follows the alcoholic fermentation. It is produced, it is true, by other species of ferments, but largely upon materials susceptible to the alcoholic fermentation or already changed by it into alcohol-containing products. The close association in nature of these two changes is readily understood when the chemical relationship of alcohol and acetic acid is looked at. The latter is the simple oxidation product of the former, and the processes for developing the alcoholic change in any sugary liquid, such as a beer-wort or a grape-must, have to be controlled carefully that they do not allow of this supplementary change whereby the alcohol goes over into acetic acid. The conditions under which the acetic fermentation sets in may be summarized as follows:

1. A liquid weak in alcohol, containing not more than twelve per cent. by weight of this compound.
2. Abundant access of air.
3. A temperature of from 20° to 35° C. (68° to 95° F.).
4. Acetic ferments (*Mycoderma aceti*, etc.), together with the food necessary for these organisms. Under this heading of acetic ferments Nägeli distinguishes besides the *Mycoderma aceti*, the *Mycoderma cerevisiæ* and *Mycoderma vini,* although the latter of these is said by De Seynes to arrest the growth of the acetic ferment proper. Hansen also mentions a second ferment as found at times in beer along with the *Mycoderma,* or, as it is often termed now, *Bacterium aceti,* to which he gives the name *Bacterium Pasteurianum.*

The acetic ferment, as before stated (see p. 203), develops not by the budding process characteristic of the yeast ferment, but by splitting or fissure of the elongated cell. When these germs, which originally drop from the air, like the yeast-cells, into the fermenting or sugary liquids, find a liquid specially suited for their growth, as, for example, a mixture of wine and vinegar, they develop rapidly over the surface of the liquid, where they have the necessary oxygen supply, and form a gelatinous skin, which thickens and falls to the bottom of the vessel because of its increasing weight. Another skin forms at once again, and this in turn is replaced by a third, and so on until the liquid is completely exhausted of assimilable material. This skin, called the "mother of vinegar," consists of a multitude of these minute fissure ferments.

I. Raw Materials.

Only such materials will be considered here as give rise to a vinegar by the normal acetic fermentation. The manufacture of acetic acid and technically important acetates will be spoken of later under pyroligneous acid as derived from the destructive distillation of wood.

The materials referred to as furnishing vinegar under the influence of the acetic fermentation are, first, wine; second, spirits; third, malt-

The *wines* used are both red and white wines, and are such as are of inferior vintages, and considered unfit for drinking as wine. Such wines are gathered together from all sections and are made into vinegar largely in France at Orleans and at Paris. The wines do not exceed ten per cent. alcoholic strength. Wines about a year old are the best for vinegar-making, as the new wines are prone to undergo putrid or ropy fermentation, and older wines do not contain sufficient extractive matter.

The *spirits* used are chiefly the potato brandy of Germany and whiskey in this country, the vinegar in either case being made by the "quick-vinegar" process. These spirits, when used for vinegar-making, are so diluted with water and vinegar already formed that the alcoholic strength ranges between three and ten per cent.

The *malt-wort* used for vinegar-making is exactly like that prepared for grain spirit manufacture, unmalted grain and malt being used admixed, and the alcoholic fermentation being pushed so as to produce the maximum amount of alcohol from the converted starch of the grain. When the alcoholic fermentation is completed it is allowed to stand for some days in the fining-vats, where all dead yeast and cloudiness subside, and it is then made to pass through a filter-bed of wood-chips into the acetifier. The unmalted grain used in the preparation of the wort must be thoroughly dried in a kiln previous to crushing in order that many of the glutinous and albuminoid matters may be destroyed. These would otherwise interfere with the keeping qualities of the vinegar. Sour ale or beer is said not to yield good vinegar, but a product very liable to undergo putrid fermentation, a very disagreeable smell being imparted to the vinegar in consequence.

Cider from apples and *Perry* from pears are about the only fruit juices besides wine fermented for the production of vinegar. Cider from good, sweet, and ripe apples serves for the manufacture of cider vinegar in this country. The cider is the product of a spontaneous alcoholic fermentation of the apple juice, and the vinegar formation may be merely a continuation of this spontaneous change, but much is now made by the quick-vinegar process, using casks containing beechwood shavings.

Sugar-beets are used somewhat in France for vinegar-making. The beets are rasped to a fine pulp and pressed. The juice is diluted with water and boiled. After cooling, yeast is added and the alcoholic fermentation developed, and this product mixed with vinegar and treated as the other alcoholic liquids before mentioned for the development of the acetic fermentation.

Artificial glucose, cane-sugar, and molasses have also been used in England for the production of vinegars which are used to adulterate malt vinegar.

II. Processes of Manufacture.

1. The Orleans Process.—This is the process by which wine vinegar is made in France and Germany, and is the oldest in practical use of the several methods now employed. The wine which is to be acetified

vessels, holding from fifty to one hundred gallons, known as "mother-casks," are first steamed out and then soured with boiling vinegar, which is made to fill one-third of the cask. The wine is now added in instalments of ten litres every eight days until the cask has become more than half-full, when one-third of its contents are siphoned off into storage-vats and the periodical addition of wine continued as before. The "mother-casks," or acetifiers, can be used in this way continuously for years until the sediment of yeast, argols, and impurities makes it necessary to give them a thorough cleaning. The vinegar obtained in this way has a very agreeable aroma, that made from white wines being most esteemed. When the wines employed in the Orleans process are too weak it often happens that the vinegar is ropy and wanting in transparency. In such case it must undergo the firing process. The progress of the acetification is judged of by plunging in a rod and examining the froth upon it when withdrawn. This should be white and copious. The temperature that is found to answer best is between 24° and 26.6° C. (75° and 80° F.)

Hengstenberg has proposed a modification of the Orleans process, whereby a series of the "mother-casks" are connected together at the base by short pieces of glass tubing. After the acetification of the first addition of wine in each cask the new wine is added only to the first cask, into which it runs slowly, while from the last cask of the series, by means of a siphon-tube fixed in the side, the excess flows off as finished vinegar. The increase of yield by this modification is, however, only slight.

2. THE QUICK-VINEGAR PROCESS.—This process was first introduced by Schutzenbach in 1823, and has been considerably improved since. It is used exclusively in the case of spirit vinegar in Germany and in this country, and, with slight modifications, in England for malt vinegar. The vinegar-formers are upright casks from six to twelve feet in height and three to five feet in diameter. About a foot above the true bottom of the cask it has a false bottom perforated like a sieve. Upon this beech-wood shavings are heaped, extending nearly to the top of the cask. Between the true and false bottoms and just under the latter a series of holes is bored in the cask in a direction slanting downward and extending around the entire cask. The beech-shavings are first boiled in water and dried. They are then soured or soaked in warm vinegar for twenty-four hours, filled into place and covered by a wooden disk perforated by fine holes in which pack-thread is loosely filled. This disk also is perforated by four larger glass tubes open at both ends, which serve as air-vents. The cask is then closed on top by a wooden cover with a single hole in the centre, through which the alcoholic liquid is to be poured and from which air may escape. The entire arrangement may be understood from Fig. 69. During the oxidation of the alcoholic liquid considerable heat is developed, and a current of air is thus made to enter through the circle of holes under the false bottom and rise through the wet shavings, escaping through the opening at the top. The diluted spirit or

flow off, by the aid of a siphon arrangement from the base they are introduced into the top of the second vat. If not over four per cent. of alcohol were contained in the original liquid, that drawn off from the second vat will be converted into good vinegar. The temperature of the vinegar-forming casks should be about 35° C. (95° F.). Above this there is too much loss of alcohol and aldehyde by evaporation; below it, the oxidation goes too slowly. If the minute organisms known as "vinegar eels" show themselves, hot vinegar is poured in on top until it shows a temperature of 50° C. (122° F.) on running off, which kills them.

Fig. 69.

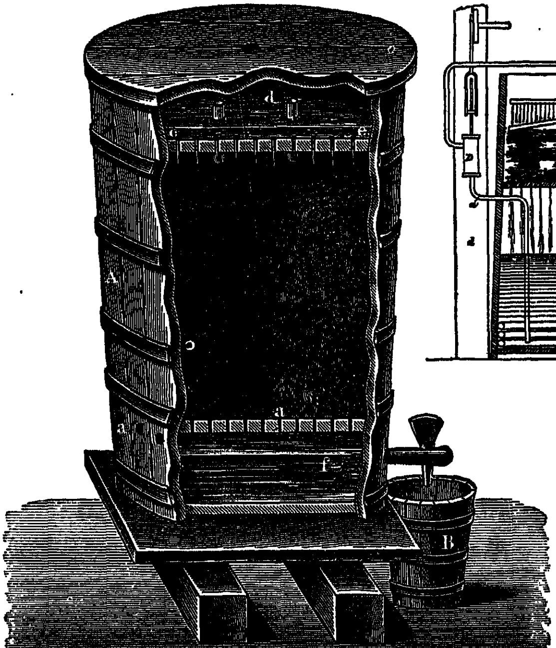
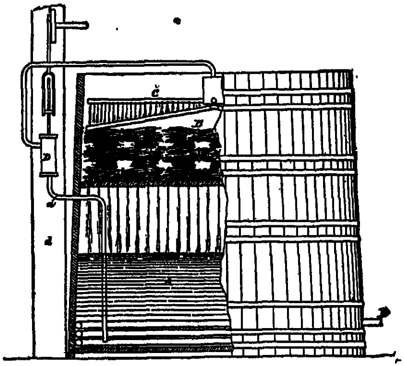


Fig. 70.



Whiskey, brandy, and grain spirit properly diluted are all acetified by the aid of this quick-vinegar process. To these diluted spirits a small amount of malt infusion is generally added to furnish nutritive matter for the development of the acetic ferment, which in this process as in the preceding is the agency whereby the atmospheric oxidation becomes effective in changing alcohol into acetic acid.

3. Manufacture of Malt Vinegar.—This is effected by a process much resembling the quick-vinegar process. The acetifiers are, however, much larger, holding from eight thousand to ten thousand gallons. Their construction is shown in Fig. 70. Bundles of birch-twigs, *B*, are supported upon a perforated bottom, from which the liquid trickles in fine streams. The malt-wort fed in below is warmed by a closed steam coil

sprinkled, in fine streams over the birch-twigs, and the process repeated until the vinegar shows the requisite strength. These birch-twigs have been previously freed from all juice and coloring matter by repeated boiling with water, and are soured before starting the sparging. The entire process of making malt vinegar requires about two months. The temperature at the beginning of the process is about 43° C. (110° F.), and later is kept at 38° C. (100° F.).

4. The Manufacture of Cider Vinegar.—As before stated, this is largely a spontaneous fermentation. The fresh cider is allowed to ferment in barrels having the bung-hole open, which are exposed to the sun or placed in a warm cellar. The acetification is often made a progressive change by adding fresh quantities of cider to the barrel every few weeks; the addition of "mother of vinegar" also is made to accelerate the change.

5. Pasteur's Process for Vinegar-making by Direct Use of the Vinegar Fungus.—Pasteur takes an aqueous liquid containing two per cent. of alcohol and one per cent. of vinegar and small amounts of phosphates of potassium, magnesium, and lime, and in this propagates the acetic ferment (*Mycoderma aceti*). The plant soon spreads out and covers the whole surface of the liquid, at the same time acetifying the alcohol. When one-half of the alcohol has been changed small quantities of wine or alcohol mixed with beer are added daily until the acetification slackens, when the vinegar is drawn off and the "mother of vinegar" collected, washed, and used again with a freshly-prepared mixture. When wine or beer is used, the addition of the phosphate salts as food for the plant is unnecessary, but when pure alcohol is used they are needed. Vinegar prepared by this process is said to possess the agreeable aroma of wine vinegar.

III. Products.

Wine Vinegar varies in color from light yellowish to red, according as it has been derived from white or red wines, that from the former being the most highly esteemed. The vinegar from red wines, however, can be decolorized by filtration through purified bone-black. Skimmed milk is also used for the same purpose. When thoroughly agitated with the vinegar the casein coagulates and carries down with it the greater part of the coloring matter of the vinegar, besides clarifying it. It is not used, however, so much as the filtration through charcoal. Wine vinegar has a specific gravity 1.014 to 1.022, and contains from six to nine per cent. (rarely twelve) of absolute acetic acid. When freshly made, it contains traces of alcohol and aldehyde. The amount of acid potassium tartrate (tartar) contained in wine vinegar averages .25 per ent. Its presence is peculiar to this variety of vinegar.

Malt and Beer Vinegars have a higher specific gravity (1.021 to .025) and contain dissolved dextrine, maltose, soluble albuminoids, and imilar constituents of the malt extract. This kind of vinegar on evaporation leaves a glutinous residue only sparingly soluble in alcohol. It

Spirit Vinegar is colorless as produced, but is frequently colored with caramel-color to imitate the appearance of wine or cider vinegar. It contains from three to eight per cent. of acetic acid, although the so-called "vinegar essence" (double vinegar) may contain as much as fourteen per cent.

Cider Vinegar is yellowish-brown, has an odor of apples, a density of 1.013 to 1.015, and contains from three and a half to six per cent. of acetic acid. It is distinguished from the other varieties by yielding on evaporation a mucilaginous extract smelling and tasting of baked apples and containing malic acid, which replaces the tartaric acid of the wine vinegar. The differences between cider vinegar and whiskey vinegar as manufactured in this country are shown in the accompanying analyses by Battershall: *

	Cider vinegar.	Whiskey vinegar.
Specific gravity	1.0168	1.0107
Specific gravity of the distillate from neutralized sample	0.9985	0.9973
Acetic acid	4.66	7.36
Total solids	2.70	0.15
Total ash	0.20	0.038
Potassa and phosphoric acid in ash..	Considerable.	None.
Heated with Fehling's solution......	Copious reduction.	No reduction.
Treated with basic lead acetate......	Flocculent precipitate.	No precipitate.

Glucose, or Sugar, Vinegar, prepared from different saccharine and amylaceous materials by conversion with dilute acid, followed by fermentation and acetification, contains dextrose, dextrine, and often calcium sulphate (from commercial glucose). It is said to be employed in France and England for adulterating wine or malt vinegars.

Factitious Vinegars are often made from pyroligneous acid flavored with acetic ether and colored with caramel-color. Such a product differs from malt vinegar in containing no phosphates, and from wine or cider vinegar in the absence of tartaric or malic acids respectively.

IV. Analytical Tests and Methods.

The determination of the *acetic acid* is usually done by titration with standard alkali, using phenolphthaleïn as indicator. In the presence of free sulphuric acid, it is necessary to distil a measured quantity of the sample almost to dryness and titrate the distillate, it being assumed that eighty per cent. of the total acetic acid present passes over.

The determination of the *extract* or solid residue in vinegar is executed in the same manner as described under beer or wine.

The test for *sulphuric acid* is an important one. In England, the manufacturers were allowed by law to add one part of sulphuric acid by volume to one thousand of vinegar in order to protect weak vinegar from the putrid fermentation. This addition is not necessary in good vinegar and is not generally followed at present. Still, it may be present, and is to be looked for in all vinegars. The usual test with basic chloride is inoperative here, as sulphates may be present in the vinegar from the water used, etc. Hehner's test for *free mineral acids* (sulphuric and hydrochloric), now regarded as satisfactory in this case, is based on the fact that acetates and most other salts of organic acids are decomposed by ignition into carbonates, having an alkaline reaction to litmus, while sulphates and chlorides of the light metals are unchanged on ignition and possess a neutral reaction. To determine the amount of free mineral acid it is sufficient therefore to carefully neutralize the vinegar with standard solution of soda before evaporation to dryness (the same process serving for a determination of the total free acid), ignite the residue, and titrate the aqueous solution of the ash with standard acid. If the free acid originally present were wholly organic, the ash will contain an equivalent amount of alkaline carbonate, which will require an amount of standard acid for its neutralization exactly equivalent to the amount of standard alkali originally added to the vinegar. Any deficiency in the amount of standard acid required for neutralization is due to the *free mineral acid* originally present in the vinegar.

The *tartaric acid,* a normal constituent of wine vinegar, may be tested for by evaporating to dryness and treating the extract with alcohol, which dissolves nearly everything but the tartar or acid potassium tartrate. On pouring off the alcohol and dissolving this in a little hot water its nature can be easily shown by the usual tests for tartaric acid.

Caramel is recognized by extracting the solid residue with alcohol and evaporating the solution to dryness; in its presence the residue now obtained will possess a decidedly dark color and a bitter taste.

Metallic impurities, such as lead, copper, and zinc, are at times to be found arising from the use of metallic vessels for storing the vinegar. Arsenic has also been found as an impurity through the use of impure sulphuric or hydrochloric acid. They are all detected by the usual qualitative tests.

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1895.—Die Essigfabrikation, Dr. J. Bersch, 4te Auf., Wien.
1907.—Die Untersuchungs methoden, etc., des gährung-essigs, Dr. Fritz Rothenbach, Berlin.

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1884.—Die Fabrikation des Mehls und seine neben Producte, H. Meyer, 2 Theile, Leipzig.
1886.—Bread Analysis, Wanklyn and Cooper, 2d ed., London.
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1889.—Handbuch der Presshefe-Fabrikation, Otto Durst, Berlin.
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1890.—Presshefe, Kunsthefe und Backpulver, A. Wilfert, 2te Auf., Wien.
1892.—Le Pain et la Viande, J. de Brevans, Paris.
The Dietetic Value of Bread, J. Goodfellow, London.
1895.—Text-Book of Science and Art of Bread-Making, W. Jago, London.
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STATISTICS.

I. PRODUCTION OF HOPS THROUGHOUT THE WORLD.

From the U. S. Consular Reports the total crop of hops throughout the world for the last three years is given as follows:

TOTAL CROP IN CWT. OF 110 LBS.

Countries	1909	1910	1911
Germany	119,000	384,000	222,000
Austria-Hungary	164,000	297,000	178,000
France	27,000	54,000	45,000
Belgium and Holland	29,000	58,000	52,000
Russia	60,000	58,000	62,000
England	205,000	296,000	354,000
America	310,000	400,000	400,000
Australia	10,000	10,000	15,000
	924,000	1,557,000	1,328,000

The United States imports a limited quantity of hops, but exports a much larger amount. The figures for recent years were:

	1906.	1907.	1908.	1909.	1910.
Imports in pounds	9,630,206	5,733,386	8,636,192	7,383,907	3,185,991
Valued at	$2,266,333	$1,813,306	$1,911,602	$1,335,300	$1,492,77
[illegible]	[illegible]	[illegible]	[illegible]	10,446,884	10,589,25

II. *a*. BEER PRODUCTION IN THE UNITED STATES.

According to the reports of the Commissioner of Internal Revenue, there were brewed in the United States the following amounts of malt liquors:

	Bbls. (31 gallons or 117.3 litres).
1905	49,459,540
1906	54,724,553
1907	58,546,111
1908	58,747,680
1909	56,364,360
1910	59,544,775

II. *b*. PRODUCTION OF DISTILLED SPIRITS IN THE UNITED STATES (IN GALLONS).

	From grain and cereals.	From fruit.	Totals.
1906	145,666,125	4,444,072	150,110,197
1907	168,573,913	6,138,305	174,712,218
1908	126,989,740	6,899,823	133,889,563
1909	133,450,755	6,440,859	139,891,613
1910	156,237,526	7,656,433	163,893,960

II. *c*. BEER PRODUCTION AND CONSUMPTION OF THE WORLD FOR 1904 AND 1905.

	Production in hectolitres.		Consumption per capita in litres.	
	1904.	1905.	1904.	1905.
Great Britain	56,395,360	54,842,670	129.60	124.65
Russia	6,560,140	....	4.54	......
Norway	295,020	307,890	13.05	13.50
Sweden	2,751,210	....	52.20	......
Denmark	2,451,460	2,415,010	92.25	92.25
Germany	69,538,590	72,027,450	115.65	118.35
Belgium	15,163,830	15,592,500	216.90	219.60
France	14,125,320	13,283,820	34.45	33.75
Switzerland	2,093,850	....	64.35	......
Italy	227,700	235,620	0.90	0.99
Austria	19,621,800	10,908,010	68.40	64.35
Hungary	1,500,840	1,485,990	8.10	8.10
Bulgaria	64,340	88,110	1.67	2.21
Servia	75,240	....	2.97	......
United States	57,546,310	63,591,840	68.80	75.60
	248,410,000	245,778,910	58.25	68.48

(English Parliamentary Report on Alcoholic Beverages, 1905.)

III. WINE PRODUCTION OF THE WORLD FOR 1897 AND 1898.

	1897. Hectolitres.	1898. Hectolitres.
France	32,350,700	32,282,300
Algeria and Tunis	4,457,758	5,341,000
Italy	25,958,500	31,500,000
Spain	18,900,000	24,750,000
Portugal	2,500,000	2,100,000
Austria-Hungary	3,000,000	2,800,000
Russia	2,500,000	3,120,000
Switzerland	1,250,000	1,160,000
Germany	2,775,576	1,406,818
Roumania	3,200,000	3,900,000
United States	1,147,000	1,300,000
Other countries	10,261,000	9,075,000

IV. *a*. CONSUMPTION OF SPIRITS, WINES, AND MALT LIQUORS IN THE UNITED STATES.

	Distilled spirits (proof gallons).	Per cap.	Wine (gallons).	Per cap.	Malt liquors (gallons).	Per cap.
1905	120,869,649	(1.45)	35,059,717	(0.42)	1,538,526,610	(18.50)
1906	127,851,583	(1.52)	46,485,223	(0.55)	1,700,421,221	(20.19)
1907	140,084,436	(1.63)	57,738,848	(0.67)	1,823,313,525	(21.24)
1908	125,379,314	(1.44)	52,121,646	(0.60)	1,828,732,448	(20.98)
1009	121,130,036	(1.37)	61,779,549	(0.70)	1,752,634,426	(19.79)

(Statistical Abstract of United States.)

IV. *b*. CONSUMPTION OF SPIRITS, WINES, AND BEER DURING 1901–1908 PER CAPITA IN DIFFERENT COUNTRIES (IN IMPERIAL GALLONS).

	Spirits.	Wine.	Beer.
Australia	0.89	1.29	11.88
Belgium	1.06	1.02	47.75
Canada	0.86	0.09	5.01
Denmark	2.54	....	20.58
France	1.35	30.67	7.92
Germany	1.55	1.45	26.25
Holland	1.50	0.37	6.50
Italy	0.25	25.04	0.14
Norway	0.62	.....	3.45
Russia	0.94	.....	0.98
Sweden	1.46	.....	12.60
Switzerland	0.97	13.65	13.88
United Kingdom	1.00	0.32	29.45
United States	1.45	0.52	18.50

(Webb, Dictionary of Statistics, 1910.)

CHAPTER VII.

MILK INDUSTRIES.

I. Raw Materials.

Milk is the fluid secreted by the females of the mammalia for the nourishment of their young, and is therefore a food specially adapted for the needs of the animal organism at this stage, furnishing all the nutrients required and furnishing them in the proper proportion. As will be seen from its analysis, it occupies an intermediate position between the cereal and the strictly animal foods, approximating, of course, more nearly the latter, but showing in one important constituent, milk-sugar, its relationship to the former.

Milk is a secretion of the mammary glands, in which it is produced proximately by certain processes of diffusion from the blood and immediately by the breaking down of the gland-cells themselves, so that milk is described as cell-material liquefied. The milk of all mammalia is essentially the same in its constituents, although these vary somewhat in their relative proportions.

The essential constituents of milk are water, fat, casein, albumen, milk-sugar, and salts. The relative proportion of these constituents in the milk of different animals may be seen from the following table of analyses from Wynter Blyth: *

	Fat.	Casein.	Albumen.	Milk-sugar.	Ash.	Total solids.	Water.
Human milk	2.90	2.40	0.57	5.87	0.16	12.00	88.00
Cow's milk	3.50	3.98	0.77	4.00	0.17	13.13	86.87
Camel's milk	2.90	3.84		5.66	0.66	13.06	86.94
Goat's milk	4.20	3.00	0.62	4.00	0.56	12.46	87.54
Ass's milk	1.02	1.09	0.70	5.50	0.42	8.83	91.17
Mare's milk	2.50	2.19	0.42	5.50	0.50	11.20	88.80
Sheep's milk	5.30	6.10	1.00	4.20	1.00	17.73	82.27

In taking up milk as a raw material for industrial utilization, we shall refer to cow's milk exclusively unless otherwise specified.

The fat exists in the milk in the form of minute globules suspended in a thin liquid, forming for the time a perfect emulsion with the aqueous solution of the other constituents. The fat is essentially an intimate

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* Foods, Composition and Analysis, 1882, pp. 214, etc.

mixture of the glycerides of the fatty acids, palmitic, stearic, and oleic, not soluble in water, and of the glycerides of certain soluble volatile acids, such as butyric, caproic, caprylic, and capric.

The casein of milk exists in the fresh milk as a diffused colloidal compound of albumen and calcium phosphate, which by the action of rennet (a ferment from the calf's stomach) is converted into the insoluble one known as casein. The casein precipitated by rennet contains five to eight per cent. of ash, consisting almost entirely of calcium phosphate. If, however, this calcium phosphate compound of albumen is decomposed by mineral acids or acetic acid, the casein precipitated contains only traces of ash. Lactic acid gives the same result, so that the casein coagulated by the souring of the milk shows less ash than that precipitated by rennet from sweet milk. On the other hand, carbon dioxide will act like rennet. The soluble compound existing in the fresh milk is considered to be that of the tricalcium phosphate with albumen, while the insoluble one precipitated by rennet is the acid calcium phosphate with albumen. Pure casein is a perfectly white brittle crumbling substance, insoluble in water, but soluble in very dilute acids or very dilute alkalies. In the action of rennet and acids upon casein a portion is apparently altered into what are called peptones (*lacto-protein* or *lacto-peptone*) and remains dissolved in the whey of the milk. The albumen (or soluble nitrogenous matter) of milk seems to be analogous to the albumen of blood. It may be obtained by precipitation with basic acetate of lead or by dialysis as a yellowish flaky mass. The proportion of albumen in milk is always, according to Wynter Blyth, about one-fifth of the casein.

Two additional nitrogenous compounds have been found by Blyth t exist in small amounts in milk, to which the names *galactine* and *lacto-chrome* have been given.

Milk-sugar, which is an important and characteristic constituent o the milk, is obtained from the serum, or "whey." After the separatio of the curd has been effected by the addition of rennet the whey i evaporated on the water-bath, and yields the milk-sugar in hard crystals. These when purified by animal charcoal and recrystallized sho the composition $C_{12}H_{22}O_{11} + H_2O$. It is easily distinguished fro other sugars of the same formula. It is converted by boiling wit dilute acids into dextrose and galactose, which latter has one-fifth les copper-reducing power than dextrose. It undergoes the lactic fermentation readily but the alcoholic with some difficulty.

The ash of milk consists of calcium citrate and the phosphates an chlorides of potassium, sodium, calcium, and magnesium, the salts tha are specially needed for the growth of the bone-material in the youn nourished by the milk.

Cow's milk is a white or yellowish-white liquid nearly opaque, except in very thin layers, when it has a bluish opalescent appearance, an a specific gravity of from 1.029 to 1.035. It has a mild sweetish tast and a slight but characteristic odor, stronger when still warm from th cow. Upon allowing milk to remain at rest for some time it undergoes two changes: First, a yellowish-white layer forms on the surface known as "cream," due to the rising of the specifically lighter fat-globules from the body of the liquid where they were held back in emulsion with the aqueous liquid; and, second, the aqueous liquid after a time undergoes further separation into a thick coagulum or "curd" of casein and a thinner liquid or "whey," holding the sugar of milk, any lactic acid formed from it, and the salts in solution. Both of the changes are of the greatest importance, as upon them are based the great milk industries, butter-making and cheese-making respectively.

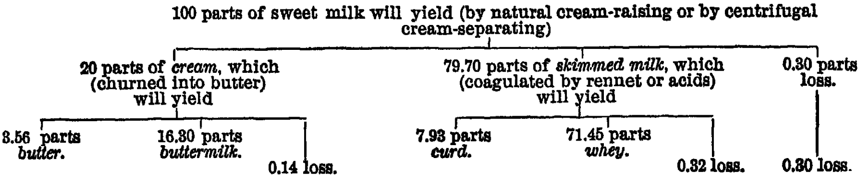
The rising of the cream is largely dependent ordinarily upon two conditions: First, the temperature,—a low temperature being favorable to the separation; and, second, complete freedom from agitation. These conditions are not, however, indispensable, as will be seen later (p. 282) in speaking of the use of centrifugals for the separation of cream.

The rising of the cream is generally allowed to be an entirely spontaneous change on the part of the milk and the first one which it undergoes, but in some creameries a little sour milk (containing lactic acid) is added to the fresh milk, when first put in the cream-rising pans, so that the curdling of the casein may facilitate the escape of the fat-globules and the rising of the cream. In such a case what remains on removal of the cream is not ordinary skimmed milk, but a sour curdled milk. The second change mentioned, that of curdling, is really preceded by a change of some of the milk-sugar into lactic acid (due to lactic fermentation, which sets in very quickly in hot weather or if the milk has not been kept in clean vessels). This souring of the milk may be retarded by the addition of a little carbonate of soda or boric acid. The lactic acid as soon as liberated decomposes the soluble casein compound, before referred to (see p. 279), and the casein is thrown out or coagulated as "curd." The separation of the curd is aided by heat. The liquor in which this coagulated casein floats, the serum of milk, or "whey," contains about one-fourth of the nitrogenous matter of the milk, all of its sugar, and most of its mineral matter. The whey is "sour whey" in case lactic acid has formed as the antecedent of the coagulation, or "sweet whey" in case the casein is thrown out by the action of rennet without the formation of lactic acid.

The composition of the several parts into which the milk is divided by these changes is thus given by Fleischmann:

	Water.	Fat.	Casein.	Albumen.	Milk-sugar.	Ash.
Whole milk	87.60	3.98	3.02	0.40	4.30	0.70
Cream	77.30	15.45	3.20	0.20	3.15	0.70
Skim-milk	90.34	1.00	2.87	0.45	4.63	0.71
Butter	14.89	82.02	1.97	0.28	0.28	0.56
Buttermilk	91.00	0.80	3.50	0.20	3.80	0.70
Curd	59.30	6.43	24.22	3.53	5.01	1.51
Whey	94.00	0.35	0.40	0.40	4.55	0.60

And the relative yield of these several constituents from one hundred parts of milk is thus given by the same author:



II. Processes of Manufacture.

1. Manufacture of Condensed and Preserved Milk.—Condensed milk is milk from which a large portion of the water originally present has been driven off, increasing, of course, in a proportionate degree the percentage of the other constituents. This condensed product may or may not have cane-sugar added to it as a preservative. That to be preserved with cane-sugar is made much more concentrated, and is that which is manufactured for export and preservation in sealed tin cans. In its preparation, the milk is first heated to 65.6° to 80° C. (150° to 175° F.) by placing the cans containing the milk in hot water, and is then strained and conveyed to the evaporating vessels, which are usually vacuum-pans. Refined sugar is added during the boiling to the amount of one to one and a half pounds for every quart of the condensed milk produced. The product is drawn off into cans, cooled to about 70° F., and then weighed into tins, which are at once soldered down.

Condensed milk free from cane-sugar is only concentrated to about one-half the degree attained in the other product, and is then cooled and filled into stone or glass flasks provided with ordinary air-tight stoppers. It will remain fresh for from one to two weeks, and requires only to be diluted with its own bulk of water in order to yield the counterpart of the original milk.

Preserved milk is either prepared by Appert's process, which consists in boiling the milk to destroy ferments and keeping it then in hermetically-sealed vessels, or by Scherff's improved process, whereby the milk is filled into glass bottles which are stopped with corks previously steamed and then fastened in by clamps, and then heated in closed boilers under a pressure of from two to four atmospheres to about 120° C. The bottles are then taken out of the pressure-vessel and cooled down, with the corks covered with flannel soaked in paraffin, so that as they cool the air entering through the pores of the corks shall be filtered. When cooled down, the cork, which has been drawn into the neck of the bottle considerably, is covered with a layer of paraffin. This kind of preserved milk is used largely in Germany for invalids and children.

2. Of Butter.—The first operation in this connection is the separation as completely as possible of the cream from the rest of the milk. This is generally a spontaneous process, it is true, but its completeness

various ways in which the raising of the cream is allowed to take place. We may mention the Holstein process, in which the fresh milk is at once set to raise cream in wide shallow pans at a temperature of 12° to 15° C. (53.6° to 59° F.), the Dutch process, in which it is first rapidly cooled down in large vessels immersed in cold water to about 15° C. (59° F.) and then transferred to the shallow pans for the raising of the cream, and the Schwartz process, largely used in Northern Europe, which differs from the Dutch process chiefly in using much deeper pans at a lower temperature, 4.4° to 10° C. (40° to 50° F.). Very similar to this last mentioned are the Hardin and the Cooley methods, which also use deep cream-raising pans. In the former of these, ice and not ice-water is used to effect the cooling, the pans being exposed to the influence of air cooled by ice, the claim being made that the cream is obtained in more solid condition. In the Cooley method, used largely in this country, the water not only surrounds the can outside as high as the milk inside, but is made to rise an inch or two above the lid, so that the can is completely submerged and all contamination from external sources prevented.

Fig. 71.

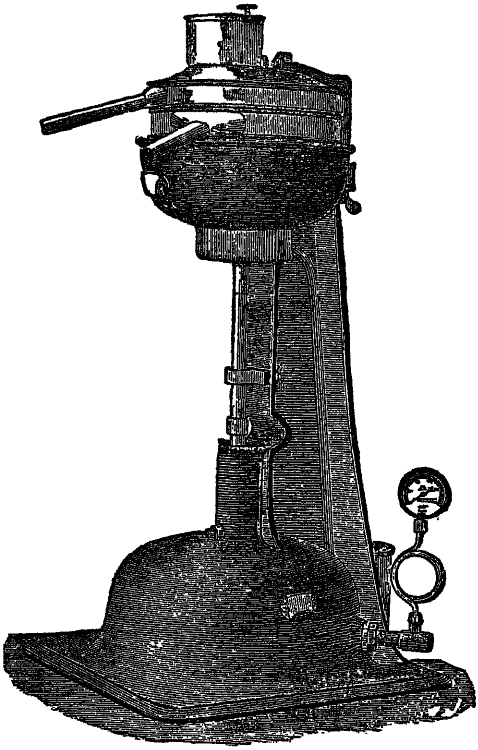
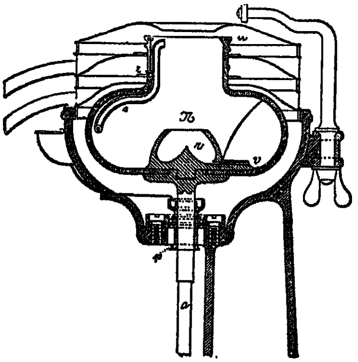


Fig. 72.



The processes which use shallow pans give a larger yield of cream but take a longer time (thirty-six to forty-eight hours as against eighteen to twenty-four for those using deep pans). Within twenty years past the principle of the centrifugal has been applied to the separation of the cream from the milk, and this has proven itself so successful that in most large creameries it is now utilized. The milk is placed in a horizontal rotating vessel driven at a high rate of speed, which causes the heavier milk fluid to gravitate towards the circumference of the vessel, whilst the cream remains nearer the centre and rises towards the upper part of the rotating bowl, whence it is removed by a conveniently-placed aperture on the side of the vessel. An exit is also provided for the gradual removal of the skimmed milk, thus making room for fresh milk to be added to the apparatus and allowing the process to be carried on continuously. Figs. 71 and 72 show the Laval cream separator in general view and in section. The fresh milk is admitted through a funnel, the tube of which is prolonged so as to deliver the milk near the bottom of the revolving drum. The skim-milk flows out through an opening, *t*, and the cream through a higher opening, the relative position of which can be changed by an adjustable screw above. The cream obtained by these centrifugal separators seems to be freer from mechanically-enclosed casein than that gotten in any of the old separation processes, as is seen in the appended cream analyses by Bell,* where samples 2 and 6 were separated by the centrifugal separator:

		Water.	Fat.	Milk-sugar.	Casein.	Ash.
1.	Raw cream	54.02	39.40	1.85	3.76	0.57
2.	Raw cream	60.66	33.60	2.43	2.90	0.41
3.	Raw cream	67.93	24.44	2.96	4.04	0.63
4.	Raw cream	58.07	35.67	2.20	3.55	0.51
5.	Raw cream	63.07	30.74	2.61	3.04	0.54
6.	Thick cream	37.62	58.77	1.46	1.83	0.32
7.	Devonshire clotted cream	33.76	59.79	1.01	4.97	0.47

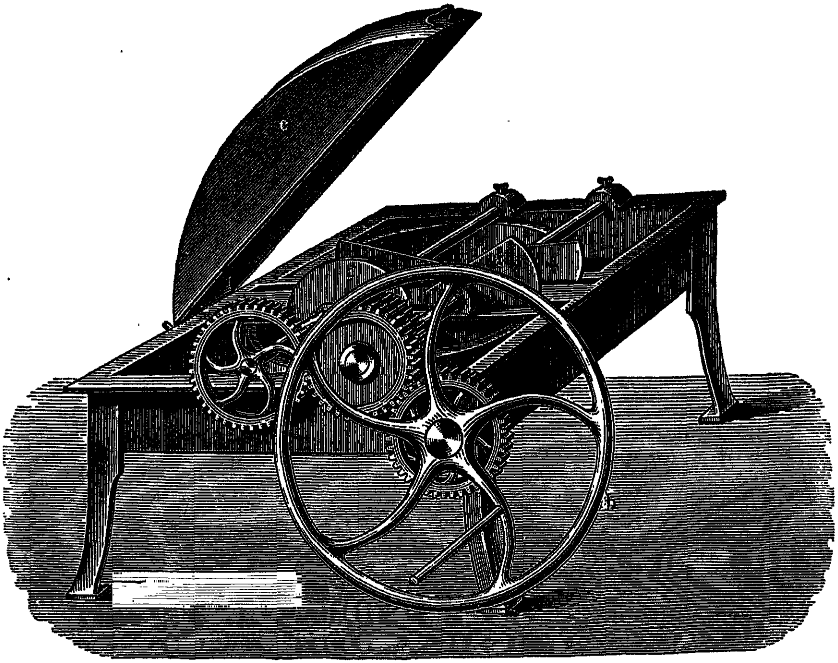
The composition of the skimmed milk of course varies according to the extent to which the cream has been removed. The following analyses by Voelcker represent its average composition as obtained in the ordinary way and as obtained by the Laval separator:

	Water.	Butter-fat.	Casein.	Milk-sugar.	Ash.
Ordinary skimmed milk	89.25	1.12	3.69	5.17	0.78
Skimmed milk by Laval separator	90.82	0.31	3.31	4.77	0.79

The coalescence of the fat-globules separated in the cream layer is now to be effected to form the compact butter. This is almost universally accomplished by mechanical agitation in the process called churning. The churns may be of very diverse construction, either for hand or power. The cream may be taken as "sweet cream" freshly separated in the centrifugal or raised from deep pans where the skim-milk is still sweet, or it may be "sour cream," which has stood longer and has separated slowly in shallow pans. The sour cream is more easily churned, but the butter will contain more casein, while sweet cream yields a butter with pleasanter taste and better keeping qualities because containing less casein. The temperature most favorable for churning is about 15.5° C. (60° F.). Sometimes cream is heated to a much higher temperature first, and then cooled down to 60° F. before being churned. Butter thus made keeps well.

Butter has almost invariably some salt added to it even when for immediate consumption; the quantity in this case need not be large (five-tenths to two per cent.), but when it is to be packed for preservation or for export considerably more is added, so that it is known as "salt butter." Export butter has also a small addition of sugar, and sometimes saltpetre, added, as well as salt, to preserve it. Genuine butter will always have a yellowish color, which, however, becomes deeper in summer when the cows have an abundance of fresh pasture. Most butter manufacturers now add a little vegetable coloring matter like annotto, carrot-color, or saffron, to give the butter this desired yellow tint in winter, when the butter would otherwise be very much lighter in color. All butter will in time become rancid and take a strong disagreeable odor. This is due to the gradual spontaneous decomposition of the butyric ether under the influence of air and light whereby free butyric acid is liberated.

Fig. 73.

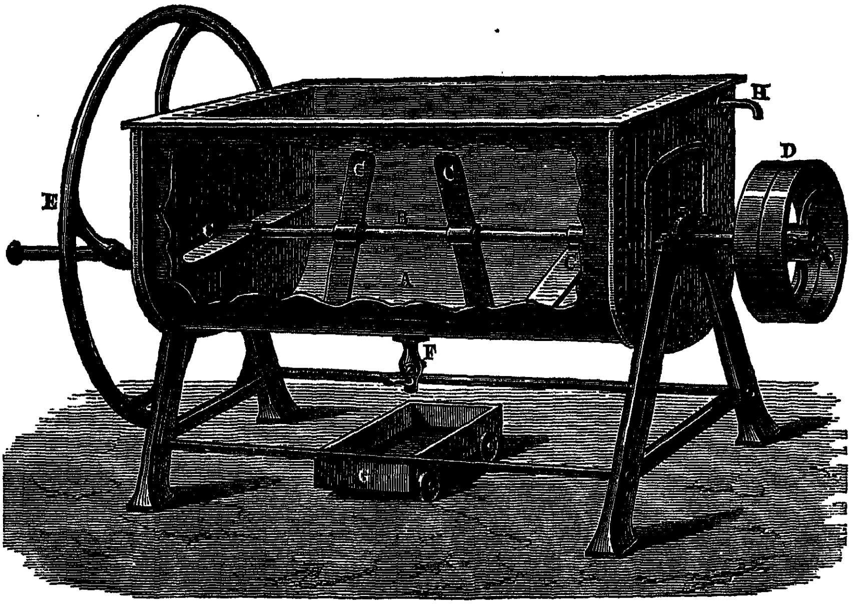


The composition of butter will be more fully spoken of later on in discussing the products of these industries.

3. Of Artificial Butter (*Butterine, Oleomargarine*).—The manufacture of substitutes for normal dairy butter began with the experiments of the Frenchman Mège-Mouries in 1870. He found that carefully-

washed beef-suet furnished a basis for the manufacture of an excellent substitute for natural butter. The thoroughly-washed and finely-chopped suet was rendered in a steam-heated tank, taking for one thousand parts of fat, three hundred parts of water, one part of carbonate of potash, and two stomachs of pigs or sheep. The temperature of the mixture was raised to 45° C. After two hours, under the influence of the pepsin in the stomachs, the membranes are dissolved and the fat melted and risen to the top of the mixture. After adding a little salt, the melted fat is drawn off, stood to cool so as to allow the stearin and palmitin to crystallize out, and then pressed in bags in a hydraulic press. Forty to fifty per cent. of solid stearin remains, while fifty to sixty per cent. of fluid oleopalmitin (so-called "oleomargarine") is pressed out. Mège then mixed the "oleo oil" with ten per cent. of its weight of milk and a little butter-color and churned it. The fat-cutting process of Mège-Mouries is shown in Fig. 73 and the churning of the "oleo oil" in Fig. 74. The product was then worked, salted, and constituted the "oleomargarine," or butter substitute. Various improvements have been made in the process of Mège, and it has been found that leaf-lard can be worked in the same way as beef-suet, and will yield an oleopalmitin suitable for churning up into a butter substitute.

FIG. 74.



The processes now followed are given substantially as described by Mr. Phil. D. Armour in his testimony before a committee of Congress:* "The fat is taken from the cattle in the process of slaughtering, and after thorough washing is placed in clean water and surrounded with ice, where it is allowed to remain until all animal heat has been removed. It is then cut into small pieces by machinery and cooked at a temperaaure of about 150° F. (65.6° C.) until the fat in liquid form has separated from the fibrin or tissue, then settled until it is perfectly clear. Then it is drawn into graining-vats and allowed to stand for a day, when it is ready for the presses. The pressing extracts the stearin, leaving a product commercially known as 'oleo oil,' which when churned with cream or milk, or both, and with usually a proportion of creamery butter, the whole being properly salted, gives the new food product, oleomargarine. In making butterine we use 'neutral lard,' which is made from selected leaf-lard in a very similar manner to oleo oil, excepting that no stearin is extracted. This neutral lard is cured in salt brine for forty-eight to seventy hours at an ice-water temperature. It is then taken and with the desired proportion of oleo oil and fine butter is churned with cream and milk, producing an article which when properly salted and packed is ready for the market.

"In both cases coloring matter is used, which is the same as that used by dairymen to color their butter. At certain seasons of the year—viz., in cold weather—a small quantity of sesame oil or salad oil made from cotton-seed oil is used to soften the texture of the product."

It will be seen that in this process a higher temperature is used in rendering the fat than was used originally by Mège. He obtained about fifty per cent. of oleo oil. The manufacturers now obtain sixty-two per cent. or more. The oleo oil from beef-suet and the neutral lard from leaf-lard are frequently mixed, the proportions varying according to the destination of the product; a warm climate calling for more "oleo," a cold one for more "neutral." In ordinary practice about forty-eight gallons of milk are used for churning with the oil per two thousand pounds of product. Plain oleomargarine is the cheapest product made. By adding to the material in the agitator or churn more or less pure butter what is known as butterine is produced, two grades of which are commonly sold,—viz., "creamery butterine," containing more, and "dairy butterine," containing less, butter.

Large quantities of oleo oil are now manufactured and exported as such from the United States to Europe, notably to Holland, where it is made up into oleomargarine butter. There are said to be seventy manufactories of this kind in Holland which work up oleo oil from all parts of the world.

4. CHEESE-MAKING.—The manufacture of cheese depends upon the property possessed by casein of being curdled by acids or ferments. In the case of sour milk, the milk-sugar has developed by the lactic fermentation some lactic acid, and this, as before stated, promptly throws out the casein in the insoluble form. In the case of sweet milk we usually accomplish the curdling of the casein not by the use of an acid, but with a ferment contained in the preparation called rennet. This is prepared from the fourth stomach of the calf by first cleansing the stomach,

active properties, so that a small quantity will curdle a large quantity of milk. We would have then, according as one or the other method is followed, a sour-milk cheese or a sweet-milk cheese. The former have a very minor value commercially, being made mainly for immediate domestic consumption. The latter class include all the more valuable commercial varieties. Of these we may distinguish fat, half-fat (or medium), and lean cheeses, or as they are also designated to indicate their origin, cream cheeses, whole milk cheeses, and skim-milk cheeses. As these last names indicate, the material may differ. We may have, moreover, all gradations or mixtures of cream, whole milk, and skim-milk used for the various grades manufactured.

In cheese-making from sweet milk, the milk, whether whole, mixed with cream, or skimmed, is heated to about 30° C. (86° F.) and the rennet added. It curdles usually in from thirty to forty minutes. After the curd has formed and been cut, or "broken down," the heat is raised to 98° F. (36° C.) to insure the souring of the whey and its more complete separation from the curd. Or the curd produced at not over 86° F. (30° C.) is after being cut collected in a heap, covered with a cloth to preserve the heat, and allowed to stand an hour to develop the acidity which serves to harden the curd and promote its separation from the whey. The curd is now cut up, worked to free it from the whey, salted and pressed. After it has acquired sufficient coherence (which requires from twelve to fourteen hours) it is taken from the press and placed in the curing-room to "ripen." This ripening process is essentially a fermentative one, and during its progress the curd loses its insipidity and acquires the characteristic taste and flavor of cheese.

In this process of ripening, the milk-sugar remaining in the cheese becomes transformed partly into lactic acid and partly into alcohol and carbon dioxide. In some varieties the carbon dioxide swells up ("huffs ") the cheese-mass and gives it the porous character so noticeable in the ripened cheese.

Fresh cheese has an acid reaction, but this diminshes more and more in the ripening, as the casein is gradually altered, soluble albuminoids peptone-like bodies, and organic bases like leucine, tyrosine, and amines being formed.

Some cheeses, especially the cream cheeses, are not pressed, but come on the market as soft cheeses. In these the curdling by rennet has also been effected at a lower temperature than in the case of the hard cheeses

Cheese has also been manufactured extensively in this country from skimmed milk to which oleomargarine or "oleo oil " has been added so a to give the finished product the character of a whole-milk cheese. Thi product is now quite supplanted, however, by the "lard cheese," which according to Caldwell,* was made in 1882 at over twenty factories i the State of New York. In this process an emulsion of lard is made b bringing together in a "disintegrator " lard and skimmed milk bot previously heated to 140° F. in steam-jacketed tanks; the "disintegrator consists of a cylinder revolving within a cylindrical shell: the surface of the cylinder is covered with fine serrated projections, each one of which is a tooth with a sharp point; as this cylinder revolves rapidly within its shell the mixture of melted lard and hot skimmed milk is forced up into the narrow interspace; and the lard becomes very finely divided and most intimately mixed, or "emulsionized," with the milk. This emulsion consists of from two to three parts of milk to one of lard. In making the cheese, a quantity of this emulsion, containing about eighty pounds of lard, is added to six thousand pounds of skimmed milk and about six hundred pounds of butter-milk in the cheese-vat, and the lard that does not remain incorporated with the milk or curd, usually about ten pounds, is carefully skimmed off. These quantities of the materials yield from five hundred to six hundred pounds of cheese containing about seventy pounds of lard, or about fourteen per cent. About one-half of the fat removed as cream in the skimming of the milk is thus replaced by lard. It is claimed that no alkali or antiseptic is used, and that only the best kettle-rendered lard can be employed, because of the injurious effect of any inferior article on the quality of the cheese, and that before even this lard is used it is deodorized by blowing steam under eighty pounds pressure through it for an hour. According to many witnesses the imitation is excellent, for experts have been unable to pick out lard cheeses from a lot of these and full-cream cheeses of good quality together.

III. Products.

1. Condensed and Preserved Milk.—The distinction between condensed milk prepared with the addition of cane-sugar and that prepared without sugar has already been referred to in speaking of the manufacture of this class of products. The first of these classes forms a white or yellowish-white product of about the consistency of honey and ranging in specific gravity from 1.25 to 1.41. It should be completely soluble in from four to five times its bulk of water without separation of any flocculent residue, and then possess the taste of perfectly fresh sweetened milk.

The second class of condensed milk preparations, those without addition of cane-sugar, are not boiled down to the same degree and remain perfectly liquid, and are put up therefore in glass bottles instead of being sealed in cans. Analyses of both classes are given on the authority of Battershall.*

Condensed Milk with Addition of Sugar.

BRAND.	Water.	Fat.	Cane- and milk-sugar.	Casein.	Salts.
Alderney	30.05	10.08	46.01	12.04	1.82
Anglo-Swiss (American)	29.46	8.11	50.41	10.22	1.80
Anglo-Swiss (English)	27.80	8.24	51.07	10.80	2.09
Anglo-Swiss (Swiss)	25.51	8.51	53.27	10.71	2.00
Eagle					

Condensed Milk without Cane-sugar.

Brand.	Water.	Fat.	Milk-sugar.	Casein.	Salts.
American	52.07	15.06	16.97	14.26	2.80
New York	56.71	14.13	13.98	13.18	2.00
Granulated Milk Company . .	55.43	13.16	14.84	14.04	2.53
Eagle	56.01	14.02	14.06	13.90	2.01

2. Butter and Butter Substitutes.—Commercial butter is more or less granular, and the more perfect the granular condition the higher is its quality considered. Special effort has been made in the case of oleomargarine or butterine to imitate this granulation, as the artificial product does not naturally tend to show such appearance. A good butter when fresh has a pleasant fragrant odor and agreeable taste, but the flavor, like the color, varies with the food of the cow, certain plants, like garlic, giving a quite pronounced flavor to both milk and butter. At ordinary temperatures butter is easily cut or moulded, and it readily melts to a transparent, light-colored oil. It always contains, according to the thoroughness with which it has been kneaded and washed, more or less casein, which is very liable to undergo decomposition, and hence the necessity for the addition of larger or smaller amounts of salt, which acts as a preservative. When the butter-fat is freed from curd and water by melting the butter and drawing off the oily layer it may be kept for a long time without change.

This butter-fat is made up, as was stated in speaking of the fat of milk, of the glycerides of oleic, palmitic, and stearic acids (the so-called insoluble acids) and the glycerides of butyric, caproic, caprylic, and capric acids (the so-called soluble acids). The proportion in which they exist in butter-fat varies within very slight limits only, so that five to six per cent. may be called the average percentage of the soluble acids, and eighty-eight per cent. the average percentage of the insoluble acids present in butter-fat. This gives a very important means of distinguishing between a natural butter and oleomargarine or natural butter adulterated with the imitations. In such butter the glycerides of the soluble acids (butyric, etc.), are either wanting entirely or, if a little cream was used in the churning with "oleo oil," present in very much smaller amount than the normal. This distinction will be evident from the analyses of normal butter and oleomargine butters, given on the authority of Dr. Bell. *

Genuine Butter, showing Range of Variation in Composition of the Fat.

	Water.	Salt.	Curd.	Butter-fat.	Specific gravity at 100° F.	Percentage of fixed acids in fat.	Percentage of soluble acids as butyric.	Melting point, Fahrenheit.
1. . .	7.55	1.03	1.15	90.27	913.89	85.56	7.41	85° F.
2. . .	11.71	3.60	0.95	83.74	911.45	88.24	5.41	90° F.
3. . .	11.42	1.29	1.12	86.17	910.47	88.53	4.84	90° F.
4. . .	12 55	0.89	0.74	85.82	910.20	89.00	4.57	90° F.
5. . .	14.62	1.48	1.88	82.02	910.70	89.00	4.50	91° F.

Analyses of Oleomargarine Butter or Butterine.

Water.	Salt.	Curd.	Fat.	Specific gravity at 100° F.	Percentage of fixed acids.	Percentage of soluble acids.	Melting point, Fahrenheit.
14.30	3.81	0.48	81.41	903.84	94.34	. .	82° F.
11.21	1.70	1.73	85.36	902.34	94.83	0.66	78° F.
12.33	4 00	1.09	82.58	903.15	95.04	0.47	79° F.
5.32	1.09	0.67	92.92	903.79	96.29	0.23	81° F.
13.21	3.99	1.07	81.73	901.36	95.60	0.16	78° F.

The best grades of artificial butter do not differ in appearance from ordinary butter. To induce the proper granulation of the oleomargarine, it is chilled thoroughly with fragments of ice immediately after it is taken from the churn and before kneading or salting it. In color, consistence, and taste it may be made to imitate the natural butter so as to deceive most persons. A distinction, it is said, however, can always be noted in the taste when it is melted upon hot boiled potatoes, to which it imparts a peculiar taste recognizable as distinct from that of a true butter.

3. CHEESE.—The general classification of the cheeses has been given in speaking of the methods of manufacture, and the distinctions between the fat and lean cheeses, between cream cheese, whole-milk and skimmed-milk cheeses given. The terms hard and soft cheeses are applied according as the curd has or has not been pressed in the process of manufacturing. Most of the names which have been attached to the different varieties of cheese are those of localities. We will indicate the character of a few of these.

Neufchâtel cheese is a Swiss cream cheese.

Limburger cheese is a soft fat cheese.

Fromage de Brie is a soft French cheese rapidly ripening and developing ammoniacal compounds.

Camembert cheese is also a cream cheese.

Roquefort cheese is a cheese made from the milk of the ewe.

Gruyère cheese is a peculiarly flavored Swiss cheese.

Cheddar cheese is a hard cheese made with whole milk.

Single and double Gloucester are made, the first from a mixture of skimmed and entire milk, and the second from the entire milk.

Parmesan cheese is a very dry cheese, with a large amount of casein and only a moderate percentage of fat.

Eidam cheese is a Dutch cheese, also relatively dry, and covered with red coloring.

In illustration of the chemical composition of these different varieties of cheese we will append three tables, the first of analyses from miscellaneous sources, and the second and third from Bell,* giving a fuller study of the composition of the cheeses and showing the difference between the fat normally belonging to the cheese and the fat added in the shape of lard or "oleo oil" in adulterated cheeses.

	Water.	Fat.	Casein.	Non-nitrogenous and loss.	Ash.
Neufchâtel (Fleischmann)	34.50	41.90	13.00	7.00	3.60
Emmenthaler (Fleischmann)	36.10	29.50	28.00	3.30	3.10
Limburger (Fleischmann).	35.70	34.20	24.20	3.00	2.90
Brie (Wynter Blyth)	51.87	24.83	18.30	. .	5.00
Camembert (Wynter Blyth)	51.30	21.50	19.00	3.50	4.70
Parmesan (Wynter Blyth)	27.56	15.95	44.08	6.69	5.72

	100 Parts contain					Proportion of fat in 100 parts of dry cheese.	Proportion of fat in 100 parts of casein and fat.	Salt percentage in cheese.	Percentage Composition of the Fat.	
	Water.	Fat.	Casein.	Free acid as lactic.	Ash.				Soluble acid.	Insoluble acid.
Stilton	23.57	39.13	32.55	1.24	3.51	51.19	52.50	0.67	4.42	88.96
American (red) .	28.63	38.24	29.64	. .	3.49	53.57	54.12	0.72	4.26	89.06
American (pale) .	31.55	35.93	28.83	0.27	3.42	52.49	53.34	0.82	4.81	88.49
Roquefort	32.26	34.38	27.16	1.32	4.88	50.75	54.24	3.04	4.91	88.70
Gorgonzola . . .	31.35	34.84	27.88	1.35	4.58	49.02	53.08	2.11	4.40	89.18
Cheddar (medium)	35.60	31.57	28.16	0.45	4.22	46.26	50.49	1.43	4.55	88 75
Gruyère	33.66	30.69	30.67	0.27	4.71	48.78	47.02	0.81	4.41	88.97
Cheshire	37.11	30.68	26.93	0.86	4.42	48.78	50.84	1.69	5.55	87.76
Single Gloucester	35.75	28.35	31.10	0.31	4.49	44.12	45.24	1.28	6.68	86.89
Dutch (Eidam) . .	41.30	22.78	28.25	0.57	7.10	38.80	42.41	4.45	5.84	87.58

Analyses of Oleomargarine and Lard Cheeses.

	100 Parts contain				Per cent. of salt.	100 Parts of Fat contain		Melting point of fat.
	Water.	Fat.	Casein and free acids.	Ash.		Insoluble acids.	Soluble acids.	
Oleomargarine cheese . .	30.95	28.80	36.27	3.98	1.14	92.43	2.16	77° F. (25° C.).
Lard cheese	31.30	24.66	38.87	5.17	1.55	92.88	1.55	92° F. (33.3° C.).

4. Milk-sugar.—The manufacture of crystallized milk-sugar (lac tose) has developed greatly in recent years, and a perfectly white, well crystallized product is now obtained. For its preparation, the swee skim-milk as it comes from the cream separator is precipitated wit acetic acid, filtered, and boiled either in open steam-heated evaporator or in vacuum pans. This first boiling should take several hours. Th whey during the boiling becomes more cloudy, but suddenly clears, an the remaining albuminoids will separate in large flocks that can readil be filtered. It is to be filtered hot and boiled to crystallization in vacuum pan. The raw sugar so obtained can be refined and made whit exactly as described under cane-sugar. As the first crystallization is al that can be brought to satisfactory color and purity, the yield is no much over ten per cent. of the total sugar contained in the milk.

5. Koumiss.—Koumiss is an alcoholic drink made by the fermenta

been a favorite beverage with the Tartars and other Asiatic tribes. Cow's milk has been used chiefly in making it in both Europe and America. Mare's milk is the more suitable for fermentation because of the larger percentage of milk-sugar which it contains.

The fermentation is started by mixing fresh milk with some already soured. Both the lactic and the alcoholic fermentations are set up, with the production of lactic acid, alcohol, and carbonic acid gas. Some of the albuminoids are also changed into peptones. The composition of the koumiss as prepared from both mare's and cow's milk is shown in the accompanying analyses from various sources:

	Water.	Milk-sugar.	Lactic acid.	Albuminoids.	Fat.	Alcohol.	Carbon dioxide.	Ash.
Koumiss from mare's milk (Fleischmann)	91.53	1.25	1.01	1.91	1.27	1.85	0.88	0.29
Koumiss from cow's milk (Fleischmann)	88.93	3.11	0.79	2.03	0 85	2.65	1.03	0.44
Koumiss from mare's milk (König)	92.47	1.24	0.91	1.97	1.26	1.84	0.95	. .
Koumiss from mare's milk (London, 1884)	91.87	0.79	1.04	1.91	1.19	2.86	. .	. .
Koumiss from cow's milk (Wiley)	89.32	4.38	0.47	2.56	2.08	0.76	0.83	. .

6. Kephir.—This is a Caucasian product somewhat similar to koumiss, but prepared from cow's milk in leathern bottles by the aid of a peculiar ferment known as "kephir grains." According to Kern, as quoted by Allen (Commercial Organic Analysis, 2d ed., vol. iv, p. 242), the kephir ferment is an elastic cauliflower-like mass found below the snow line on certain bushes. The fungus consists of bacilli and yeast-cells, each cell containing two round spores, whence the name *Dispora caucasina*. When dried, the kephir fungus forms hard yellowish grains about the size of peas. By soaking these in water and adding them to milk, alcoholic fermentation ensues and the kephir is matured in a few days.

The following figures show the comparative percentage composition of fresh milk, kephir, and koumiss:

	Fresh Milk.	Kephir.	Koumiss.
Fat	3.8	2.0	2.05
Proteids	4.8	3.8	1.12
Sugar	4.1	2.0	2.20
Lactic acid	Trace.	0.9	1.15
Alcohol	None.	0.8	1.65
Water and salts	87.3	90.49	91.83

7. Casein Preparations.—Casein is now utilized on a large scale, first, as a basis of food preparations; second, as a fixing agent in calico printing instead of albumen; and third, as a substitute for glue in cements. For the first class of compounds, the casein salts of the alkalies and alkaline earths are used, and are obtained by dissolving casein in the calculated amount of caustic alkali, alkaline carbonate or phosphate or milk of lime and evaporating the solution

erally dissolved in ammonia or in borax solution and used either with or without formaldehyde. A very superior paper size is thus made which is used on glazed cardboard. A mixture of casein with slaked lime sets to a hard insoluble mass, which is sometimes employed as a cement for earthenware and for similar purposes as a cheap substitute for glue.

In making these casein cements the most important point that is to be noted to insure success is the freeing of the casein from all oily matter. Therefore, when curd is prepared from milk, use only the most carefully skimmed milk quite free from cream, such as separator skimmed milk. When the casein has been separated and thoroughly washed it is uniformly mixed with quicklime and applied quickly. It then sets very rapidly. Silicate of soda solution and borax are also used instead of quick-lime, and form excellent cements with casein. *Käseleim pulver,* a ready-made Swiss preparation, will set when moistened.

8. Whey.—The aqueous liquid remaining after the separation of the butter-fat and the casein, or curd, is termed the whey. Its more important constituent is milk-sugar, which in sour whey has been changed in part into lactic acid. It also contains soluble nitrogenous constitutents, such as milk-albumen and peptonized casein. On account of these constituents it is an easily digestible preparation and one assisting digestion. Hence the use of the "whey treatment" in medical practice for dyspeptics and those suffering from enfeebled digestion. The chief importance, however, of the whey is for the extraction of the milk-sugar, which has developed into an important article of manufacture. Other products of minor and local importance only are "whey butter," "whey alcohol," from which latter "whey champagne" is made, and "whey vinegar." For the analysis of whey see p. 280.

IV. Analytical Tests and Methods.

1. For Milk.—The specific gravity of milk is an indication of value as it varies according to the content of fat, being higher for a skimme milk than for a whole milk. However, when the cream has been removed the specific gravity may be reduced to that of normal milk by the addi tion of water, and then the specific gravity determination taken alon would be fallacious. Hence the detection of the adulteration of milk b addition of water cannot be made with entire accuracy by the lactomete or specific gravity hydrometer in use. The lactometer officially used b milk inspectors in New York and other States indicates specific graviti between 1.000 (the specific gravity of water) and 1.038. A specifi gravity of 1.021 (taken as the minimum density of genuine milk) is al marked 100°, while the specific gravity of water (1.000) is called 0 Hence if the lactometer read 70°, the sample is supposed to contai seventy per cent. pure milk and thirty per cent. water. The avera lactometric strength of about twenty thousand samples of milk examin by the New York State Dairy Commissioner in the year 1884 was 110 equivalent to a specific gravity of 1.0319. Another form of lactomet used abroad is the Quevenne-Müller instrument, which is graduated

then the limits of pure milk (1.029 to 1.034) indicated, and degrees of dilution with water also indicated as the specific gravity sinks below this. The degree of adulteration of skimmed milk is also indicated on the instrument in the same way.

The *total solids* form an important element in the examination of milk. In some States the minimum percentage of total solids allowed in a milk is stated by law. (In Massachusetts thirteen per cent.; in New York and New Jersey twelve per cent.) To determine the *water* and *total solids,* five grammes of milk are placed in an accurately weighed flat-bottomed platinum dish of not less than five centimetres diameter and dried on a steam bath until constant weight is obtained. Fifteen to twenty grammes of pure dry sand may be previously placed in the dish to facilitate drying. Cool in desiccator and weigh rapidly to avoid absorption of moisture.

To determine the *ash* weigh about twenty grammes of milk in a weighed dish, add six cubic centimetres of nitric acid, evaporate to dryness and ignite at a temperature just below redness until the ash is free from carbon.

Both *fat* and *moisture* may be determined with one weighing of the sample in the Babcock asbestos method. A hollow cylinder of perforated sheet metal sixty millimetres long and twenty millimetres in diameter, closed at one end by a disk of the same material, is taken. This is filled loosely with from 1.5 to 2.5 grammes of freshly ignited woolly asbestos free from fine and brittle material, cooled in a desiccator, and weighed. Then introduce a weighed quantity of milk (between three and five grammes) and dry at the temperature of boiling water to constant weight to obtain the moisture by loss. Extract the residue now by the aid of anhydrous ether until all the fat is removed, evaporate the ether, dry the fat at the temperature of boiling water and weigh. The fat may also be determined by difference, drying the extracted cylinders at the temperature of boiling water.

The paper coil method of Adams is also often used. In this a coil of white blotting-paper (or thick filtering-paper) previously purified with ether and dried is made to soak up the milk to be analyzed from a weighed beaker or pipette. The paper coil is then dried in a hot-air oven and placed in a Soxhlet (see p. 86) or similar fat-extraction apparatus connected with an inverted condenser and the fat extracted by ether or petroleum-ether.

The *total nitrogen* is estimated by evaporating a weighed portion of milk to dryness and making a combustion of the residue with soda-lime or by the Kjeldahl method of conversion into ammonia compounds and distillation from an alkaline solution. *Casein* may be determined in fresh milk as follows: Place about ten grammes of milk in a beaker with about ninety cubic centimetres of water at 40° to 42° C., and add at once 1.5 cubic centimetres of a ten per cent. acetic acid solution. Stir with a glass rod and let stand from three to five minutes longer. Then decant on to the filter, wash first by decantation and then transfer the precipiin the washed precipitate and filter paper by the Kjeldahl method, using 6.38 as the factor to calculate the casein.

The estimation of the *milk-sugar* by the polariscope is rendered difficult by the presence in milk of various albuminoids, all of which turn the plane of polarization to the left, and the ordinary means of removing these albuminoids by a solution of basic acetate of lead is far from being perfect. Professor Wiley after extensive experiments upon this ha adopted a method of optical analysis, using acid mercuric nitrate t precipitate the albuminoids. He takes the specific rotatory power o milk-sugar as $(a)_d = 52.5$. For details of his procedure the reader i referred to Bulletin 107.* Milk-sugar may also be determined eithe volumetrically or gravimetrically with the aid of Fehling's solution (See p. 175.) In this case, it is also necessary to remove the albuminoid first, and this is done by Ritthausen's method of precipitation wit copper sulphate, all excess of this reagent being removed with causti potash solution. In calculating the results it will be remembered tha the copper reducing power of milk-sugar is 70.5° as compared wit dextrose at 100°.

The sugar is probably most accurately determined by extraction fro the fat-free residue with weak boiling alcohol, filtering the alcoholi fluid, and evaporating to dryness. This leaves the sugar with som mineral matter. On burning and determining this matter as ash th amount of sugar can be gotten.

The *artificial coloring* of milk is frequently practised to cover up th watering of the sample. The colors to be tested for are annatto, caram and anilin-orange, an azo-dye. Leach † has given the following schem for the detection of added colors in milk:

SUMMARY OF SCHEME FOR COLOR ANALYSIS.—Curdle one hundre and fifty cubic centimetres of milk in casserole with heat and acetic aci Gather the curd in one mass, pour off whey, or strain, if curd is fine divided. Macerate curd with ether in corked flask. Pour off ether.

Ether Extract.

Evaporate off ether, treat with NaOH and pour on wetted filter. After the solution has passed through, wash off fat and dry filter, which if colored orange, indicates presence of annatto. (Confirm by $SnCl_2$.)

Extracted Curd.

(1) If colorless—indicates presence no foreign color other than in ether e tract.

(2) If orange or brownish—indicat presence of anilin orange or caram Shake curd in test-tube with concentrat hydrochloric acid.

If solution gradually turns blue, indicative of caramel. (Confirm by testing for caramel in whey of original milk.)

If orange cu immediat turns pink, dicative of a lin orange.

The examination of milk for *preservatives* is constantly necessa The most important of these preservatives is formaldehyde. To det

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* U. S. Dept. of Agricult.. Bureau of Chem., Bulletin 107 (Revised), p. 118

it according to Leach add ten cubic centimetres of commercial hydrochloric acid (specific gravity 1.2) containing two cubic centimetres of ten per cent. ferric chloride per litre to an equal volume of milk in a porcelain casserole and heat slowly over the free flame, giving the vessel a rotatory movement while heating to break up the curd. The presence of formaldehyde is indicated by a violet coloration varying in degree with the amount present. With fresh milk, one part of formaldehyde in 250 of milk may be thus detected.

Hehner's test may also be used. To five or ten cubic centimetres of milk in a wide test-tube add about half the volume of concentrated commercial sulphuric acid, pouring the acid carefully down the inside of the tube so that it forms a layer at the bottom without mixing with the milk. A violet zone at the junction of the liquids indicates formaldehyde. Benzoic, salicylic, and boric acids have also been used. The latter may be readily tested for by turmeric paper. Ten cubic centimetres of the milk are thoroughly mixed with six drops of concentrated hydrochloric acid. Turmeric paper moistened with this and dried will show a red color if boric acid were present in the milk.

2. For Butter.—The *water* in butter is determined by drying five grammes of the butter in a platinum dish at a temperature of 100° C. (212° F.) or slightly higher. The melted butter is stirred from time to time to facilitate the escape of the moisture. The water will have been given off in three to four hours, and it has been found that longer heating sometimes causes the melted fat to gain in weight.

To determine the *salt,* the dried butter just obtained is treated with warm ether or petroleum spirit, and the contents of the platinum dish poured on a weighed filter and washed with ether until all fat is removed. The residue and filter are dried and weighed. The salt is then dissolved out by warm water, and the chlorides in the solution estimated volumetrically by titration with decinormal silver nitrate, using a few drops of potassium chromate as indicator. The difference between the weight of salt ascertained and the total weight of curd and salt on the weighed filter is regarded as the amount of the *casein,* or *curd,* present. If after washing out the salt the residue on the weighed filter be dried and then weighed, the amount of casein so obtained is a little less than that gotten by difference. This is partly due to the small amount of milk-sugar washed out along with the salt and undetermined, and partly to the slight solvent action of warm water on some of the curd.

The percentage of *fat* may be obtained by evaporating the ether filtrate from the previous determination of salt and curd, but the butter-fat is liable to increase in weight by this treatment, and therefore the *fat* is usually gotten by difference after determining the water, casein, salt, and milk-sugar.

The adulteration of butter and the manufacture on a large scale of butter substitutes make an examination of the butter-fat one of great importance. This examination may be both qualitative and quantitative and, after allowing the water and curd to settle, pouring the clear fat on to a dry warm ribbed filter and collecting the filtrate.

The specific gravity of the butter-fat may be taken, as first suggested by Bell, in a specific gravity bottle at a temperature of 100° F. (37.7° C.), or, as suggested by Estcourt and endorsed by Allen, with the aid of the Westphal balance (see p. 87) at a temperature of 99° to 100° C. (210° to 212° F.). Bell found by this method that the specific gravity of true butter-fat varied from 909.4 to 914 (water 1000), while butterine showed a specific gravity of 901.4 to 903.8. Allen gives the limit for pure butter-fat tested at 99° C. as 867 to 870, while butterine at the same temperature was 858.5 to 862.5.

The *melting point* of the butter-fat is also generally noted. Bell proposed determining the melting point by first suddenly cooling some melted butter-fat by floating the capsule containing it upon ice-water, and then taking a fragment of the congealed butter upon the loop of a platinum wire. This is then introduced close to the bulb of a thermometer in a beaker of water which is being heated from without. As the water becomes warmed the globule melts and the thermometer is read off. An improvement on the method insuring greater accuracy is recorded in Bulletin No. 107 (revised) of the Bureau of Chemistry, p. 133. The melting point of butter usually ranges between 29.5° C. and 33° C. (85° to 90° F.), while the melting point of butterine is stated to be between 25.5° C. and 28° C. (77.9° to 82.4° F.).

The quantitative examination of the supposed butter-fat may be made by several methods,—viz., the determination of the saponification equivalent by Koettstorfer's method,* the determination of the percentage of insoluble fatty acids present as glycerides by Hehner's method,† and the determination of the volatile fat acids after distillation by Reichert's method.‡ To these most generally received methods may also be added the method of Hübl of iodine saturation as determining the character of fatty acids, and the method of Morse and Burton, which combines the Koettstorfer and the Hehner processes, and determines the saponification equivalent of the soluble and the insoluble fat acids separately.

The term "saponification equivalent" is used to indicate the number of grammes of an oil saponified by one equivalent in grammes of an alkali. Thus, tributyrin (the glyceride of butyric acid) has a saponification equivalent of 100.67, while tristearine (the glyceride of stearic acid) has a saponification equivalent of 296.67. Butter-fat, it will be remembered, is a mixture of the several glycerides of the lower or volatile fatty acids and the higher or non-volatile fatty acids. Its saponification equivalent ranges from 241 to 253, the average being 247; butterine has a saponification equivalent ranging from 277 to 294, the average being 285.5. In Hehner's method, the weighed quantity of the fat is saponified by alcoholic potash, the soap solution evaporated down, taken up with water

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* Allen, Commercial Organic Analysis, 2d ed., vol. ii, p. 40.

† Bell, Analysis and Adulteration of Foods, Part ii, p. 56.

and the fatty acids set free by an excess of hydrochloric acid. They are now brought upon a weighed filter, washed with boiling water until no longer acid, and then chilled into a cake by immersing the filter in cold water. The filter is then transferred to a weighed beaker-glass and the contents dried at 100° C. until constant in weight. The soluble fat acids can also be determined in this process by collecting the washings which were obtained with boiling water and making them up to one hundred cubic centimetres and then carefully titrating an aliquot portion with decinormal soda solution. This will give the amount of soluble fat acids plus the excess of standard hydrochloric acid used originally in liberating the fat acids. The amount of this excess can be ascertained by carrying through a blank experiment with alcoholic potash and hydrochloric acid, but without the fat. In the analysis of butter-fat the sum of the insoluble fatty acids and of the soluble fatty acids calculated as butyric acid should always amount to fully ninety-four per cent. of the fat taken. The soluble fatty acids calculated as butyric acid should amount to at least five per cent., any notably smaller proportion being due to adulteration. As an average, eighty-eight per cent. of insoluble and five and a half per cent. of soluble acids should be obtained.

While the true percentage of the volatile fatty acids cannot be easily obtained, the amount of alkali needed to neutralize them after distillation can be determined by Reichert's process. According to this, as improved by Meissl, five grammes of the fused and filtered fat are placed in a flask of about two hundred cubic centimetres contents with about two grammes solid caustic potash and fifty cubic centimetres of seventy per cent. alcohol, saponified on the water-bath and evaporated down until all alcohol is driven off. The thick soap-mass remaining is now dissolved in one hundred cubic centimetres of water, forty cubic centimetres of dilute sulphuric acid added, and, after adding a few fragments of pumice-stone, distilled with the aid of a Liebig condenser. About one hundred and ten cubic centimetres of distillate are collected, which requires about an hour. Filter and collect one hundred cubic centimetres in a graduated flask. Add phenol-phthalein as an indicator, and titrate with decinormal alkali. Increase the result by one-tenth, and reckon the result upon five grammes of the substance. It is found that two and a half grammes of butter-fat, examined by Reichert's method, require about thirteen cubic centimetres of the decinormal alkali, while butterine requires only one cubic centimetre. As the difference between these is twelve cubic centimetres, it may be calculatd that there is 8.5 per cent. real butter-fat present in a mixture for every cubic centimetre of alkali required over the one cubic centimetre required for ordinary butterine.

Hübl's method is founded on the fact that the three series of fatty acids (acetic, acrylic, and tetrolic) unite in different proportions with the halogens, like chlorine, bromine, and iodine, to form addition products. The number of grammes of iodine absorbed is calculated to one hundred grammes of fat, and this is Hübl's "iodine number." Thus genuine butter has an iodine number from 30.5 to 43.0, while oleomar-

Morse and Burton * saponify the combined fatty acids, liberate the free acids, wash out the soluble portion of the mixture, and then saponify again the soluble and the insoluble acids separately. They thus combine the Koettstorfer and the Hehner processes and get a greater certainty as to the character of the fat mixture. Thus they find that with butter 86.57 per cent. of potassium hydrate is required to neutralize the insoluble acids and 13.17 per cent. to neutralize the soluble acids, while with oleomargarine 95.40 per cent. of potassium hydrate is required for the insoluble acids and 4.57 per cent. for the soluble acids.

A physical test frequently applied to distinguish oleomargarine and process (renovated) butter from true butter is the foam test. True butter melted in a spoon over a free flame will foam abundantly, while the other butter named will only burn and sputter like melted grease.

The presence of annatto coloring in butter is shown by treating two or three grammes of the melted and filtered fat (freed from salt and water) with warm dilute sodium hydroxide and after stirring pouring the warm mixture upon a wet filter. If annatto is present the paper will absorb the color so that when the fat is washed off by a gentle stream of water the paper appears dyed straw yellow and on application of a drop of stannous chloride solution turns pink.

For azo colors, melt a small amount in a test-tube and add an equal amount of a mixture of one part concentrated sulphuric acid and four parts glacial acetic acid and heat nearly to boiling, shaking the contents of the tube. Then set aside. The acid solution when settled will show a wine-red color in the presence of azo colors.

3. For Cheese.—The methods employed in cheese analysis are in most respects the same as those employed in the examination of butter. The *fat* is best extracted with light petroleum-ether, as common ether dissolves the free lactic acid as well as the fat. The remaining solids not fat can then be dried and weighed. The fat should be examined by Koettstorfer's saponification equivalent method, as the oleomargarine and lard cheeses may be detected in this way. Genuine cheese-fat, according to Muter,† should not consume less than two hundred and twenty milligrammes of potassium hydrate for each gramme used. If the cheese should give unfavorable indications with Koettstorfer's test, then the soluble and insoluble fatty acids are determined in the fat according to Hehner. The percentage of insoluble fat acids in genuine cheese, according to Muter, averages 88.5, while in oleomargarine cheeses it is from 90.5 to 92 per cent.

The *acidity*, calculated as lactic acid, may be determined by treating the residue from the fat determination with water and titrating the washings with decinormal soda solution. The washed residue then is the non-fatty solids.

The *ash* is determined by ignition of the dried cheese before extraction of the fat.

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* Amer. Chem. Journ., x, p. 322.

V. Bibliography and Statistics.

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STATISTICS.

The only general statistics of the milk industry are those gathered able. The figures for the main products of the milk industry are as follows:

	1905.	1900.	Increase.
Products, total value	$168,182,789	$130,783,349	$37,399,400
Butter (lbs.)	531,478,141	420,126,546	111,351,595
Value	$113,189,453	$84,079,754	$29,109,699
Cheese (lbs.)	317,144,872	281,972,324	35,172,548
Value	$28,611,760	$26,519,829	$2,091,931
Condensed milk (lbs.)	308,485,182	186,921,787	121,563,395
Value	$20,149,282	$11,888,792	$8,260,490
All other products	$6,232,294	$8,294,974	$2,062,680

(Report of Census Bureau, 1905.)

The oleomargarine production, as reported by the Internal Revenue Bureau, has been:

	1909.	1910.
Uncolored oleomargarine (lbs.)	86,572,514	135,685,289
Colored oleomargarine (lbs.)	5,610,301	6,176,991
Total oleomargarine (lbs.)	92,282,815	141,862,282

The exportation of dairy products from the United States has decreased in recent years and was as follows:

	1906.	1907.	1908.	1909.	1910.
Butter (lbs.)	27,360,537	12,544,777	6,463,061	5,981,265	3,140,545
Valued at	$4,922,913	$2,429,489	$1,407,962	$1,268,210	$785,771
Cheese (lbs.)	16,562,451	17,285,230	8,439,031	6,822,842	2,846,209
Valued at	$1,940,620	$2,012,626	$1,092,053	$857,091	$441,017
Oleomargarine (lbs.) .	11,794,174	5,397,609	2,938,175	2,889,058	3,418,632
Valued at	$1,033,256	$520,406	$299,746	$293,746	$349,972
Oleo oil (lbs.)	209,658,075	195,337,176	212,541,157	179,985,246	126,091,675
Valued at	$17,455,976	$16,819,933	$19,278,476	$19,126,745	$14,305,080
Condensed milk (lbs.)	....	....	....	....	13,311,318
Valued at	$1,889,690	$2,191,111	$2,455,186	$1,375,104	$1,023,633

Of miscellaneous products, there were produced in 1905, according to the Census Bureau, 1,161,414,457 pounds of skimmed milk valued at $1,368,738, and from this was extracted 11,581,874 pounds of casein, valued at $554,099. The whey from which sugar of milk is obtained amounted to 166,451,226 pounds, valued at $111,907.

CHAPTER VIII.

VEGETABLE TEXTILE FIBRES.

General Characters.

All the fibres which have been found of technical value for manufacturing purposes may be divided into the two great classes, vegetable fibres and animal fibres, the few found in the mineral kingdom among fibrous minerals being of relatively slight importance in textile manufacturing. Moreover, the distinction is not merely, as the name chosen would indicate, one of origin, but fundamental structural and chemical differences also exist and make themselves evident upon the slightest examination. The vegetable fibres are exclusively cell-growths of relatively simple structure, which during their life form integral parts of the plant organisms, while the animal fibres may be either a hardened secretion like silk or a more complicated cell-growth like wool, distinguished by its scale-like surface.

Thus the vegetable fibres are without exception some form of cellulose $(C_6H_{10}O_5)_n$ in more or less pure condition or an alteration product of the same, while the animal fibres are composed of protein matter, and hence are nitrogenous.

The radical character of their chemical difference just referred to will be more thoroughly appreciated when we note the action of reagents upon the two classes respectively. The vegetable fibres are not dissolved or weakened by alkalies even at a boiling temperature, while the animal fibres are speedily disintegrated, with eventual liberation of ammonia from the nitrogenous material; on the other hand, sulphuric acid or hydrochloric acid rapidly causes a disintegration of the vegetable fibres by their action upon the cellulose, and nitric acid either oxidizes the cellulose or gives rise to nitrated derivatives, while the animal fibres are only slightly affected even when the acids are concentrated. These reactions will be referred to more fully in speaking of the analytical tests used for distinguishing the fibres in mixed goods. (See p. 353.)

The several vegetable fibres may be classified according to botanical or morphological character into three groups: (1) *Seed-hairs* (filaments composed of individual cells); (2) *bast fibres* (filaments or fibre-bundles made up of individual fibre-cells aggregated together); and (3) *fibro-vascular bundles.* Sometimes the term bast fibres is made to include both the second and third classes as just given.

Chemically, all vegetable fibres are composed of cellulose. However, it has long been known that it is frequently more or less contaminated with altered products, which have been known have given us a clear understanding of the nature of the lignin and the alteration products of cellulose. The combination of cellulose and lignin, to which they apply the name of *bastose,* may make up the whole bundle of fibres, as in jute, or may be merely a covering upon the unaltered cellulose. By distinguishing between the cellulose and the bastose and mixtures of the two we may establish a chemical classification of the vegetable fibres. We are enabled to do this by the aid of the solutions of iodine (potassium iodide solution saturated with free iodine) and sulphuric acid (concentrated glycerine and strong sulphuric acid), which were first proposed by Vétillart.* Pure cellulose when tested with the iodine and sulphuric acid solutions, one after the other, will give a pure blue color, while bastose shows under these conditions a yellow coloration. A complete classification, taking both botanical and chemical characters into account, is the following, which is that of Cross and Bevan's † with some additions:

	A. Seed-hairs.	B. Dicotyledonous bast fibres.	C. Monocotolydonous fibres corresponding to bast fibres.
Blue reaction with iodine and sulphuric acid.	Cotton.	Linen. Hemp. China-grass. Ramie. Nettle. Sunn fibre.	Straw. Pineapple. Esparto. Alfa.
Yellow reaction with iodine and sulphuric acid.		Hibiscus. Jute.	New Zealand flax. Aloe. Yucca. Manila hemp. Coir.

1. COTTON FIBRE.—The cotton, as already noted, is a seed-hair and envelops the seeds, which are at first enclosed in a capsule. With the ripening of the plant this capsule bursts and the contents spread out widely, consituting the cotton-boll, which is easily picked. The separation of the fibre from the enclosed seed is afterwards accomplished by the mechanical operation called "ginning," in which it is torn from the seed, so that while one end of an individual fibre is always closed the other is irregularly broken.

The genus *Gossypium,* to which all cotton-plants are referred, includes several well-marked varieties, the most important of which are *G. Barbadense,* or "sea-island cotton," grown off the coast of Georgia, South Carolina, and Florida, which yields the longest and strongest fibre or the finest "staple;" the *G. hirsutum,* or upland cotton, grown inland in Georgia, Alabama, Louisiana, and Mississippi, which yields a shorter staple; the *G. herbaceum,* grown in Egypt, Asia Minor, and India; the *G. Barbadense,* or "sea-island cotton," grown off the coast of Georgia, China and India and yielding the so-called "nankin " cotton of brown-yellow color; and the *G. Peruvianum,* yielding the long-stapled Brazilian and Peruvian cotton.

The structure of the cotton fibre is very characteristic. It presents a flattened and collapsed tube slightly twisted in spiral form, with comparatively thick walls and a small central opening. This structure is illustrated in Figs. 75 and 76, in the first of which the fibre is magnified thirty times and in the second of which it is magnified two hundred times. The first illustration shows the spiral twist of the fibres distinctly, but the collapsed character of the tube only slightly; this latter feature, however, is shown very distinctly in the second illustration. This flattening is not seen in the unripe fibre, which is a tube filled with liquid protoplasmic matter, but in the ripening of the plant this liquid dries up and the walls of the tube collapse and flatten out. The adhesion of the fibre to the seed also becomes less, so that the ripe cotton is easily separated in the ginning process. In some species (as in *G. Barbadense*) this separation of hair from the seed is so perfect that the seed shows after the ginning a lustrous black appearance, whence the name locally applied of "black-seed cotton" as distinguished from the upland variety, known as "green-seed cotton."

FIG. 75.

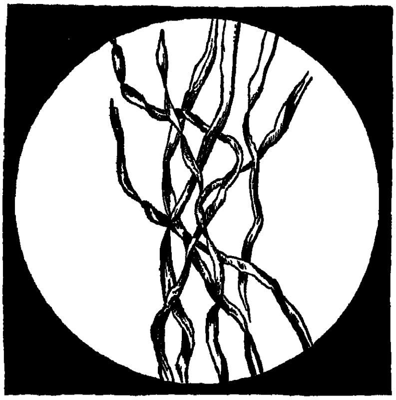
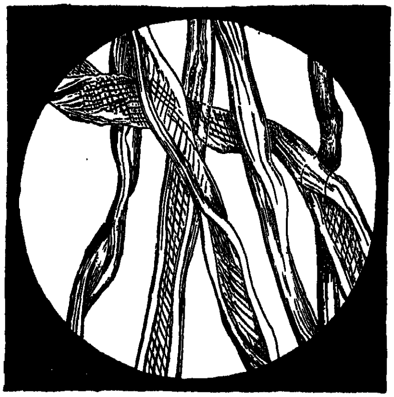


FIG. 76.



The fibre must be picked when mature or it becomes "over-ripe" and deteriorates. The length of the "staple," or fibre, varies considerably with the different varieties of the cotton, the long-stapled sea-island cotton grown on the shores of Georgia and Florida attaining a length of nearly two inches (five centimetres), while the short native cotton of India scarcely exceeds three-quarters of an inch (eighteen millimetres) in length.*

Chemically, the cotton fibre contains about ninety-one per cent. of pure cellulose, seven per cent. of moisture, and small amounts of fat, nitrogenous material, and cuticular substance. An ammoniacal solution of copper oxide causes the cellulose material of the fibre to soften and swell up, whereby the cuticle, which is not softened, takes the appearance of yellowish constricting rings binding the swollen cellulose at regular intervals. Prolonged action of the reagent dissolves the cellulose. When

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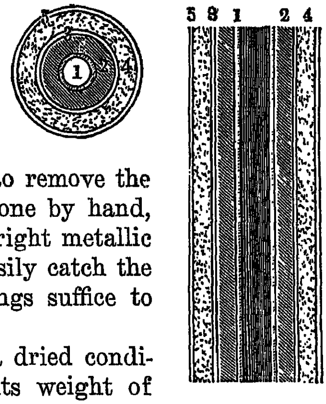
bleached by boiling with sodium carbonate or hydrate, the cuticle is decomposed and the fibre yields easily a very pure form of cellulose.

2. Flax.—The flax-plant, *Linum usitatissimum,* yields the best known and probably the most valuable of the bast fibres as well as other products, like the linseed oil and linseed cake. (See p. 54.) It is not grown for both fibre and seed together, however, as when the fibre is desired in best condition the plant is gathered before it is fully matured, while if the plant is allowed to ripen fully for production of seed, the fibre obtained is more stiff and coarse.

The plant is grown through a wide range of climate, although that grown in the tropics, as in India, is chiefly used for seed, the fibre being of little value, while that grown in colder countries, as in the Russian East Sea provinces, yields the best fibre. When the plant is cultivated for the production of fibre, it is either sowed more thickly or, as in Holland and Belgium, forced to grow up through a net-work of brushwood, thus yielding a more slender plant with a longer and finer fibre, known as *lin ramé.* The plant is not cut, but is always carefully pulled up by the roots, and the freshly pulled-up flax is at once submitted to the process of seeding, or "rippling," which is to remove the leaves and seed capsules. This is usually done by hand, drawing the bundles of the flax through upright metallic combs, or "ripples," the prongs of which easily catch the seed capsules, so that three or four drawings suffice to clean the stems or flax straws.

Fig. 77.

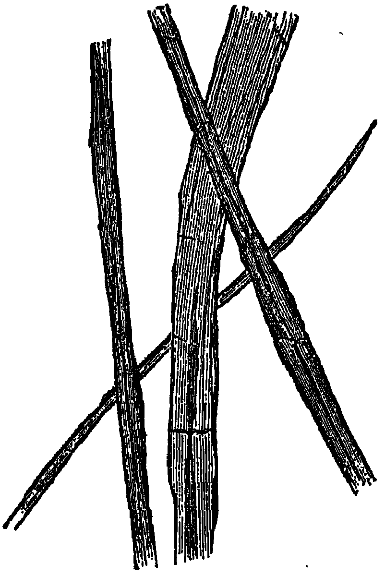


This straw, as it is termed, contains in a dried condition seventy-three or eighty per cent. of its weight of woody matter and encrusting material and twenty to twenty-seven per cent. of bast fibre.

The distinction between the several parts of the stem in the flax and similar plants yielding bast fibres is shown in Fig. 77 by both transverse and longitudinal cross-sections, where 1 represents the pith, 2 the woody tissue, 3 the cambium or partially lignified tissue, 4 the bast fibre, and 5 the crust or rind. To free these several parts of the stem from each other so as to obtain in a clean state the bast fibre is the object of the process of "retting." This is done either by natural means, as in the case of *dew retting* and *cold-water retting,* or by the help of an artificial process, as in *warm-water retting* and *chemical retting.* The dew retting, applied most largely in Russia, consists in leaving the flax thinly spread exposed to dew and rain, air and light, for eight or ten weeks, when, by the fermentation of the pectose matter of the rind, the bast fibre is thoroughly loosened. In cold-water retting either running or stagnant water may be used, the former being used in Belgium and the latter in Ireland. The bundles of flax are placed in crates and submerged, when actual fermentation ensues. The water must be soft, and undue heating up during the fermentation. The warm-water retting requires a temperature of 30° to 35° C., and can be carried to completion in fifty to sixty hours, yielding an excellent product. The chemical process consists in the use of dilute sulphuric acid or hydrochloric acid, which allow of the completion of the process in a few days. After the retting process the flax is well washed and dried, and is then submitted to the mechanical processes of "breaking," "scutching," and "hackling" to thoroughly free the fibre from the woody layer and draw out the fibre-bundles into filaments.

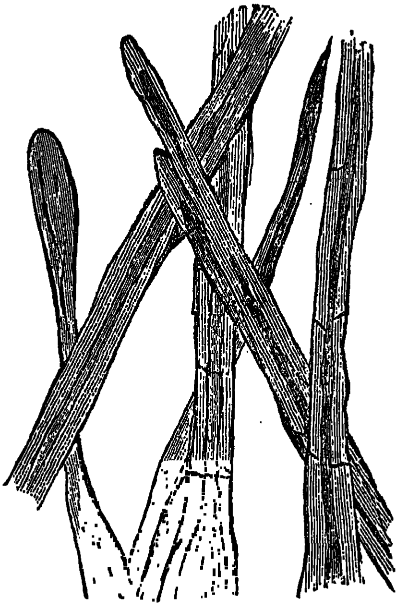
The flax fibre as seen under the microscope seems to be a long straight and transparent tube with thick walls and a minute central canal. Fig. 78 shows these characters of the flax fibre. Characteristic transverse markings also are shown, which may be nodal divisions or slight breaks or wrinkles produced by bending. Longitudinal fissures also show after vigorous rubbing. The linen fibre when cleansed has a blonde or even white color, a fine silky lustre, and great strength. It is less pliant and elastic than cotton, but is a better conductor of heat, and hence seems colder than cotton. Chemically it is, like cotton, a pure cellulose, but when swollen by the action of ammoniacal cupric oxide solution does not show the same uniform series of constricting bands of cuticle. Linen is in many respects more readily disintegrated than cotton, especially under the influence of caustic alkalies, calcium hydrate, and strong oxidizing agents like chlorine and hypochlorites.

Fig. 78.



Flax ($\frac{250}{1}$).

Fig. 79.



Hemp ($\frac{250}{1}$).

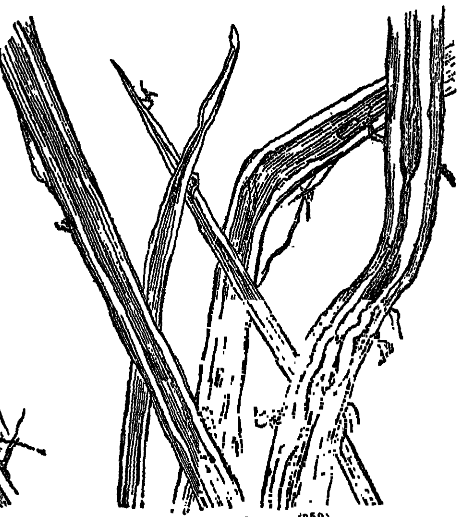
3. Hemp.—The fibre known by this name is the product of the *Can-*

Italy, while the seed is grown in India. It is a bast fibre similar to that of the flax-plant, but coarser, stronger, of deeper color and less lustre. Fig. 79 shows the microscopical characters of the hemp fibre. Its cultivation is very similar to that already described under flax, and differs according as the fibre or the seed are sought. The freshly-plucked hemp loses sixty per cent. of its weight in drying, and from the air-dried hemp straw twenty per cent. of bast fibre is obtained in the case of the male plant and twenty-two per cent. in the case of the female plant. It is used chiefly for ropes and cordage, and the fabric woven from it, known as canvas, is used in sail-making. Much of the finer fibre, however, is combined with linen fibre in weaving other goods. The iodine and sulphuric acid test shows that the hemp fibre is not composed of pure cellulose, but is a mixture of cellulose and bastose.

FIG. 80.

Jute, *Corchorus capsularis* ($\frac{450}{1}$).

FIG. 81.



Manila hemp ($\frac{250}{1}$).

4. JUTE is the bast fibre of two species of the genus *Corchorus*, and is grown chiefly in India and Ceylon. The fibre is separated from the plant by methods similar to those employed with flax and hemp, the process of cold retting in stagnant water being followed generally. The bast fibres attain a length of 2.5 metres or even more, are of a yellowish-white color, and have a fine lustre. It is seen under the microscope to consist of bundles of stiff lustrous cylinders with walls of very irregular thickness. These characters of the jute are shown in Fig. 80. Chemically, jute differs from the bast fibres hitherto mentioned in that it contains no free cellulose, but consists of the chemical compound of cellulose with lignin, to which Cross and Bevan, who investigated it, gave the name of *bastose*. It gives, treated with iodine and sulphuric

colors, like the aniline dyes, as if it had been mordanted with tannin, and can therefore be dyed directly without previous treatment. It is much more easily affected by the action of acids and alkalies than flax or hemp. The influence of air and moisture will also rot the jute fibre. It cannot be bleached safely with chloride of lime because of the readiness with which the fibre is oxidized, but it may be bleached with a weak solution of sodium hypochlorite or by the successive action of potassium permanganate and sulphurous acid. It may be considered as showing more resemblance to the animal fibre in lustre and appearance than any of the other vegetable fibres, and is therefore frequently mixed with wool, mohair, and silk in certain classes of goods.

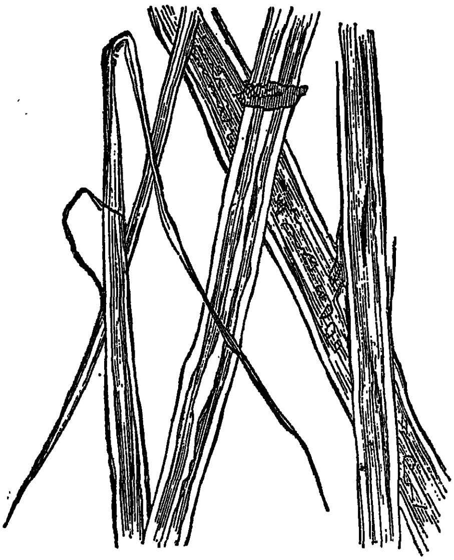
Among the fibres of lesser importance which serve as substitutes for hemp and jute are *Manila hemp, Sunn hemp,* and *Sisal hemp.* The first of these is a tropical fibre, obtained on the Philippine Islands from the leaves of the wild plantain. The fibre is obtained by cutting open the leaf-stalks, which are from six to nine feet in length, and then scraping them free from pulpy matter. It furnishes a very superior rope-making fibre because of its combined lightness and strength, and the finer grades are used for woven goods. The color is yellowish or white, and the white variety has a fine silky lustre. It is shown in Fig. 81.

The Sunn hemp is grown in India, and furnishes a fibre of light-yellowish color and resembles jute, although less lustrous. It is well adapated for cordage and netting.

Sisal hemp (or henequen) is derived from the fleshy leaves of a species of agave grown in Yucatan, British Honduras, and the West Indies and Bahamas. It is used largely in the United States as a substitute for jute in the manufacture of bagging and for cordage, being stronger and lighter than jute.

Ramie fibre (*China-grass*).—The bast fibre from two varieties of *Boehmeria nivea,* known in India as Rhea, in the Malay Archipelago as Ramie, and to Europeans as China-grass, has in recent years attracted very favorable attention from all interested in textile industries. It seems to thrive best in the tropics and requires a great deal of moisture. The bast fibre cannot be removed from the woody stems by the retting process used for flax and hemp, as the intercellular substance is so easily decomposed that the water retting rapidly resolves the fibre into a magma of separated cells. The fibre must be removed from the woody stem while the plants are in the green state, as when dried, even by several hours' exposure to the sun, the fibre becomes difficult to remove from the woody portion. The length of the cells makes it possible to cut the ramie fibre into short lengths and to treat the cleansed fibre like cotton rather than like a long bast fibre. Hence the name "cottonized" ramie which has been applied to that exported from China. With improved methods it is found possible to cleanse it in full lengths, and the fibre is worked like flax rather than with cotton-spinning machinery. The machines for breaking and decorticating the ramie are numerous, but few if any are entirely satisfactory. The properly-prepared fibre edly the most perfect of all the vegetable fibres, and will play a great part in the industries of the future, especially as the plant, being a perennial, can be grown continuously for years, spreading of itself very rapidly and yielding several crops yearly. Its cultivation has been begun successfully in Louisiana and Mississippi, and it can probably be extended through the Southern States and Mexico, where is has also been tried. The iodine and sulphuric acid test shows the ramie fibre to be composed of a pure cellulose, which swells easily and voluminously when treated with ammoniacal solution of cupric oxide. The appearance of the China-grass is shown in Fig. 82.

FIG. 82.



China-grass ($\frac{140}{1}$).

Nettle Fibre.—The bast fibres of the common nettle (*Urtica dioica*) were at one time prior to the development of the cotton industry used extensively in spinning and weaving on the Continent of Europe, the cloth made being known as grass-cloth, the name now given to the product of the China-grass, or ramie. The fibre when cleansed is soft, of good length and strength, and quite lustrous and white. The bast fibres of the linden (*Tilia Europæa*) and of the paper-mulberry-tree (*Broussonetia papyrifera*) are also used, the former for the manufacture of mats in Russia and the latter by the paper-makers of China and Japan.

New Zealand Flax is a fibre obtained from the leaves of *Phormium tenax*, which acquires a length of one to two metres. The fibre as prepared by hand-scraping, the method of the native Maoris, is soft, white, and of silky lustre; as prepared by machinery it is distinctly inferior in character. Its chief value is for rope-making and for coarse textiles. The rope made from this fibre is, however, weakened when wet by sea-water, and therefore must be kept well oiled.

Pineapple Fibre.—The leaves of the several varieties of *Bromelia* yield a fine, nearly colorless, fibre, which is worked, especially in Brazil, for the manufacture of the so-called "silk-grass."

Esparto.—This is a grass, cultivated especially in North Africa and Spain, where ropes and cordage are made from it. Its chief use, however, is in connection with paper-making. (See p. 313.)

Fibre (Coir).—The coarse fibrous covering of the nut of carpeting. The fibre is coarse, stiff, very elastic, round, and smooth like hair. It also has great tenacity, and is well adapted for cordage.

The classification of the vegetable fibres just enumerated has already been made upon the basis of the iodine and sulphuric acid reaction according to Vêtillart. Two groups were thus established, the one composed essentially of unaltered cellulose and the other of lignified cellulose bastose. Other reactions of these two classes of materials are given in the accompanying table from O. Witt:*

Reagent.	Cellulose.	Bastose (compound of cellulose with lignin).
Iodine and sulphuric acid.	Produces blue color.	Produces a yellow or brown color.
Sulphate of aniline with free sulphuric acid.	Indifferent.	Colors deep yellow.
Basic aniline dyes.	Indifferent.	Produces fast colors.
Weak oxidizing agents.	Indifferent.	Rapid disintegration.
Ammoniacal cupric oxide.	Immediate solution.	Swelling up, blue color, and slow solution.

To distinguish the several more important vegetable fibres from each other when admixed, a number of chemical and physical tests have been proposed in addition to the microscopical study of the structural differences already mentioned under the individual fibres.

Thus, according to Kindt's test, the presence of cotton fibre in linen goods can be distinguished, after first removing the size or dressing by thorough boiling with distilled water and drying again, by dipping them from one-half to two minutes, according to the texture of the goods, in concentrated sulphuric acid. They are then well washed with water, rubbed, dipped for a moment in ammonia-water, and dried. The cotton fibre is either dissolved or gelatinized and removed by the rubbing, while the linen fibre remains unchanged or but slightly attacked. By counting the flax fibres remaining for a given superficial area the relative proportion of cotton admixture can be determined.

The different effect of strong caustic potash solution upon cotton and linen fibres is also taken as decisive at times, although the difference is not so marked. Both kinds of fibres shrink in size, the cotton fibres remain whitish or grayish yellow, while the linen fibres are colored deep yellow or orange.

A very characteristic test is that given by Boettger. A piece of the mixed goods frayed out in three sides is first dipped in a one per cent. solution of fuchsine, then taken out, washed in running water until this runs off clear, and dipped in ammonia-water for from one to three minutes. The cotton fibre is quickly decolorized, while the linen fibre remains bright rose-red in color. A test easily applied and satisfactory is the oil test, but it is only applicable to white goods which are free from size. The well-dried sample is dipped into olive oil, and then well pressed. The linen fibres become translucent from the capillary action upon the oil, while the cotton fibres remain white and dull in appearance.

An alcoholic cochineal solution (one part of powdered dyestuff c gested with twenty parts of alcohol of .847 specific gravity for twent four hours) is also recommended by Bolley. Cotton fibres take a cle red color in this solution, while linen fibres are colored violet.

A special test to distinguish the fibre of the *Phormium tenax* (Ne Zealand flax) from linen or hemp is given by Vincent. It is in the u of concentrated nitric acid, which colors the New Zealand flax distinct red, but does not change the other fibres mentioned. (For tests to d tinguish the vegetable fibres as a class from the animal fibres, see p. 302

The use of the microscope, however, is much the most reliable mea of distinguishing the several fibres when occurring in admixtures, as t structural characters are sufficiently distinct to allow of easy recogniti to those possessed of some practice.

INDUSTRIES BASED UPON THE UTILIZATION OF VEGETABLE FIBRES.

The great utilization of these fibres is of course in the manufacture textile fabrics of all grades. Having described the fibres which cons tute the raw materials of these industries, we shall pass the mechani side of their treatment and shall note the chemical processes of bleac ing, dyeing, and color-printing in a later section of the work (see p. 52 after the preparation of natural and artificial dye-colors has been scribed. Other industries based upon utilization of some one or more the vegetable fibres are *Paper-making, Pyroxylin and Gun-cotton, C lodion, Celluloid,* and most recent *Artificial Silk.*

A. PAPER-MAKING.

I. Raw Materials.

1. RAGS.—The first in order of use for paper-making and still most important raw materials for the finer grades of paper are li and cotton rags. As the cellulose of these rags has already underg a process of purifying from the coloring and incrusting matter w which it was first associated in nature in its preparation for ma facture into textile fabrics, it is well adapted for use in paper-maki the basis of which is also a cellulose fibre. Of course, the rags may of all grades of cleanliness. They may be cuttings obtained in the co of manufacture of garments, and being unworn may be relatively cl or they may be fragments of cast-off wearing apparel gathered f waste-heaps and reeking with filth. Indeed, so great is the demand paper-making stock that rags are gathered from Japan, Egypt, and parts of the world, and the bales generally require careful disinfec before they can be used. They may contain sizing and China clay other loading materials, or they may be colored with various dyes metallic salts. Rags considered as paper-making stock must therefor assorted, and for trade purposes they are divided into a large nun

Linen rags are distinctly superior for paper-making to cotton rags, as they make a stronger and more durable paper.

2. Wood Fibre.—Two varieties of pulp for paper-making may be obtained from wood,—viz., mechanically and chemically prepared pulp. Of these, the mechanical wood-pulp obtained by shredding the wood serves for the inferior grades of paper only, as its fibres are too short and do not "felt" or interlace sufficiently. It can therefore be used only as a filling material. Moreover, the resin present resists strongly the action of bleaching agents, and the paper becomes yellowish after a time. This mechanical wood-pulp is known to the trade as "ground wood" and it is obtained by forcing the barked timber cut in short lengths against rapidly revolving stones or grinders, keeping a steady stream of water in contact with it to prevent the development of heat. This fibre, although, as said, very short, is used in enormous quantities to "fill in" in the manufacture of newspapers. No attempt is made to bleach it before making paper, it being merely necessary to incorporate in the stock sufficient coloring matter to overcome the yellowish tinge which otherwise would be evident. On the other hand, what is termed chemical wood-pulp has met with great favor as a very pure and easily obtainable form of cellulose. Chemical pulp is made by three distinct processes, known to the trade as the sulphite, soda, and sulphate processes. In all of these cases the timber is thoroughly denuded of bark and is then split and put through a "hog" or chipper which produces short, coarse heavy chips of about a half-cubic inch in volume. These are screened to obtain a fair degree of uniformity and separate the dust.

In the sulphite process, there are two methods of cooking, known as the "quick cook" and the "slow cook" or Mitscherlich method. The former is now more extensively used by large manufacturers of newspaper and by book paper manufacturers to obtain their raw sulphite stock. The cooking liquor is made from a dolomitic milk of lime saturated with sulphur dioxide, thus forming a mixture of magnesium and calcium bisulphite; or by another method high wooden towers are kept packed with lime-stone while water is allowed to pass down over the stone against a counter current of sulphur dioxide which displaces the carbon dioxide in the limestone. The digestors in most common use are about forty feet high, vertical, with conical bottom, and of boiler steel lined with rough or glazed firebrick set in an alkaline silicate cement. The "cook" lasts six to eight hours, during which time a steam pressure of about 120 pounds is maintained, while the excess of sulphur dioxide developing is frequently allowed to pass off through relief pipes. The pulp when "blown" from the digestor is washed and if for book or writing paper is bleached with chloride of lime, or if for news, wrapping or bag paper is allowed to go to the beating engines unbleached.

In the case of the "slow cook" or Mitscherlich process, a horizontal cylindrical digestor is used having the same kind of lining as above described, but in which the heating is indirect by leaden steam coils lasts about forty hours under a comparatively low pressure. Although the resulting material has had the lignin dissolved from it, it retains the original form of the uncooked chips and though soft must be ground before beating. Cross and Bevan explain the efficacy of the bisulphite processes by saying, "The chief agency is the hydrolytic action of sulphurous acid, aided by the conditions of high temperature and pressure; and the subsidiary agencies are, (1) the prevention of oxidation; (2) the removal from the sphere of action of the soluble products of resolution in combination with the sulphite as a double compound, for it is to the class of aldehydes that we have shown that the non-cellulosic constituents of wood belong; and (3) the removal of a portion of the constituents in combination with the base,—*i.e.*, with expulsion of sulphurous acid."

At the present writing, the large consumption and rapidly diminishing supply of timber adapted to the sulphite process will cause a search for new fibres and an abandonment of the sulphite process in favor of the other chemical processes of treatment.

The *soda process* is used for the working of a variety of woods such as different kinds of long-leaf pine, spruce, hemlock, poplar, bass, etc. The cooking of the wood is comparatively simple. A vertical clyindrical welded digestor is used without any lining. The cooking liquor is generally a caustic soda solution testing about 12° B. The time of digestion is the same as in the "quick cook" sulphite process. The soda takes up the ligneous and resinous portion of the wood, and, when separated from the pulp, is evaporated, incinerated, and recausticized, with a loss of ten to fifteen per cent. in recovery, for cooking purposes. In this country, a large proportion of the soda pulp mills use poplar, spruce, and hemlock for the production of a fine grade of pulp for book paper. Others, using the long-leaf pine, produce a long, coarse fibre for wrapping paper.

The *sulphate process,* in large use in Sweden and Norway and to a small but increasing extent in the United States, produces what is known as a "kraft" pulp, which as the name denotes, has an extremely strong fibre and makes excellent wrapping paper. To obtain this, long-leaf pine is digested in soda digestors, and the process corresponds with the soda process except that before the incineration of the concentrated spent soda or "black liquor" sulphate of soda is introduced, which in the incineration causes the formation of a certain amount of sodium sulphide from the action of the carbon on the sulphate. This mixture of the caustic soda and sodium sulphide in cooking has the proper influence on the chemical changes taking place and produces long strong fibre.

3. ESPARTO.—This grass, mentioned under the vegetable fibres (see p. 309), is of great importance as a paper-making material, particularly in England. The Spanish variety, according to Hugo Müller, contains 48.25 per cent. and the African variety 45.80 per cent. of cellulose, but the yield of bleached fibre obtained in practice probably does not much exceed forty per cent. The fibre is tough and it makes an excellent paper whether used singly or in admixture with other materials.

pulp is largely used. The varieties of straw so utilized are oat, wheat, rye, and barley. Of these, rye is the most suitable on account of its yielding the largest amount of fibre, and next in value is wheat. The amount of cellulose in winter rye is given by Hugo Müller as 47.69 per cent. and in winter wheat as 46.60 per cent., but probably not more than thirty-five per cent. is actually obtained as pulp, much being lost in the treatment on account of the loose aggregation of the cellular tissue. Straw contains more silica than Esparto, and hence requires more soda in the after-treatment to free the cellulose and adapt it for use.

5. JUTE.—The "butts" or "cuttings" rejected by the textile manufacturer are largely used in the manufacture of the common grades of paper. It possesses a large percentage of cellulose (63.76 per cent. in the best fibre and 60.89 per cent. in the "butts"), but it cannot be economically bleached to a white color.

6. MANILA HEMP.—This is very like jute in its adaptability for cheap and colored papers, and as the fibre is a lignified cellulose it requires considerable boiling with soda to prepare it for use.

7. PAPER-MULBERRY.—In China and Japan, where the paper-makers excel the best European workmen in the making of some delicate but strong papers, the material chiefly used is the inner bark of the paper-mulberry-tree (*Broussonetia papyrifera*), the leaves of which can be used in feeding silk-worms. The strength of this paper is due to the fact that in making the pulp the long bast-cells are not broken and torn as in European pulping-machines, but merely softened and separated by beating. In taking up the pulp in the mould the cells are made to lie in one direction, and the paper may be strengthened by taking one or more dips in which the cells are made to lie in other directions. Some gum is added to make the cells of the pulp adhere.

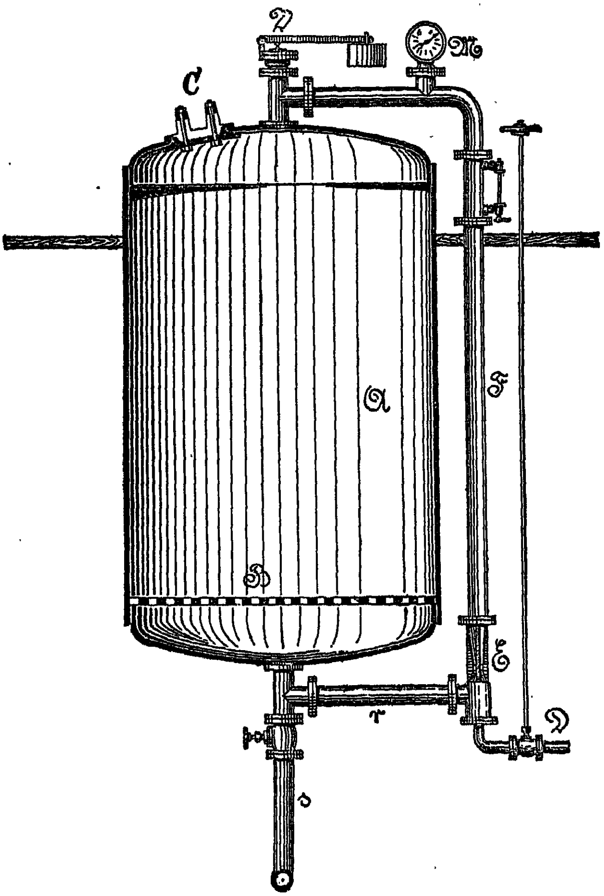
II. Processes of Treatment.

1. MECHANICAL PREPARATION OF THE PAPER-MAKING MATERIAL.—This differs, of course, according as the raw material is composed of rags or other cellulose-containing substance. With rags, a preliminary sorting always takes place, more or less complete according to the make-up of the bales. Numerous commercial designations are in use for these different grades so obtained. We need only speak of white linen, blue or gray linen, white cotton, colored linen or cotton, sacking, half wool, etc. They are then cut into coarse fragments by hand, being passed rapidly over broad knives fixed at a set angle in tables, and all buttons and hard substances removed. A thorough dusting or "thrashing" is now necessary to remove the dust and detachable dirt. This is effected in large wooden boxes with revolving arms. A more thorough cutting now ensues with the aid of revolving knives, followed in most cases by a final and thorough dusting, so as to eliminate as much dirt as possible and save in the amount of boiling necessary as the next operation.

With Esparto a mechanical sorting or "picking" is also the first etc., carefully removed, as these would be difficult to boil and bleach and would give rise to dark-colored specks in the finished paper known as "sheave." Machines for this cleansing of the Esparto are also used quite largely.

The preparation of mechanical and chemical wood-pulp has already been referred to.

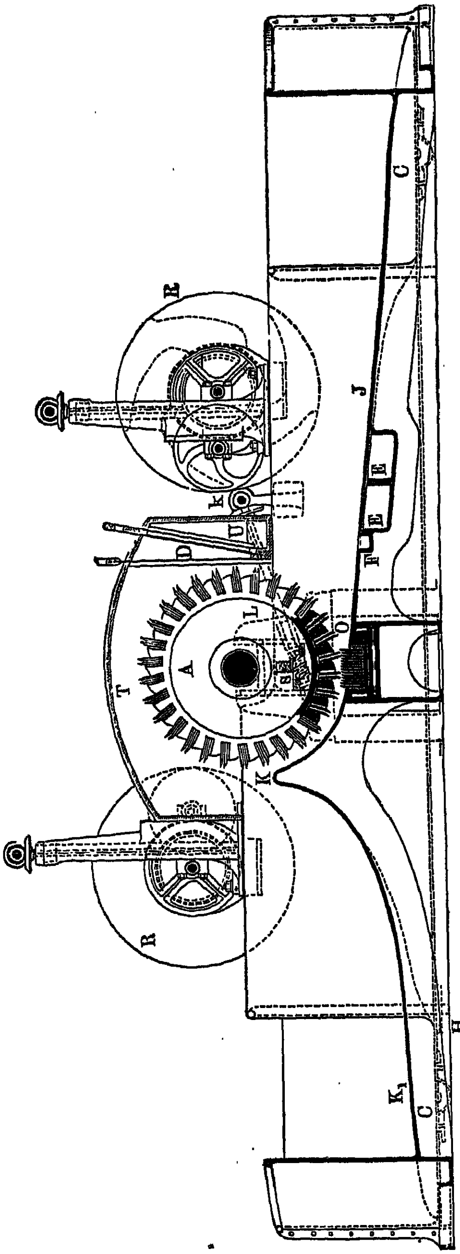
FIG. 83.



2. BOILING.—The boiling of the rags with caustic soda, caustic lime or a mixture of soda ash and lime, which is the next operation, i designed to free them from grease, dirt, and coloring matter. This ma be done either in rotating spherical or cylindrical boilers or in th so-called "vomiting" boilers described later. The boilers are often larg enough to take two tons of rags at a charge. The amount of alka usually ranges from five to ten per cent. on the weight of the rag Soda is preferred by many paper-makers to lime on account of th greater solubility of the compounds it forms, although both are in ge

the quality of rags, the alkali employed, and the pressure. The use of high pressure is to be avoided as far as possible, as it may result in fixing the dirt and coloring matter instead of dissolving them. A pressure of from three to four atmospheres is commonly employed. After the pressure has been allowed to fall, the liquor collected at the bottom of the boiler is drawn off and the water run in to give the rags a slight preliminary washing. The charge is then drawn off.

FIG. 84.



In the case of Esparto, the "vomiting" boiler or other form of apparatus for keeping up a continuous circulation of the liquor is used. A form of boiler in which this circulation is kept up by the use of a steam injector is shown in Fig. 83. The grass is put in through the man-hole *C* and rests upon the false bottom *B*. Circulation is set up by the steam from the pipe *D* passing through the injector *E* and drawing the liquor through the small pipe *r*. In order that this circulation may proceed uniformly, it is necessary that the steam shall enter at a pressure one atmosphere higher than the pressure existing in the boiler. A manometer, *M*, shows the pressure, and a safety-valve, *V*, allows of the adjustment of the necessary conditions. The contents of the boiler are discharged through *s* at the end of the operation. The quantity of soda necessary depends upon the nature of the grass, Spanish requiring less than African, and the pressure employed varies from five to forty-five pounds per square inch.

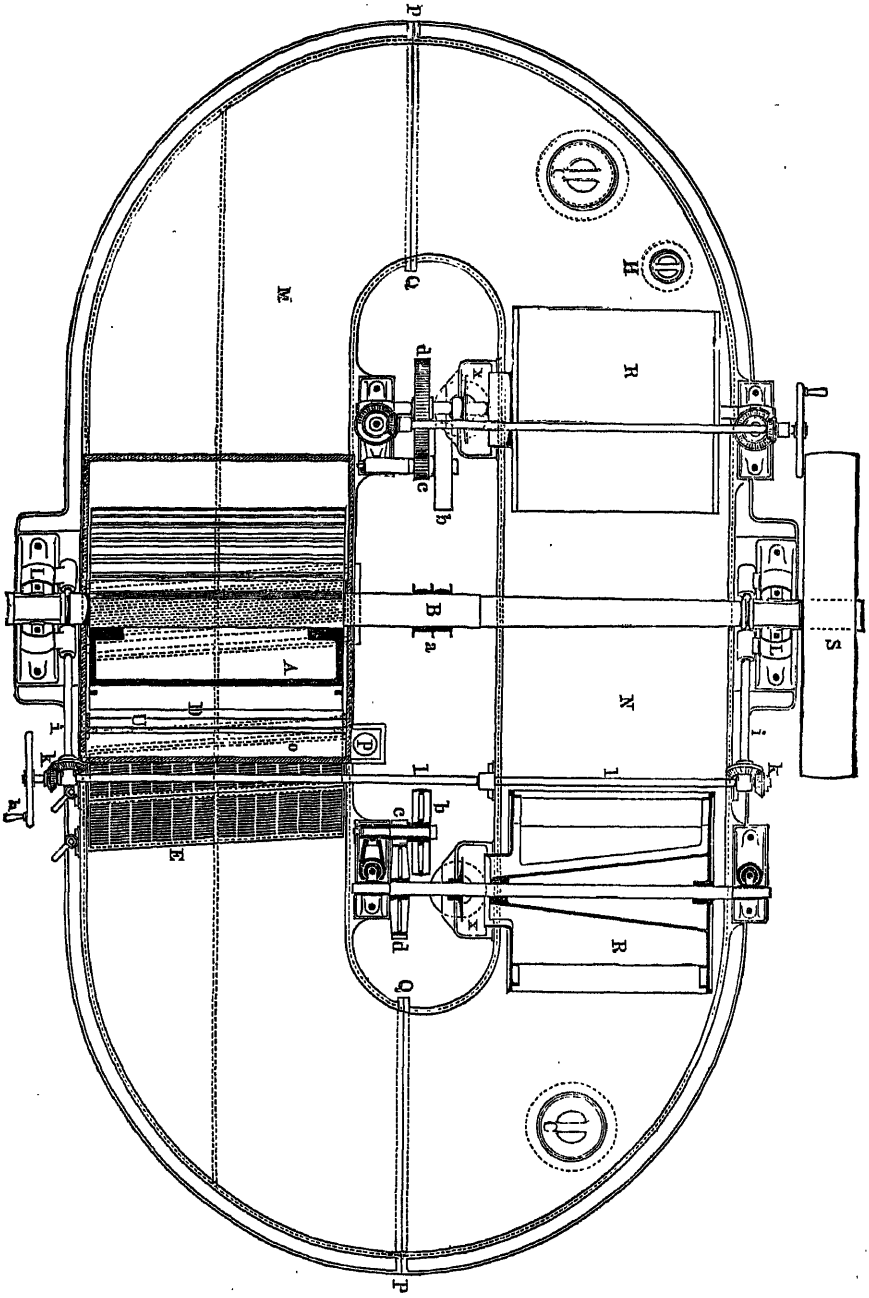
erally given to this machine as well as to the similar one in which the beating or mixing is done. The hollander is an oval iron tube, from ten to twenty feet long, four to six broad, and about three feet high, divided for two-thirds or more of its length by an upright partition known as the "mid-feather." The details of its construction may be seen from Figs. 84 and 85. The roll *A* carries upon its circumference a number of steel knives and revolves on one side of the "mid-feather," or longitudinal division *Q Q* (Fig. 85). The floor on this side is raised in such a way as to bring the pulp well under the roll, as shown by the line *J O K* (Fig. 84). Immediately under the roll is the "bed-plate," shown at *O*, and provided with knives similar to those in the roll *A*, but set with their edges in the opposite direction. The distance between the roll and the bed-plate can be varied at will by means of the hand-wheel *h* and the mechanism shown at *k* and *i* (Fig. 85). After passing between the roll and the bed-plate, the pulp flows down the "back-fall" *K K*, and finds its way around to the other side of the mid-feather. On the inclined part of the floor and immediately in front of the bed-plate a small depression is made at *E*, covered with an iron grating, for the purpose of catching buttons, small pieces of stone, and other foreign substances that may have found their way into the rags or other paper stock. The dirty water from the rags is removed by the "drum-washers" *R R*. The ends of the drums are of wood, and the circumference is covered with fine copper or brass wire-cloth. The wash-water passes through the wire-cloth into the compartment shown in *R*, and passing towards the narrower end of the inner conical tub, flows out through the side of the drum into a trough placed to receive it.

In washing the rags in this machine, the tub is partly filled wit water, the rags from the boiler dumped in, and the operation begun The action of the roll thoroughly mixes pulp and water and sweeps th rags up the incline and over the back-fall *K*. The dirty water the passes away through the drum-washer, the supply of pure water bein so regulated as to keep the level constant. When the water begins t run off clear the supply is stopped, the washer still being kept i action. As the level falls, the drum is lowered by means of the handle *h* When sufficiently drained, the pulp is discharged through the valve *C C* in the bottom of the washer. It is now ready to be bleached. Thi may be done in the washer itself or in separate engines called "potchers.' If done in the washer, a solution of bleaching-powder is run in afte the withdrawal of the wash-water and the action of the roll continue

Esparto is generally washed in exactly the same way as that jus described for rags, but in some mills the grass is washed in a serie of connected lixiviating tanks like those used in alkali-works. Pur water flows in at one end, passes through fresh lots of grass in succe sion, and issues at the farther end highly charged with the soluble pro ucts of the grass. The washed and broken pulp now goes by the nam of "half-stuff."

4. Bleaching.—This is done with the aid of chlorine or a solutio

FIG. 85.



tions, as chlorine is liable to form difficultly removable compounds, and it also tends to attack and weaken the fibre of the pulp. When chlorine is used, 2.5 to 5 kilos. of salt are taken as needed for 100 kilos. of "half-stuff."

The solution of calcium hypochlorite must be used perfectly clear and free from undissolved hydroxide or carbonate. A solution of 6° Twaddle, which contains about half a pound of bleaching-powder to the gallon, is commonly used. An addition of hydrochloric or sulphuric acid to the bleaching-liquor is sometimes made, but this must be done with care so as not to liberate chlorine instead of hypochlorous acid. This danger from free chlorine is greater when highly lignified fibres, such as wood or jute, are used. The bleaching is often effected by combining a preliminary treatment in the "potcher" or washer with a subsequent prolonged steeping in tanks. A process has been recently proposed by Professor Lunge involving the use of acetic acid. The quantity required is very small, as during the process of bleaching it becomes regenerated. Any free lime in the solution is first nearly neutralized with a cheaper acid, such as hydrochloric or sulphuric acid, followed by the addition of the acetic acid. The process is said by Cross and Bevan to give excellent results with high-class material, such as the best cotton and linen rags, but is not to be recommended for materials like straw or Esparto.

A process invented by Thompson is also said to be very effective for the bleaching of rags. It consists in saturating the materials with a weak solution of bleaching-powder and then exposing them to the action of carbonic acid gas. The bleaching action is thus made very rapid and effective.

One of the most recent innovations in bleaching is the application of electricity in this connection. The earliest process that attracted much attention was that of M. Hermite. It is thus described by Cross and Bevan: * "This process is based upon the electrolysis of a solution of magnesium chloride, this salt having been found to give the most economical results. The solution, at a strength of about 2.5 per cent. of the anhydrous salt ($MgCl_2$), is electrolyzed until it contains the equivalent of about three grammes of chlorine per litre. This solution is then run into the 'potcher' containing the pulp to be bleached; a continuous stream is then kept up, the excess being removed by means of a drum-washer. This excess, which, after being in contact with the pulp in the engine, is more or less deprived of its bleaching properties, is then returned to the electrolyzing-vat, where it is again brought up to normal strength. It is claimed that the bleaching effect is much stronger than that of the corresponding amount of calcium hypochlorite solution. Moreover, the bleaching is much more rapid and the loss of weight which the substances undergo is less for equal degrees of whiteness obtained.' In this country several successful electrolytic bleaching processes have been introduced in connection with the paper and pulp industry, such as the Carmichael electrolytic process and the Whiting electrolytic process, both extensively used.

The removal of any excess of chlorine or bleaching-liquor must now be looked to. This is done either by careful washing or by the use of an "antichlor." The first method has the advantage of not only removing the bleach but also of the chloride of calcium which has been formed from it. It, however, takes some time and consumes a large amount of water. Much more general is the use of an "antichlor." The commonest of these is sodium thiosulphate (or hyposulphite, as it is commonly called). This is ordinarily decomposed according to the reaction $2(Ca(ClO)_2) + Na_2S_2O_3 + H_2O = 2CaSO_4 + 2HCl + 2NaCl$, but when the solutions are very dilute, sodium tetrathionate, $Na_2S_4O_6$, and caustic soda and lime are formed. For the first equation two hundred and forty-eight parts of commercial thiosulphate are required to neutralize four hundred and nine parts of bleaching-powder of thirty-five per cent. available chlorine strength. The various sulphites are also in use as antichlors, sodium sulphite being the most important. A cheap antichlor is also made by boiling together lime and sulphur, the resultant calcium sulphide solution containing a mixture of calcium thiosulphate and calcium pentasulphide. This last-mentioned preparation is, however, objectionable on account of the free sulphur formed, as this affects the pulp injuriously. Whatever antichlor is used, an excess should be avoided, as it may act upon the color or size added subsequently. The antichlor should therefore be added in successive small portions, and any hypochlorite solution still remaining be tested for from time to time with iodide of starch paper, which will be turned blue as long as hypochlorite remains.

5. BEATING.—The bleached pulp, or "half-stuff," is not yet in condition for making an even paper, as the fibre has not been sufficiently disintegrated. This is now effected in the beating-engine, which is a hollander very similar to the breaker already illustrated, except that the roll carries more knives and it is usually let down much nearer the bed-plate. The half-stuff is furnished in successive portions to the beater previously partially filled with water, each successive portion being allowed to mix thoroughly with the water before another lot is added. This is continued until the mass is so thick that it will only just turn round under the action of the roll. The operation of beating is designed to be a more complete breaking or tearing apart of the fibres rather than a cutting, as this latter result would interfere with the felting of the fibres so necessary in paper-making. Cotton and linen rags naturally take longer than most other paper-making material, taking often as much as ten hours; wood-pulp requires to be very gently and slowly beaten, so that it requires some six hours; while Esparto is sufficiently disintegrated in from two to four hours. In making the finer grades of paper, the roller bars or knives instead of being made of steel are made of bronze, so that contamination with oxide of iron is avoided.

cone, fitted with knives and revolving in an iron box of corresponding shape, and also fitted with knives set at an angle. In the Kingsland engine and the Gould engine a circular plate furnished with knives revolves against one or more stationary plates similarly fitted, somewhat after the manner of millstones. The half-stuff is even more thoroughly disintegrated in these beaters than in the ordinary forms.

6. LOADING, SIZING, COLORING, ETC.—Except in the very finest papers, some mineral loading material is incorporated with the pulp when in the beater. This is, of course, in the main for cheapening purposes, but also serves the useful purpose of filling the pores of the paper and enabling it to take a better surface in the subsequent operations of calendering. Such loading materials are China clay, or kaolin, sulphate of lime, or "pearl hardening," barium sulphate, precipitated chalk, bauxite, precipitated magnesia, and magnesium silicate, or "agalite." The amount added varies from two or three per cent. to twenty per cent., or in rare cases even more.

All papers except blotting-papers have also to be sized. This is for the purpose of filling the pores with some material that will, to some degree at least, resist the action of water. Thus, all writing-papers, and in general printing-papers also, are sized to prevent the ink applied to them from running. This is done either by what is termed "engine-sizing"—that is, in the beating-engine itself—or by "tub-sizing," when the paper as it goes through the Fourdrinier machine (see below) passes through a tub of gelatine size and takes a layer of the same on either surface.

In "engine-sizing" a rosin soap is first added to the pulp in the beater, and when this is thoroughly incorporated a solution of alum is run in, forming, as it has been generally supposed, a resinate of alumina, which is water resistant when dried. Wurster * claims to have shown, however, that the sizing in this case is not due to the formation of a resinate of alumina but to a separation of free resin, and in this result he has been supported by Conradin.†

With the resin soap is also added some starch, and the quantity of mixed rosin and starch is usually from three to four pounds to the one hundred pounds of pulp.

The pulp although bleached is rarely white enough to produce a clear white paper, and the yellowish tint requires to be neutralized by the addition of small quantities of blue and pink coloring material Ultramarine, smalt, and aniline-blue are used for the first color, and either cochineal, Brazil-wood, or aniline-red for the second. The paper may be colored throughout any desired color by using rags previously dyed, or by adding to the bleached pulp in the beater the necessary dyes or pigments.

7. MANUFACTURE OF PAPER FROM THE PULP.—We have to consider here two different products,—viz., hand-made paper and machine-made paper. The former is made by taking in the mould upon the "deckel,'

water to make a sheet of paper. As the water drains through the wire-cloth and leaves the fibres spread out upon the surface, the felting operation is assisted by shaking the frame gently from side to side. The mould with the sheet of paper is then turned over, and the sheet thus transferred from the wire to a piece of felt. When a number of sheets have been thus prepared, they are piled up with alternate sheets of felt and the whole subjected to strong pressure to expel water. They are then sized if required by dipping them into a solution of gelatine, again pressed, and hung up to dry. When dry they are calendered or pressed between hot metal rolls.

Machine-made paper is made on what is universally known as the Fourdrinier machine, of which an improved form, as manufactured by the Pusey and Jones Company, of Wilmington, Delaware, is shown in Fig. 86. We cannot here describe the various mechanical details of this machine, but may summarize by saying that it consists of an endless mould of wire-cloth on to which the prepared pulp flows from the “stuff-chest” through a “regulating-box” and over the “sand-table” and the “screen.” From the deckel wire it now passes through a series of rolls, at first covered with felt and later of smooth heated metal known as the “dandy-roll,” the “couch-rolls,” the “press-rolls,” the “drying cylinders,” and, finally, the “calenders.” The action of the machine is a continuous one, and the speed of the Fourdrinier is from sixty to two hundred and forty feet per minute,—the latter for cheap newspaper, the former for the best paper requiring the most care.

What is known as “tub-sizing” is applied to many machine-made papers in the course of their passage through the Fourdrinier. A filtered solution of gelatine is used to which about twenty per cent. of its weight of alum has been added. A certain quantity of soap is also often added, a white soap free from resin being used.

Instead of the Fourdrinier, what are termed cylinder-machines are also in use, in which a large drum or cylinder covered with wire-cloth revolves in the vat containing the pulp. As it revolves the fibres attach themselves to the wire and the water is sucked through the meshes by a partial vacuum within. The sheet of paper thus formed is taken on to an endless felt passing over a couch-roll, which revolves in contact with the hollow drum, and thence passes to a large drying cylinder heated by steam. Paper made on such a machine is weaker, however, than that made on the Fourdrinier, because it has not been found possible to give the shaking motion to the cylinder necessary to produce the felting of the fibres.

III. Products.

The products are almost without number, and vary not only in different countries, but even locally from time to time as different mills change their production. We will therefore attempt only a general classification of the main varieties.

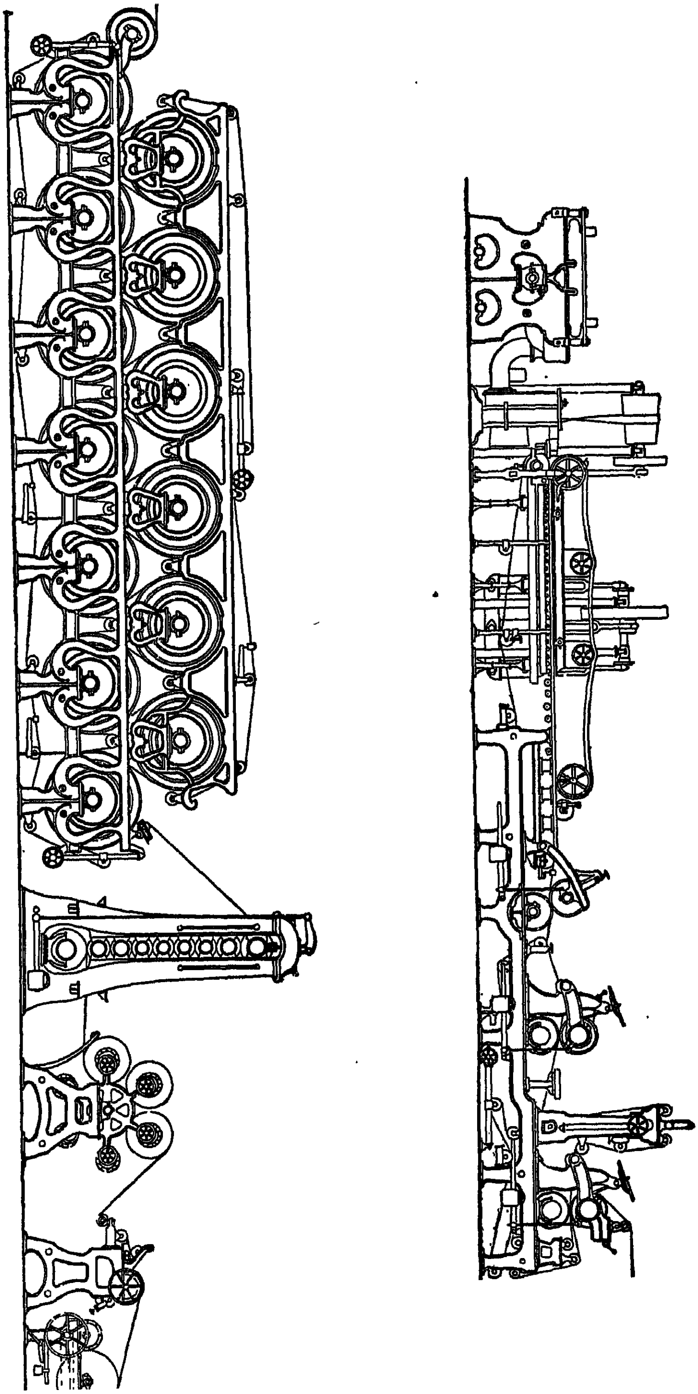


FIG. 86.

any loading or filling material, and therefore is capable of easily and quickly taking up water or other liquids. It may be white, gray, or colored to any shade by the addition of the proper dyes. Tissue-papers, which as the name indicates are the thinnest of all papers, are made from very strong fibres, such as that of hemp-bagging and cotton canvas, and on machines somewhat different from the ordinary Fourdrinier.

2. WRAPPING-PAPERS.—These are partially-sized papers of coarse materials, such as straw, jute, Manila hemp, common rags, etc. They may show the natural color of the materials or may be colored, as in the case of the blue wrapping-paper commonly used for packing sugar. A more strongly sized and calendered wrapping-paper is made for use with linens and other textile goods.

3. PRINTING-PAPERS.—These are white papers, generally with filling and sizing material, although some special grades are given a smooth surface by calendering instead of sizing. The cheaper grades for newspaper use are frequently largely adulterated with filling material, and mechanical wood-pulp is also largely used in their manufacture.

4. WRITING-PAPERS.—These are thoroughly-sized papers, for which the best materials are generally used, linen rags alone being taken for the finer grades.

5. CARDBOARD, PASTEBOARD, AND PAPIER-MACHÉ.—Pasteboard may be made by pressing a number of sheets of freshly-formed unsized paper in powerful presses, or cementing them together by the use of glue or other cementing material, and then pressing the mass so formed. Cardboard is made direct upon machines adapted for heavy layers of pulp and pressed and calendered like similar grades of ordinary paper. Papier-maché is made chiefly from old paper by boiling to a pulp with water, pressing, mixing with glue or starch paste, and then pressing in moulds previously oiled. After drying, the articles are soaked with linseed oil and then dried at higher temperature.

PARCHMENT-PAPER.—If a pure unsized paper be dipped in sulphuric acid of 60° B. a portion of the cellulose is changed into *amyloid* (hydrocellulose, according to Girard), which forms a gelatinous coating over the swollen fibres and effects in some degree a sizing of them. The paper is made hereby translucent and parchment-like, the strength is increased from three to fourfold, and the specific gravity by perhaps forty per cent. For the manufacture of this parchment-paper the long-fibred, unfilled paper is to be chosen. After treatment the paper is quickly washed, first with water, then with weak ammonia, and again with water.

In place of sulphuric acid we have the treatment with ammoniacal cuprous oxide solution or zinc chloride. The former reagent furnishes the *Willesden ware,* which always retains the light blue-green color; the latter yields the valuable product known as *indurated* or *hard fibre.* In preparing this latter material the paper, which is either unsized or prepared with a rosin size and then nearly dried, is dipped or run while in the roll through a bath of zinc chloride of about 65° to 70° B. kept then dried in a heated room, given a coating of paraffin oil, and calendered. The material so obtained is very strong, tough, and can be washed.

6. Side-products.—*Recovered Soda.*—The alkaline liquors in which rags, esparto, and other paper-making material have been boiled were at one time run off as waste products. This is no longer done in properly conducted mills, as the alkali used can be recovered in the form of carbonate by evaporation of the waste-liquor and ignition of the residues, and this carbonate can then be causticized and fitted for renewed use. The soda during the process of boiling with the paper-making materials takes up a large amount of non-cellulose fibre constituents, such as resin, coloring matter, and silica. These on evaporation and ignition become either carbonate or silicate. It will not be possible for us here to describe the forms of evaporators in use for this soda recovery. One of the best-known evaporators is that of Porion, used largely in England on the Continent. For a description of this and other forms, see Cross and Bevan's "Text-book of Paper-Making," p. 182. In this country the Swenson form of evaporator has been largely used for the "black liquor" of the soda pulp works.

The recovered soda consists essentially of carbonate of soda, togethe with a certain amount of silicate of soda if the liquor had been obtaine by boiling straw or esparto. The causticizing is done in the usual wa with caustic lime and the clear alkali decanted from the separated calcium carbonate, which is then thoroughly washed.

IV. Analytical Tests and Methods.

1. Determination of the Nature of the Fibre.—This may be don
in part, if not wholly, by either of two methods,—viz., by the aid of th
microscope or by the use of chemical tests for individuals fibres. Th
fibre is always torn or cut and often somewhat attacked. By some pra
tice, however, it is possible to distinguish between cotton and linen o
to identify both in admixture. Wood and straw can also be identifie
In making these tests, it is best to take strips of the paper in questio
and boil them in succession with alcoholic potash solution, with wate
with two per cent. hydrochloric acid, and then again with water. I
they are now shaken up with a little warm water, we obtain a fine magm
of fibres, which when mixed with an equal volume of glycerine is we
adapted for examination under the microscope. The distinctive cha
acters of some of the chief paper-making materials as seen under t
microscope may be thus summarized, according to Cross and Bevan:
Cotton,—flat, ribbon-like fibres, frequently twisted upon themselve
The ends generally appear laminated. *Linen*,—cylindrical fibres, simil
to the typical bast fibre. The ends are frequently drawn out into nume
ous fibrillæ. *Esparto*,—the pulp consists of a complex of bast fibres a
epidermal cells. The most characteristic feature of esparto pulp is t
of a number of fine hairs which line the inner surface of t

The presence of these hairs may be taken as conclusive evidence of the presence of esparto. *Straw,*—this closely resembles esparto pulp in microscopical features, except that the hairs are absent. On the other hand, a number of flat oval cells are always present in paper made from straw. *Chemical wood-pulp,*—flat ribbon-like fibres, showing unbroken ends. The presence of pitted vessels is eminently characteristic of pulp prepared from pine-wood. *Mechanical wood-pulp* may be recognized by the peculiar configuration of the torn ends of the fibres and from the fact that the fibres are rarely separated, but generally more or less agglomerated. The pitted vessels of pine-wood also show, and usually more distinctly than in chemical wood-pulp.

The chemical reagent most useful in testing paper-pulp is aniline sulphate. With most of the fibres which consist of cellulose simply it gives no reaction. Straw, esparto, and mechanical wood-pulp can, however, be identified by its means. Thus, where paper containing straw or esparto is treated for some time with a boiling one per cent. solution of aniline sulphate, a pink color is produced. Esparto gives the reaction with greater intensity than straw. Mechanical wood-pulp treated with this solution develops even in the cold a deep-yellow color. According to Bolley,* the moistening of paper containing mechanical wood-pulp with nitric acid will give the same result, and a naphthylamine salt produces a deeper orange color. According to Wiesner, phloroglucin is also a delicate reagent for wood fibre in paper. A drop of dilute solution of phloroglucin put upon the paper and this followed by moistening with hydrochloric acid develops an intensely red color. Fuchsine also colors wood fibre red, but has no effect upon paper from linen fibre alone.

M. Wurster in "Journ. de Pharm. et Chemie" has extended Wiesner's observation on phloroglucin to a number of the phenols, finding them as a class to serve as reagents for distinguishing between wood-pulp and other cellulose. The results are:

Reagent.	Wood-pulp.	Cellulose paper.
Orcin	Dark red.	No color.
Resorcin	Deep green.	Violet.
Pyrogallol	Blue-green	Violet.
Phenol	Yellow-green.	Violet.
Phloroglucin	Blue-violet.	No color.

According to Godeffroy and Coulon, mechanical wood-pulp from pine-wood possesses the property, after it has been extracted with water, alcohol, and ether, of reducing gold solutions on boiling. This property is not possessed by wood-pulp prepared by the caustic soda or sulphite processes, after similar extraction with solvents, nor by the pulp prepared from linen or cotton fibres. This property depends upon the fact that in mechanical wood-pulp ligno-cellulose remains, and to this composition is due the reducing power upon gold solutions. This ligno-cellulose is destroyed in the preparation of chemical wood-pulp, and does not exist at all in the linen or cotton fibre. It has been found that on solvents and dried at 100° C., will reduce fourteen thousand two hundred and eighty-five grammes of gold. It is thus made possible by weighing the reduced gold to estimate the amount of mechanical wood entering into the composition of the paper. For details of the analytical method based upon this gold reaction, see Bolley's "Handbuch der Technisch-Chem. Unterschungen," 6te Auf., p. 1007.

2. Determination of the Nature of Loading Materials.—The total amount of the mineral loading material is determined by igniting a weighed quantity of the paper until the ash is white or grayish and then accurately weighing this. The ash from a paper containing the China clay is insoluble in boiling dilute hydrochloric acid; that from paper containing calcium sulphate is soluble, and deposits on standing needle-shaped crystals of gypsum easily recognizable by chemical tests.

3. Determination as to Nature of the Sizing Materials.—The iodine test serves to indicate the use of starch in the size, as it produces the well-known blue color. Extraction of the paper with alcohol containing a few drops of acetic acid serves to show the resin used in the size. The alcohol, after cooling, is poured into four or five times its bulk of water, when the resin separates, producing cloudiness or turbidity. Or, after extraction, the alcohol is evaporated, leaving the resin capable of being identified by its properties. Notable quantities of alumina in the ash also point to the use of resinate of alumina as sizing material. According to Wurster, if between two sheets of paper which have been sized with resin is pressed paper moistened with tetramethyl paraphenylen-diamine solution, a bluish-violet color is produced, while paper free from resin is not affected. Boiling of the paper sample with distilled water, filtering, and adding a few drops of tannic acid solution will serve to show the presence of gelatine sizing. If present, a whit curdy precipitate is formed on the addition of the tannic acid.

4. Determination of the Nature of the Coloring Material.—In deciding as to the presence of coloring matter, we must bear in mind the reactions of the commoner pigments used. Ultramarine is destroyed and decolorized on addition of acids; Prussian blue is decolorized by heating with alkalies; indigo is decomposed by heating with chlorin or nitric acid; smalt withstands the action of both acids and alkalie and remains in the ash as a blue glass; the aniline colors are capable o extraction with alcohol as solvent.

B. GUN-COTTON, PYROXYLINE, COLLODION AND CELLULOID.

I. Raw Materials.

The basis of these preparations is the class of nitrates formed from cellulose by the action of nitric acid, either taken singly or admixed wit strong sulphuric acid, or as developed by the action of sulphuric aci upon a nitrate. Using the doubled formula $C_{12}H_{20}O_{10}$, we may note th following five stages of nitration:

mixture of the strongest nitric acid (specific gravity 1.52) with two or three parts of concentrated sulphuric acid, in which the cotton is immersed for twenty-four hours at a temperature not exceeding 10° C. (56° F.). The hexanitrate so prepared is insoluble in alcohol, ether, or a mixture of both, in glacial acetic acid, or in methyl alcohol. Acetone dissolves it very slowly. According to Eder, mixtures of nitre and sulphuric acid do not give this nitrate. It contains 14.14 per cent. nitrogen.

Pentanitrate, $C_{12}H_{15}O_5(NO_3)_5$. It is difficult, if not impossible, to prepare this nitrate in a state of purity by the direct action of the acid upon cellulose. The best method (that of Eder) is to dissolve gun-cotton (hexanitrate) in nitric acid at about 80° to 90° C. (176° to 194° F.) and then precipitate as pentanitrate by concentrated sulphuric acid after cooling to 0° C.; after mixing with a larger volume of water and washing the precipitate with water and then with alcohol, it is dissolved in ether-alcohol and again precipitated with water, when it is obtained pure. This nitrate is insoluble in alcohol, but dissolves readily in ether-alcohol and slightly in acetic acid. It contains 12.75 per cent. nitrogen. Strong potash solution converts this nitrate into the dinitrate.

The *tetranitrate* and *trinitrate* (collodion pyroxyline) are generally formed together when cellulose is treated with a more dilute nitric acid and at a higher temperature and for a much shorter time (thirteen to twenty minutes) than in the formation of the hexanitrate. It is not possible to separate them, as they are soluble to the same extent in ether-alcohol, acetic ether, acetic acid, or wood-spirit. On treatment with concentrated nitric acid and sulphuric acids, both the tri- and tetranitrates are converted into pentanitrate and hexanitrate. Potash and ammonia convert them into dinitrate.

The *dinitrate,* $C_{12}H_{18}O_8(NO_3)_2$, always results as the final product of the action of alkalies on the other nitrates, and also from the action of hot, somewhat dilute nitric acid upon cellulose. The dinitrate is very soluble in ether-alcohol, acetic ether, and in absolute alcohol.

The chief raw material for the manufacture of these nitrates at present is the waste from cotton-spinning, which has already been freed from the impurities of the raw cotton. It is first picked clean by hand from admixture with foreign matter and then torn and opened up by machinery so as to fit it for easy action of the nitrating acids. It is then treated for a few minutes with boiling potash solution, thoroughly washed, and dried by steam. For the manufacture of celluloid a specially prepared and perfectly pure tissue-paper is now used, which is torn into shreds by machinery preparatory to the nitrating.

II. Processes of Manufacture.

1. Gun-cotton.—The following is the procedure at Waltham Abbey, where gun-cotton is made for the English government under Sir F. Abel's improved method. A mixture of fifty-five parts of nitric acid

nitrating mixture is placed in cast-iron vessels, cooled from without by flowing water, and the cotton immersed. It may either remain in these until ready for washing, or may after a brief immersion be transferred to smaller stone-ware vessels, similarly cooled, in which it then remains for twenty-four hours, for the double purpose of completing the nitration, so that the product shall contain a maximum of the highest, or hexanitrate, and of allowing the contents of the jar to cool down perfectly. The nitrated cotton is then centrifugated, stirred up thoroughly with cold water, again centrifugated, and then washed systematically with warm water to which some soda has been added. The gun-cotton so obtained may either be used in the loose form or, when designed for manufacture into cartridges, is beaten in a hollander after the manner of paper-pulp, and then washed and pressed in the desired forms. The gun-cotton when finished is usually preserved in a moist state, and dried only when needed for use. It, however, does not require to be sharply dried, as with fifteen to twenty per cent. of moisture it can be made to develop its full explosive powers.

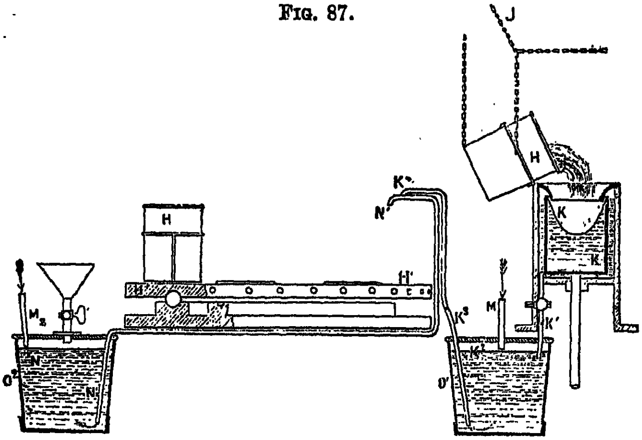
2. PYROXYLINE AND COLLODION.—Pyroxyline of various grades of solubility can be prepared according to the strength of acids used and length of immersion given the cotton. In general, the nitric acid taken is less concentrated than that used for making gun-cotton, and a somewhat higher temperature is employed. Potassium or sodium nitrate is also used along with the sulphuric acid as the nitrating mixture, as the presence of nitrous acid in the nitric acid generated is considered as playing some part in the result. A mixture of twenty parts pulverized potassium nitrate with thirty-one parts of sulphuric acid of 1.835 specific gravity is given as a suitable pyroxyline mixture. After the nitre has entirely dissolved in the sulphuric acid and the mixture has fallen in temperature somewhat below 50° C. the cotton is put in, stirred around thoroughly, and then the vessel left covered for twenty-four hours at a temperature of from 28° to 30° C. The pyroxyline is then washed with cold water until it shows no acid reaction, and finally with boiling water to remove the last traces of potassium sulphate. A similar mixture, using sodium nitrate, is thirty-three parts of sulphuric acid of 1.80 specific gravity, seventeen parts of sodium nitrate, and one-half part cotton.

A special grade of pyroxyline for the manufacture of collodion, put upon the market by the Schering factory in Berlin, is made by immersing cotton for fifteen minutes in a mixture of equal volumes of sulphuric acid of 1.845 specific gravity and nitric acid of 1.40 specific gravity, taken at a temperature of 80° C.

The pyroxyline made from tissue-paper for the celluloid manufacturers is made by taking fifty cubic centimetres of nitric acid of 1.47 specific gravity, one hundred cubic centimetres nitric acid of 1.36 specific gravity, and one hundred cubic centimetres of sulphuric acid of 1.84 specific gravity. In this mixture eighteen grammes of the finely-shredded tissue-paper are immersed at a temperature of 55° C. for one hour. The patentee of celluloid, is shown in the annexed illustration. (See Fig. 87.) The shredded paper is filled into the container *H*, in which has been placed a mixture of strong sulphuric and nitric acids heated to from 26° to 32° C. The mixture having been vigorously stirred by a mechanical stirrer which can be raised and lowered at will, it is allowed to remain at rest for twenty minutes to allow of the completion of the nitration. It is then swung around on the revolving table H^1, caught by a crane from above, and emptied into the centrifugal *K*, which quickly drains off the excess of acid from the mass, the liquid flowing through the pipe K^1 into the reservoir O^1. The container *H* can be filled from this reservoir through the pipe K^3 by the application of air pressure at *M*, as the lid of the acid reservoir is fitted on air-tight. O^2 is a reservoir for fresh acid mixture.

The proportions of ether and alcohol used in dissolving pyroxyline to make collodion solutions vary very greatly. The United States Pharmacopœia prescribes for four grammes of pyroxyline seventy-five cubic centimetres of ether and twenty-five cubic centimetres of alcohol; the British Pharmacopœia takes for one ounce of pyroxyline thirty-six fluidounces of ether and twelve fluidounces of rectified spirit; the German Pharmacopœia takes one part of pyroxyline to twenty-one parts of ether and three parts of alcohol.

FIG. 87.



3. CELLULOID.—The conversion of pyroxyline into celluloid is accomplished by effecting a thorough incorporation with the former of a certain amount of camphor. This may, however, be done in a number of ways, several of which have been carried out in practice. First, it is possible to effect it by heat alone, without the use of any solvent for either the camphor or the pyroxyline. The camphor at the temperature of its fusion becomes a sufficient solvent for the pyroxyline to effect complete physical admixture. This process is essentially that used in this country. The weighed amount of camphor is added to the pyroxyline [illegible] in a partially moist condition some alcohol

mixture may now be put through heated rolls to effect the melting of the camphor and cause it to penetrate and take up the pyroxyline in every part of the mass. It is then put through a heated masticating machine to complete the admixing and make the mass of uniform composition throughout. Coloring matter is added when desired to the materials before the camphor takes up the pyroxyline, so that it may be thoroughly distributed or dissolved as the case may be.

A solution of camphor in either ethyl or methyl alcohol has also been used as the means of converting the pyroxyline into celluloid. This may be either with the aid of heat or, if sufficient of the solvent be used, it may be carried out at ordinary temperatures.

A solution of camphor in ether has also been used in the celluloid factory of Magnus & Co. in Berlin. For fifty parts of pyroxyline are taken twenty-five parts of camphor dissolved in one hundred parts of ether to which five parts of alcohol have been added. The mixture is covered up and stirred from time to time. A gelatinous and glutinous mass results, which must be rolled between calender rolls until it acquires plastic characters. The process is distinctly more dangerous than the others mentioned, as the ether is all allowed to evaporate, and it does not yield anything better in the way of product.

III. Products.

1. GUN-COTTON.—The explosive variety of gun-cotton, whether in the form of loose fibre or as compressed cartridge or paper sheets, cannot be readily told by outward characteristics from untreated cotton. On close examination a slight yellowish tint is recognizable; it is slightly rougher to the touch, and crinkles slightly when pressed; when rubbed it is easily electrified and sticks to the fingers. When lighted it burns quickly without smouldering or leaving any residue. When heated slowly it begins to decompose with evolution of acid fumes, and above 130° C. it explodes. It is therefore necessary to exercise great care in the drying of it, and especially if all traces of acid have not been removed. It is much safer when wet than dry, although it is possible to explode it by concussion when it still contains from fifteen to twenty per cent. of water.

The explosive variety of nitrocellulose is a mixed penta- and hexanitrate and contains from 12.6 to 13.4 per cent. of nitrogen.

Gun-cotton is insoluble in water, alcohol, ether, chloroform, and acetic acid, in dilute acids and alkalies. It is somewhat soluble in acetone and wood-spirit.

Gun-cotton is chiefly used in submarine mines and blasting and for naval torpedoes. The combination of it with nitro-glycerine, known as blasting gelatine, has been referred to under another section. (See p. 85.)

2. PYROXYLINE.—This in most physical characters resembles perfectly the explosive gun-cotton. The most important difference is the ready solubility of this variety of cellulose nitrate in a mixture of alcohol and ether, in which the higher nitrate is insoluble. The ordinary pyroxyline is moreover only slightly explosive. When dissolved in the

3. Collodion.—This is a colorless liquid, which rapidly evaporates on exposure to the air, leaving a transparent film of tetranitrate, or tetra- and trinitrate mixed, insoluble in water and alcohol. It is used as a dressing for wounds under the name of "liquid adhesive plaster," and very largely in photography as a means of covering the photographic plates with a transparent film which shall hold finely divided and distributed the sensitive silver salt.

4. Pyroxyline Varnishes.—In recent years a very important class of metal varnishes or lacquers have been introduced under trade-names, such as Zapon varnish, etc., in which pyroxyline is the basis. This is dissolved in either methyl alcohol, acetone, methyl and amyl acetates, or mixtures of these. Petroleum-naphtha is also added to these solvents to facilitate the drying. These varnishes are of special value for fine metal-work in brass or bronze, as they leave a perfectly transparent and flexible film of pyroxyline, which protects the metal and will not crack or peel when properly applied.

5. Celluloid.—This valuable product of the action of camphor upon pyroxyline is prepared under a great variety of forms, both transparent and opaque, colored uniformly, or mottled and striated in imitation of ivory, coral, amber, tortoise-shell, agate, and other substances. It cannot be caused to explode by heat, friction, or percussion. When brought in contact with flame it burns with a rustling flame, and continues to smoulder after the flame is extinguished, the camphor being distilled off with production of thick smoke, while the nitro-cellulose undergoes incomplete combustion.

Celluloid dissolves in warm, moderately concentrated sulphuric acid, but is carbonized by the strong acid. It is readily soluble in glacial acetic acid, and on diluting the solution with water both camphor and pyroxyline are reprecipitated. It is rapidly soluble in warm, moderately concentrated nitric acid (four volumes of fuming acid to three of water), and is also dissolved with ease by a hot concentrated solution of caustic soda. Ether dissolves out the camphor from celluloid, and wood-spirit behaves similarly. Ether-alcohol (3 : 1) dissolves both the nitro-cellulose and camphor, leaving the coloring and inert matters as a residue. The density of celluloid ranges from 1.310 to 1.393. When heated to 125° C., it becomes plastic and can be moulded into any desired shapes. Separate pieces can also be welded together by simple pressure when at this temperature. The celluloid is easily cemented to wood, leather, etc., by the use of collodion or a solution of shellac and camphor in alcohol.

IV. Analytical Tests and Methods.

Pure hexanitrate of cellulose will keep indefinitely, but the presence of free acid, of lower nitrates, or of fatty and waxy matters renders it more or less unstable, and therefore unsafe. The most important determinations to make are the examination for free acid and for lower nitrates, and the valuation by means of the estimation of NO_2 liberated from any sample.

1. Examination for Free Acid.—This may be detected by treating twenty grammes' weight of the gun-cotton with fifty cubic centimetres of cold water. After twelve hours the water may be pressed out, filtered, and twenty-five cubic centimetres titrated with decinormal caustic alkali. With the remainder of the liquid the nature of the acid, whether sulphuric or nitric, may be ascertained by the usual tests.

2. Examination for Lower Nitrates.—These may be detected if present by treating five grammes of the sample, previously dried at 100° C., with one hundred cubic centimetres of a mixture of three parts of ether and one of alcohol. The mixture is shaken frequently during twelve hours, and then rapidly filtered through loosely-packed glass-wool, the filtrate evaporated at a gentle heat, and the residue weighed.

3. Examination for Unaltered Cellulose.—This may be estimated by treating the gun-cotton left undissolved by the ether-alcohol with acetic ether, which dissolves the hexanitrate and leaves the unchanged cotton. An alternative plan is to prepare a solution of sodium stannite by adding caustic soda to a solution of stannous chloride until the precipitate at first formed is just redissolved. This solution when boiled with gun-cotton dissolves the cellulose nitrates without affecting the unchanged cellulose. Sodium sulphide is also used for the same purpose.

4. Valuation by Determination of NO_2.—The nitrogen peroxide contained in gun-cotton and similar nitrated products is frequently determined by the aid of the reaction of sulphuric acid and mercury upon the nitrates as carried out in a Lunge's nitrometer. This is a burette provided at one end with stopcock and funnel-tube and narrowed at the other end, which is connected by a stout piece of rubber tubing with a simple graduated burette-tube. The burette with the stopcock is filled with mercury through the rubber connection with the other tube and the stopcock closed. .35 gramme of gun-cotton, dissolved in five cubic centimetres of concentrated sulphuric acid, are then put into the funnel-tube, and by opening the stopcock and lowering slightly the connecting burette are drawn into the stoppered tube, washed out of the funnel with a little additional pure sulphuric acid, and the stopcock closed. The tube is then shaken vigorously until the reaction is complete and the volume of gas no longer increases. It is then allowed to attain constant temperature and the volume read off with correction for temperature and pressure. Allen (Commercial Organic Analysis, 2d ed., vol. i, p. 328) recommends that the volume be compared with that yielded by a standard sample or a nitre solution.

ARTIFICIAL SILK.

I. Raw Materials.

The manufacture of an artificial silk (with the exception of one process, not now commercially followed—that using gelatine) starts with cellulose, usually in the form of the cotton fibre. Three processes have been developed, until at present they have assumed what may be product of great value and one that has created a field for itself in numerous special utilizations. While the raw material is primarily cellulose in all cases, in two of the processes it is first changed into a chemical derivative of cellulose which is afterwards decomposed in the process of manufacture.

1. NITROCELLULOSE OR CHARDONNET PROCESS.—The starting-point of this process, the earliest of the commercial processes (1888) is a pure cellulose, usually cotton fibre, cleansed both mechanically and then by treatment with weak alkali solutions. This is then carded so as to open it up and nitrated, as already described in the manufacture of pyroxyline or soluble cotton. The washing of the nitrocellulose must be very thorough, so that every trace of acid is removed. When washed the wet nitrocellulose is pressed in hydraulic presses until the per cent. of water retained is reduced to thirty-six per cent., which amount remains in it until after the spinning. The solution of this is then effected in a mixture of equal parts of ninety-five per cent. alcohol and ether, using one hundred litres of solvent for twenty-two kilos. of nitrocellulose, reckoned on dry weight. This solution takes place in horizontal revolving iron cylinders lined with tin and provided with mechanical agitation. From fifteen to twenty hours slow continued revolution of the cylinder is usually required and the solution, although appearing perfectly clear, is nevertheless filtered to remove any imperfectly dissolved nitrocellulose. The solution after filtration is stored in large containers to "ripen," so that it may be suited for the spinning process.

2. THE CUPRAMMONIUM PROCESS.—The raw material is here also a purified cellulose. Cotton is treated with an alkaline lye to bring it into a pure condition easily soluble in the solvent, which in this case is a copper-oxide-ammonia solution. Pauly, the first patentee of artificial silk of this kind, prepared his solution by precipitating cupric hydroxide from copper sulphate solution with ammonia in required amount, washing the same and then dissolving it in aqua ammonia to clear solution, of which one litre contained from ten to fifteen grammes of copper. This is then allowed to act on the moist purified cellulose in a hollander, in which the cellulose solution is rapidly effected. Even after perfect solution seems to have been effected, this must be filtered in order to obtain that uniform solution needed for the spinning operation. A later process (that of Bronnert, Fremery and Urban) prepares the cuprammonium solution by the action of strong ammonia water on metallic copper in the presence of a current of air. If the temperature is kept down to about 5° C. the ammonia in the presence of air has a rapid solvent action on the copper, and solutions containing eight and ten per cent. of copper are obtained.

3. THE VISCOSE PROCESS.—Cross, Bevan, and Beadle in 1892 discovered the method of preparing a water-soluble cellulose xanthogenate by the reaction of carbon disulphide upon alkali-treated cellulose, which compound decomposes with the liberation of carbon disulphide, leaving behind a pure cellulose in gelatinous form mixed with the alkali

which is mixed with the required amount of sodium hydroxide in solution and allowed to react, producing a swollen mass of crumbling granulated texture, with the development of heat. The proportions usually taken are air-dried cellulose 25 to 33, sodium hydroxide 12.5 to 16, water 62 to 55. The carbon disulphide is made to act upon the soda-cellulose in the proportion of 1 to 10. The proper mixture being put into a wooden rotating drum which can be sealed, the reaction takes place rapidly at the ordinary temperature, a few hours sufficing for its completion. The product of the reaction being transferred to a closed vessel provided with mechanical stirring attachment, water is gradually added, when the mass dissolves to a viscid jelly which, when filtered, is ready for the spinning.

II. Processes of Manufacture.

SPINNING OF THE ARTIFICIAL SILK FILAMENT.—While in each case the spinning is effected by forcing a very viscid liquid through fine jets of glass or metal, the conditions are so dissimilar in the case of the three different raw materials that the process will be described as applying to each material in turn.

1. *The Collodion or Chardonnet Process.*—The collodion filament solidifies almost in the moment that it is forced out of the jets. The passing of the filament into a bath of acidified water is no longer practised, but the filament goes into the air, liberating the vapors of alcohol and ether which are carried along by a current of warm air and pass through condensation and absorption vessels, the first containing soda and the second sulphuric acid which absorbs the vapors of ether. The Chardonnet filament is, however, a nitrocellulose which when dried thoroughly is extremely inflammable, so that it is necessary to denitrate it. This is done by the action of alkaline sulphides, such as ammonium sulphide. Following this a slight bleaching is necessary, as the ammonium sulphide leaves the filament yellow. A very small amount of bleaching powder and muriatic acid suffices to bring the silk to a white color, when it is finally washed and dried.

2. *The Cuprammonium Process.*—The material which is forced from the spinning jet in this case is cellulose in ammoniacal cupric-oxide solution. So to form the filament it must be delivered into a solution which will act at once to decompose it and liberate the cellulose, which then forms a filament semisolid at first but becoming stronger as it loses the water with which it is charged. Pauly first used fifteen per cent. sulphuric acid as the ingredient of the decomposing bath. This forms cupric and ammonium sulphates, both soluble, while the cellulose filament when thoroughly washed free from acid is dried under tension and yields a product of silky lustre that requires no denitrating or bleaching to finish it.

Bronnert, Fremery, and Urban later improved this procedure by them a firmer filament, and then, after washing this, drying it in two stages, first in a current of air at the ordinary temperature and then in heated rooms at 40° C.

3. *Viscose Process.*—The separation of cellulose from viscose solutions takes place so readily that at first it was sought to simply spin the filament from the fine jets into a vertical shaft or air-passage through which warm air was rising, but now it is effected according to the Stearns' process by spinning the filament into a solution of ammonium chloride, which causes a complete separation of the cellulose of the filament. It is left in a cold ammonium chloride bath for several hours, brought into boiling ammonium chloride for a few minutes and then thoroughly washed.

III. Products.

Artificial silk as a commercial product is of a uniform white color and possesses the characteristic lustre of natural silk. Chardonnet silk indeed possesses a higher lustre than the natural, although it does not have the rustle of true silk and is somewhat harder to the touch; cuprammonium silk (the German glanz-stoff), on the other hand, has more exactly the lustre as well as the rustle of natural silk; viscose silk resembles the collodion silk.

Several points of difference in physical characters between natural and artificial silk are thus given by Süvern: *

	Specific gravity.	Percentage of moisture at 99°C.	Absorption of moisture in moist room of silk dried at 110°-115°.
Natural raw silk	1.36	7.97	20.11
Chardonnet silk (1)	1.52	10.37	27.46
Chardonnet silk (2)	1.53	11.17	28.94
Lehner silk	1.51	10.71	26.45
Cuprammonium silk (Glanz-stoff)	1.50	10.04	23.08
Gelatine silk	1.37	13.02	45.56
Viscose	....	11.44	.....

That artificial silk fibres lose notably in strength on wetting is one of their distinguishing characters as compared with natural silk fibre. The average loss in strength on wetting is given as seventy per cent. for all varieties. A treatment of artificial silk with a formaldehyde bath to correct this defect has been proposed by Escalier and is known as "sthenosizing." It is claimed that fibres so treated lose very little of their strength on wetting.

From the chemical point of view the most important difference between artificial silk (the gelatine silk excepted) and natural silk is that while natural silk contains some seventeen per cent. of nitrogen, the artificial silk contains only traces of this element. They therefore behave to chemical reagents like the vegetable cellulose fibres.

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* Die Künstliche Seide, Dr. Carl Süvern, 2te Aufl., p. 330.

IV. Analytical Tests and Methods.

There are a number of reagents that will distinguish between natural and artificial silk. Strong potassium hydroxide solution, which will dissolve natural silk, will only swell more or less the artificial silks, with the exception, of course, of gelatine silk.

Alkaline copper-glycerine solution will dissolve natural silk (both the true and the tussah silk) but does not attack the artificial silk consisting of cellulose.

Diphenylamine sulphate, however, is one of the best of the reagents for the detection of artificial silk. Its reaction is as follows:

With natural silk	Brown coloration.
With tussah silk	Intense brown coloration.
With Chardonnet and Lehner silk	Intense blue.
With Pauly or Thiele cuprammonium silk	No reaction.
With viscose silk	No reaction.

It is claimed that artificial silk is more easily affected by heat than either cotton, wool, or natural silk fibre. On heating a fabric containing mixed fibres to 200° C., the artificial silk will be destroyed and the dust can be beaten or brushed out and the loss in weight give the proportion of the artificial silk originally present.

V. Bibliography and Statistics.

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STATISTICS.

I. *a*. PRODUCTION, CONSUMPTION AND EXPORTATION OF COTTON FROM THE UNITED STATES.

Year.	Production (in bales of 500 lbs.)	Domestic consumption (bales of 500 lbs.)	Exportations (bales of 500 lbs.)	Value of exportations.
1905	10,804,556	4,877,465	6,975,494	$401,005,921
1906	13,595,498	4,974,199	8,825,237	481,277,797
1907	11,375,461	4,493,028	7,779,508	437,788,202
1908	13,587,306	5,198,963	8,889,724	417,390,665

I. *b*. COTTON CONSUMPTION BY COUNTRIES, 1905 AND 1900. (IN BALES OF 500 LBS.

Country.	1905.	1900.
United States	4,310,000	3,856,000
United Kingdom	3,620,000	3,334,000
Continent of Europe	5,148,000	4,576,000
East Indies	1,350,000	1,139,000
Japan	875,000	712,000
Canada	130,000	105,000
Mexico	70,000	18,000
Other countries	35,000	33,000
Total	15,538,000	13,773,000

(Census Bureau, 1905.)

II. FLAX.—According to a United States consular report fro Odessa (United States Consular Reports, March, 1891, p. 365), the tot area sown in Europe with flax amounted to 5,700,000 acres, of whic Russia alone had 3,700,000 acres. The total quantity of flax fibre pr duced in Europe is there given as follows:

	Pounds.		Pounds.
Russia	900,000,000	Belgium	43,200,000
Austria-Hungary	104,400,000	Italy	43,200,000
Germany	97,200,000	All other countries	36,000,000
France	79,200,000		
Ireland	46,800,000		1,350,000,000

The world's production of flax is thus stated by J. Scott Keltie (Th Statistician's Year-Book, London, 1907):

	Tons.		Tons.
Russia	350,000	Great Britain and Ireland (1908)	9,080
Germany	44,000	Italy	5,200
France (1905)	20,645		
North America	20,000		

The importation of flax into the United States was as follows:

	1906.	1907.	1908.	1909.	1910.
Amount in tons	8,729	8,656	9,528	9,890	12,761
Value	$2,327,300	$2,086,205	$2,514,680	$2,542,256	$3,417,321

III. *a*. The importations of other vegetable fibres have been:

	1906.	1907.	1908.	1909.	1910.
Hemp (dutiable)	5,317	8,718	6,213	5,208	6,42
Value	$906,808	$1,534,371	$1,086,805	$799,164	$1,039,83
Hemp (Manila)	58,738	54,513	52,233	61,622	92,50
Value	$11,036,667	$10,876,107	$8,974,617	$7,156,091	$10,517,10
Jute (tons)	103,945	104,489	107,533	156,685	68,15
Value	$6,449,684	$8,950,684	$6,504,920	$7,216,307	$3,728,44

III. *b*. Production and exportation of jute from India:

	Production in 1000 cwts.	Export in 1000 cwts.
1905	29,075	12,875
1906	32,880	14,480
1907	35,064	15,970
1908	22,539	14,192
1908	......	17,880

(Statistical Abstracts for British Colonies, London, 1909.)

IV. *Paper and Pulp Statistics:*

The importations of crude paper stock (rags, etc.) and of wood-pulp in recent years have been:

	Crude paper stock.	Wood-pulp.	
1904	$2,900,713	289,592,000 lbs., valued at	$3,602,668
1905	3,796,595	335,008,000 " "	4,500,955
1908	3,675,926	532,031,360 " "	7,313,326
1909	3,638,034	614,244,972 " "	8,629,263
1910	5,206,877	847,440,759 " "	11,768,014

(Commerce and Navigation of U. S., 1910.)

The production of wood-pulp, according to Census Reports, has been:

	Ground wood-pulp.	Soda-fibre.	Sulphite-fibre.	Total.
900	586,374 tons	177,124 tons	416,037 tons	1,179,535 tons
905	968,976 tons	196,770 tons	756,022 tons	1,921,768 tons

CHAPTER IX.

TEXTILE FIBRES OF ANIMAL ORIGIN.

As before stated, the only animal fibres that have acquired technical importance are the wool fibre and silk. These will now be considered.

I. Raw Materials.

A. WOOL.—Wool is undoubtedly a variety of hair, found in greater or less quantity on almost all mammals, on a few of which, as the domestic sheep, it forms the principal covering of the body. It is probable that while both hair and wool occur together in wild sheep, domestication has gradually caused the rank hairy fibres to disappear and the soft under-wool to develop until the fleece of wool becomes a thick and complete covering. From ordinary hair the wool is distinguished by two important properties: First, while hair is almost smooth on the surface, the wool fibre is covered by minute overlapping scales arranged like roof-tiles. While these scales are so minute as not to be discernible to the eye, they can be felt if a woollen fibre is drawn between the fingers in the direction opposite to that in which the scales are set. Secondly, while a hair is perfectly straight, the woollen fibre is finely crimped or curled, so that it becomes longer when drawn out and shortens again when the strain is removed. The spring due to this curled structure gives woollen fabrics notable elasticity. Owing to the overlapping scale-like structure and the crimpled condition of the fibre, wool has also the power of felting, or becoming matted into a compact cloth under the fulling process without the necessity of weaving. These structural characters of the wool fibre are shown in Fig. 88.

Sheep's wool varies from the long straight coarse hair of certain varieties of the English sheep (Leicester, Lincolnshire, etc.) to the comparatively short wavy fine soft wool of the Spanish and Saxon Electoral sheep. According to the average length of the fibres or staples two principal classes of wool are established, the *long-stapled* (eighteen to twenty-three centimetres) and the *short-stapled* wools (two and five-tenths to four centimetres). The former class have hitherto been combed and then spun into *worsted* yarn, while the latter have been carded and spun, yielding *woollen* yarns. These processes will be referred to again later. (See p. 350.) In general the long straight wools, like Lincoln and Leicester wools, possess a silky lustre, and are known as *lustre* wools, while the Merino, Colonial, etc., which are shorter and curly, are known as *non-lustre* wools.

The worth of any grade of wool is determined by noting such prop-

Wool is very hygroscopic. In warm dry weather it may contain eight to twelve per cent. moisture but if kept for a time in a damp atmosphere it may take up thirty to fifty per cent. This becomes an important item in the sale of wool, and hence in France and Germany the percentage of moisture contained in wool to be sold must be officially determined in "wool-conditioning" establishments. (See silk-conditioning, p. 348.) The legal amount of moisture allowed on the Continent is 18.25 per cent.

The best kind of wool is colorless, but inferior grades are often yellowish, and sometimes even brown or black in color.

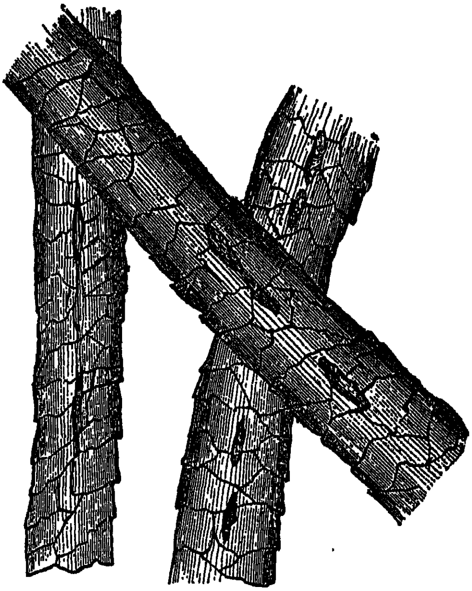
The chemical composition of the wool fibre is, as already noted (see p. 302), nitrogenous, but we must at the same time distinguish between the true fibre and the encrusting matters. These latter, independent of mechanically adhering impurities or "dirt," are of twofold character, the "*wool-fat*" (soluble in ether) and the "*wool-perspiration*" (soluble in water). These two are frequently included together under the name of the "yolk" or "suint" of the wool. The true wool fibre, when cleansed from these, has approximately the following composition: Carbon, 49.25 per cent.; hydrogen, 7.57 per cent.; oxygen, 23.66 per cent.; nitrogen, 15.86 per cent.; sulphur, 3.66 per cent. The presence of sulphur is very distinctive of wool and serves to distinguish it from silk, the other nitrogenous fibre. It can be removed in large part, but not without weakening the fibre and destroying its lustre, etc.

Wool-fat is a mixture of a solid alcoholic body, cholesterine, together with isocholesterine and the compounds of these bodies with several of the fatty acids. These free higher alcohols are soluble in boiling ethyl alcohol, while the compounds they form with the fatty acids are insoluble in alcohol but soluble in ether.

Wool-perspiration has been shown to consist essentially of the potassium salts of oleic and stearic acids, possibly other fixed fatty acids, also potassium salts of volatile acids, like acetic and valerianic acid, and small quantities of chlorides, phosphates, and sulphates. The wash-water of raw or greasy wool, it will be seen, therefore, would contain large amounts of potash salts, and when evaporated and ignited would yield an abundant product of potassium carbonate. This utilization of the wool wash-water as carried out at present in France and Belgium yields over one million kilos. of potassium carbonate. Another utilization of this yolk of wool is to submit it to dry distillation, when it yields a residue which is an extremely intimate mixture of carbonate of potash and nitrogenous carbon, of great value for the manufacture of yellow prussiate of potash.

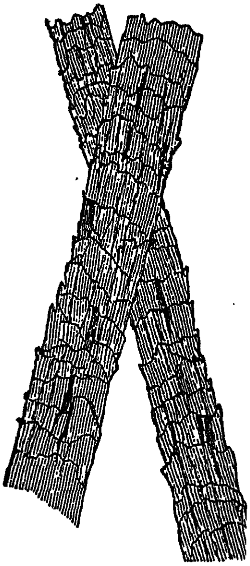
Wool is decomposed by heat at 130° C., ammoniacal vapors are given off, and at 140° to 150° C. sulphur compounds are also present in the vapors. When ignited by a flame, wool emits the disagreeable odor of burnt feathers and leaves a porous caked residue. Ammoniacal solution of cupric hydroxide has no action upon wool in the cold, but dissolves it when hot. Dilute solutions of hydrochloric and sulphuric acids have little influence whether hot or cold. This fact is availed of in separating cotton from wool in the process of "carbonizing" mixed cotton and woollen goods. The dilute sulphuric acid used attacks and disintegrates the cotton. They are then dried in closed chambers at 110° C., after which the disorganized cotton can be beaten out, while the wool remains but slightly altered. Nitric acid does not attack the wool seriously, but gives it a yellow color, hence sometimes used as a "stripping" agent for dyed woollen goods in case of re-dyeing. Sulphurous acid is the most satisfactory bleaching agent for woollens, as it removes the natural yellow tint of the ordinary wool. Caustic alkalies act rapidly and injuriously upon wool. Alkaline carbonates and soap have little or n injurious action if not too concentrated and if the temperature is no above 50° C. Chlorine and hypochlorites act injuriously upon wool an cannot be used for bleaching. A very slight action of chlorine, on th other hand, causes wool to assume a yellowish tint and gives it a increased affinity for many coloring matters.

FIG. 88.



Sheep's wool ($\frac{350}{1}$).

FIG. 89.



Alpaca goat's hair ($\frac{350}{1}$).

Closely related to sheep's wool are a few varieties of animal hai which are also utilized in some degree as textile fibres in similar class of goods.

Mohair is the product of the Angora goat of Asia Minor and Ca Colony, South Africa. It is a long silky hair, which is very soft a lustrous.

Cashmere consists of the soft under-wool which grows in winter the Cashmere goat. It furnishes the material for the costly Cashme shawls of native manufacture, but is not exported at all as fibre.

related species of South American goats found on the western slopes of the Andes, which yield valuable hair-like fibres. Of these, the alpaca is exported in largest amount to Europe and the United States. It is a long silky fibre somewhat intermediate between true wool and hair and possessing a strong lustre. It is both white and of various colors. It is shown in Fig. 89.

Camel's Hair is somewhat used in Africa, Asia Minor, and the Caucasus, and latterly in Europe, for the manufacture of woven goods, which are made from the unbleached hair.

B. SILK.—The silk fibre is, morphologically, the simplest and at the same time, because of its properties, the most perfect of the textile fibres. It differs from all the other fibres in that it is found in nature as a continuous fine thread, so that the process of spinning is superfluous in its case. In place of this we have the reeling process, whereby several of the natural threads are united into one thicker and stronger thread.

Silk is the product of the silk-worm (*Bombyx mori*) and is simply the fibre which the worm spins around itself for protection when entering the pupa or chrysalis state. From the eggs laid by the animal in the moth or butterfly state develops the caterpillar or silk-worm. The eggs are yellowish in color at first, changing to gray when dry. They are very light in weight, some thirteen hundred and fifty together weighing one gramme. For the development of the caterpillar from them a certain amount of warmth and moisture is necessary, the temperature being raised in the incubation chamber during ten or twelve days from 18° to 25° C. The young worms are at once removed to larger chambers, where are lath frame-works strung across with threads and sheets of paper. The animals are placed upon these, and fed regularly during thirty to thirty-three days, till indeed they begin to spin. They are here fed upon mulberry leaves (*Morus alba*), and during this period increase enormously in size, becoming at length about eight to ten centimetres long and about five grammes in weight. To allow of this increase in size it casts its skin some four times during this period (at intervals of from four to six days). When about the thirtieth day of its growth has been reached it ceases to take food and shows a decided restlessness. It is then placed on birch-twigs, and soon begins to spin. This spinning of the cocoon, or oval-shaped house in which the worm is to undergo the chrysalis state before emerging as the butterfly, involves the secretion of the fibre so much prized as silk. The silk substance is secreted by two glands, one on either side of the body of the caterpillar. The substance from these two glands unites in a capillary canal situated in the head of the animal, whence issues the silk as a double fibre only rarely separated, cemented throughout by the sericin, or silk-glue. The microscopical appearance of the silk fibre is shown in Fig. 90. This fibre which goes to form the cocoon varies in length from three hundred and fifty to twelve hundred and fifty metres, and has a diameter which averages about .018 millimetre. The interlacing layers of the silk cocoon are at first most layer which immediately surrounds the animal forms a thin parchment-like skin. The several stages of cocoon-spinning are shown in Fig. 91. The cocoons of the female are pure oval in shape, while those of the male are distinctly contracted in the centre. They are white or yellowish, and usually about three centimetres long and one and one-half to two centimetres thick. Some seven or eight days are allowed for the completion of the cocoon-spinning, and they are then gathered. A sufficient number of both males and females are taken for breeding purposes, and the rest put aside to be reeled for silk. Those chosen for breeding are kept for some twenty days at a temperature of from 19° to 20° C., when the silk-moth which has formed in the interior from the pupa emits a peculiar saliva, which softens the sericin, or silk-glue, at one end of the cocoon and enables the animal to push its way out to da light. The females within forty hours after their appearance lay the eggs, some four hundred in number, and shortly after die. The egg are slowly dried, and stored in glass bottles in a dry dark place till t following spring. The cocoons put aside for the reeling of silk mu be taken in hand promptly and the chrysalis contained in them kille in order to prevent the development of the silk-moth and the injury the cocoon by its pushing its way out. This is done either by heati

FIG. 91.

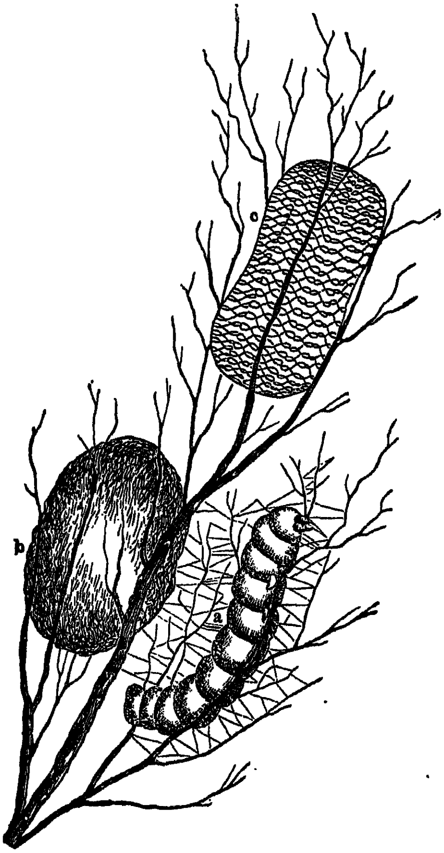
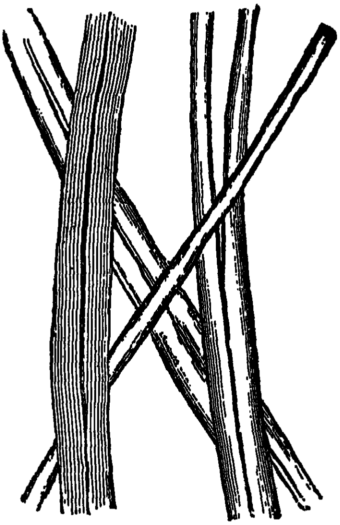


FIG. 90.



Silk fibre ($\frac{340}{1}$).

steam heat. One hundred grammes of eggs produce under favorable conditions from ninety thousand to one hundred and seventeen thousand cocoons, weighing one hundred and fifty to two hundred kilos., and these yield twelve to sixteen kilos. of reeled silk.

The silk fibre consists to the extent of rather more than half its weight of *fibröin,* $C_{15}H_{23}N_5O_6$, a nitrogenous principle. Covering this is the silk-glue, or *sericin,* $C_{15}H_{25}N_5O_8$. Whether this latter exists in the glands of the silk-worm along with the fibröin, as maintained by Duseigneur-Kleber, or is produced exclusively by atmospheric change from the fibröin as asserted by Bolley, is still in debate. This sericin, however, is easily dissolved off from the fibröin by warm soap-water and other alkaline liquids. This "boiled-off" liquid plays an important part in silk-dyeing operations. (See p. 544.) The most important physical properties of the silk fibre are its lustre, strength, and avidity for moisture. The regulation of the amount of moisture contained in raw silk as offered for sale, or "silk-conditioning," will be spoken of under the process of treatment. (See p. 348.)

Besides the true silk, the product of *Bombyx mori,* we have several so-called "wild silks," the most important of which is the Tussur silk, the product of the larva of the moth *Antheræa mylitta,* found in India. The cocoons are much larger than those of the true silk-worm, egg-shaped, and of a silvery drab color. They are also attached to the twigs of the food trees by a thread-like prolongation of the cocoon. The cocoon is very firm and hard, and the silk is of a drab color. It is used for the buff-colored Indian silks, and latterly largely in the manufacture of silk plush. Other wild silks are the *Eria* silk of India, the *Muga* silk of Assam, the *Atlas* or *Fagara* silk of China, and the *Yama-mai* silk of Japan.

II. Processes of Manufacture.

It will be beyond the province of this work to take up the manufacture of woollen and silk goods from the mechanical side. Hence we shall only notice the preliminary processes of chemical treatment which the fibres undergo to prepare them for manufacture into goods, and then take up the several classes of manufactured textiles again in speaking of bleaching and dyeing of goods.

A. Wool.—1. *Wool-scouring.*—The condition of the raw wool when first obtained from the back of the sheep has already been referred to. The fibre is covered with both natural and artificial impurities (yolk, dirt, etc.) to such an extent that mordanting and dyeing would be almost impossible. These are therefore to be removed by the process of scouring. It will be remembered, too, that the yolk was stated to be made up of the wool-fat (soluble in alcohol) and the wool-perspiration (soluble in water). Both of these have to be removed in the completed scouring operation. The full operation then must include three stages,—viz., steeping, or washing with water (*désuintage*); cleansing or scouring proper with weak alkaline solutions (*dégraissage*); rinsing or final wash-wool has been washed by the wool-grower. This is true, for instance, with Australian wools, while, on the other hand, most South American wools come into commerce unwashed and very rich in yolk. The washing of these wools is largely carried on in France and Belgium, and as has been stated (see p. 342), is made to yield large amounts of potassium carbonate by evaporating and igniting the wash-waters. The woo is systematically washed in tepid water (about 45° C.) in a series o tanks arranged so that the water passes from one to the other unti completely saturated, when it is evaporated. According to M. Chandelon, one thousand kilos. of raw wool may furnish three hundred an thirteen litres of yolk solution of specific gravity 1.25 (50° Tw.), havin a value of fifteen shillings and sixpence, while the cost of extractio does not exceed two shillings and sixpence.

The scouring and washing processes for loose wool are usually carrie out in the well-known rake scouring-machines, consisting of a larg cast-iron trough provided with an ingenious system of forks or rak whereby the wool is gradually passed forward by the to-and-fro diggin motion of the rakes. Two or three such scouring-machines are plac in series, so that the first may take the bulk of the impurities, the secon complete the scouring, and the third effect a thorough washing in stream of fresh water. The scouring liquid which has been longest use is stale urine (*lant*), which is effective because of the ammoniu carbonate it contains. It is now largely supplanted by ammonia, sodiu carbonate, soaps, etc. The most injurious effects arise from the use water containing lime or magnesia, because of the formation of t insoluble lime or magnesia compounds upon the fibre. In recent yea volatile solvents, like petroleum-naphtha, carbon disulphide, and carb tetrachloride, have also been introduced for scouring purposes, althou not generally adopted on account of the expense and risk attending th use. They must be followed at all events by a washing with water, while they dissolve fatty matters, they do not take up the oleates, e of the wool-perspiration.

The only treatment of this kind, known technically as a *degreas* process, is that with petroleum-naphtha. This has been found pr ticable and remunerative. The wool, freed from its grease and w like constituents by the naphtha and its potash salts, by a washing w water only is left in an excellent condition for the mechanical treatm such as carding and combing.

Woollen yarns and woollen cloth are also scoured to free them fr the oil which has either purposely or by accident been put upon th in the spinning and weaving operations. The scouring of "uni goods—that is, materials with cotton warp and woollen weft—is a m difficult operation on account of the differences in elasticity, hy scopic character, etc., of the cotton and the wool fibre. It includes operations of *crabbing, steaming,* and *scouring.*

2. *Bleaching Wool.*—Wool is generally bleached either as yarn cloth. The bleaching agent in general use is sulphur dioxide. It

former method being generally followed, and the yarn or cloth suspended on poles in closed chambers, called sulphur-stoves, which can be charged with the gas. In liquid bleaching with sulphurous acid, a solution of sodium bisulphite is generally used, which is either mixed with an equivalent amount of hydrochloric acid or, what is better, the goods are passed through one solution after the other in separate baths. The bleaching of sulphur dioxide differs essentially from that effected by chlorine and hypochlorites in that it is not due to oxidation, but to reduction or possibly to the formation of colorless compounds with the natural yellow color of the wool. At all events, it is not permanent in character, and the yellow color gradually returns on exposure to atmospheric influences and repeated washings in alkaline solutions.

The best liquid bleaching agent is hydrogen dioxide. The woollen material is steeped for several hours in a dilute and slightly alkaline solution of the commercial H_2O_2 and then well washed, first with water acidified with sulphuric acid and afterwards with pure water.

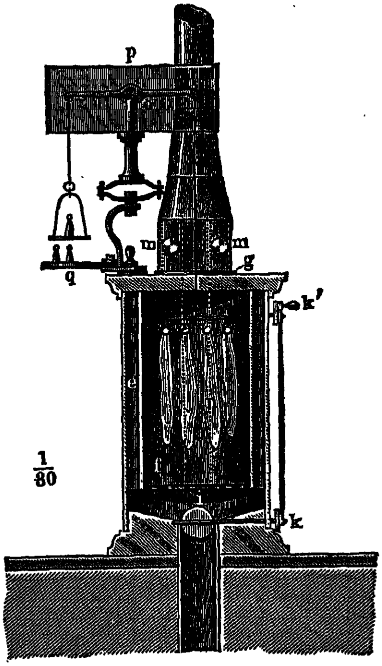
B. SILK.—1. *Reeling of Silk.*—The unwinding of the long silk fibre from the cocoon and bringing it into condition for weaving is to be accomplished in the reeling process. The cocoons are thrown into a basin of warm water to soften the silk-glue and allow of the fibres being separated. From four to eighteen fibres, according to the quality, are taken, and two threads formed by passing the fibres together through two perforated agate guides. After being crossed or twisted together at a given point they are again separated and passed through a second pair of guides, thence through the distributing guides on to the reel. The temporary twisting or crossing causes the agglutination of the individual fibres of each thread. In order to form long threads a frequent adding on the fibre of a new cocoon is necessary. Care must be taken, also, that the thread remain as nearly as possible of uniform thickness, so that as the inner fine fibres of several cocoons come through the guides another cocoon is added to the number used for the thread. One cocoon gives .16 to .20 or at most .25 gramme of raw silk. The loss through removal of the external floss varies from eighteen to thirty per cent., according to the cocoons and the care bestowed by the worker. Before this raw silk can be used for weaving two of the threads are "thrown" together and slightly twisted.

2. *Silk-conditioning.*—Raw silk kept in a humid atmosphere is capable of absorbing thirty per cent. of its weight of moisture without this being at all perceptible. It therefore becomes a matter of great importance for the buyer to know what weight of normal silk there is in any given lot. To ascertain this with accuracy, there have been established in a number of the European centres of silk industry *conditioning* establishments. The operation is carried out by means of the apparatus shown in Fig. 92, where a number of hanks of silk are shown in the drying chamber. A test hank of silk is taken from the bale, and having been suspended from the one arm of an accurate balance its initial

chamber is shown in the illustration. To the final weight obtained for the dry silk eleven per cent. is added, and the result taken as a normal silk weight. The average loss of weight in this conditioning process is about twelve per cent.

3. *Silk-scouring.*—By the scouring of silk the silk-glue is removed to a greater or less extent and the fibre is rendered lustrous and soft and able to take the dye-color. According to the amount of silk-glue removed in this operation the product is called *boiled-off silk, souple silk,* or *écru.* In the first case, the loss of silk-glue amounts to twenty-five to thirty per cent. of the weight of the raw silk; in the second, to eight to twelve per cent.; and in the third to three to four per cent. of the original weight of the silk. In preparing the first variety two operations are necessary, *stripping* or *ungumming* (*dégommage*), and *boiling off.*

FIG. 92.



The hanks of raw silk are suspended by wooden rods in a rectangular trough lined with copper and worked by hand in a thirty to thirty-five per cent. soap solution heated to 90° to 95° C. When the water is very hard it must be corrected or softened previously. Frequently two soap-baths are used one after the other as the first one becomes charged with the silk-glue. The silk at first swells up and becomes glutinous, but as the glue dissolves off it becomes soft and silky. The waste soapy and glutinous liquid obtained is called "boiled-off" liquor, and is a useful addition to the dye-bath in dyeing with coal-tar colors. (See p. 544.) For the purpose of removing the last portions of the silk-glue, it is now washed in water at 60° C., to which some soap and carbonate of soda have been added, then put in coarse hempen bags called "pockets" and boiled for half an hour to three hours, according to quality, in open copper vessels with a solution of ten to fifteen per cent. of soap. It is then rinsed with a weak tepid solution of sodium carbonate, and finally washed in cold water. Silk intended to remain white or to be dyed pale colors is then at once bleached while moist with gaseous sulphur dioxide for some six hours. The bleaching operation may be repeated from two to three times, according to the quality of the silk.

Souple silk is that which has been prepared for dyeing with a loss of less than eight per cent. of its weight. It is, however, not so always includes two operations, and if the silk is to be dyed light colors, two additional operations have to be carried out. The raw silk is first "softened," and the small quantity of fatty matter present removed (*dégraissage*) by working it from one to two hours in a ten per cent. soap solution at 25° to 35° C. It is then "bleached" by immersion for ten to fifteen minutes in a dilute solution of aqua regia (five parts hydrochloric acid to one part nitric), or as a substitute for this nitrated sulphuric acid (nitrosyl-sulphate). This is followed by "stoving," or treatment with sulphur dioxide, and then, without removing the sulphurous acid, by the treatment of soupling (*assouplissage*) proper. This consists in working the silk for about an hour and a half at 90° to 100° C. in water containing three to four grammes cream of tartar to the litre. This treatment makes the silk softer and causes it to swell up and become more absorbent. It is then finally washed in tepid water.

Ecru silk is raw silk which has been washed with hot water, with or without soap, bleached with sulphur, and again washed. It is only used for a base for other silk fabrics like velvet or dyed in blacks.

Artificial silk has already been described in detail under the vegetable fibres and the products therefrom (see p. 333.)

III. Products.

A. WOOL.—We have already alluded to the distinction between worsted and woollen yarns. Formerly all long-stapled wools were *combed*,—that is, the fibres were brought as nearly as possible parallel to one another and were then spun into what was known as worsted yarn, used in hoisery and in the manufacture of fabrics which did not undergo fulling. All short-stapled wools, on the other hand, were *carded* and spun much as cotton is spun, and the yarns so obtained were the only ones capable of being used in making milled or fulled cloths, in which the felting property of wool is availed of to thicken the cloth after weaving and in which by teasels the nap of the cloth is raised so as to present a uniform surface. All kinds of wool, therefore, were formerly divided into combing and carding or clothing wools. Machines have been invented latterly, however, capable of combing wools having as short a staple as one inch, and, on the other hand, wools with a staple as much as five inches long may be used in making milled cloth. So the distinction between the several wools is no longer as absolute as it once was.

Among the chief kinds of worsted fabrics are *serges* and *merinos* and mixed goods of wool and mohair, alpaca, and camel's hair. *Hosiery* and *carpets* also belong here, although the best of these latter are made on a ground of strong linen or hemp. The principal varieties of woollen cloth are *broadcloths*, the finest variety of woollen cloth, *cashmeres*, a fine thin twilled fabric, *tweeds*, fabrics of looser texture than broadcloth and less highly milled, *doeskin*, a strong twilled cloth, *blankets*, *flannels*, etc.

Shoddy is a material made from

mungo, which is made from remains of finer fragments, such as old dress-coats, tailor's clippings, etc.

A third grade of recovered wool, sometimes called *extract wool,* is obtained from union goods (mixed woollen and cotton goods) by the process of carbonizing the vegetable fibre and then beating it out. The carbonizing is done with dilute sulphuric acid, with aluminum chloride, or with gaseous hydrochloric acid. The last process is said to give the best results.

B. SILK.—The raw-silk threads obtained in the reeling process are not sufficiently strong for use in the loom, so several must be united. This may be done in different ways. By the union of two or more single threads, separately twisted in the same direction, which are then doubled and retwisted in the opposite direction, is obtained *organzine.* The best grades of silk are also taken for the organzine, which is to form the warp in silk-weaving. The product of the union of two or more simple untwisted threads which are then doubled and singly twisted is *tram,* which forms the weft in weaving.

Waste silk is that which proceeds from perforated and double cocoons and such as are soiled in steaming or in any other way. This waste silk is washed, boiled with soap, and dried. When carded and spun like cotton it yields the so-called *flurt-silk.*

Satins are tissues so woven that almost the only threads appearing on the right side of the tissue are weft threads, which present a uniform glossy surface.

Velvets are tissues in which the outer surface presents to view a short soft pile, made by passing the warp threads over fine wires, which are afterwards drawn out. The loops then remaining are either left as they are, in which case the tissue is called *pile-velvet,* or cut to form *cut-velvet.* This fabric is now largely imitated in cotton and mixed tissues.

IV. Analytical Tests and Methods.

GENERAL DISTINCTIONS BETWEEN VEGETABLE AND ANIMAL FIBRES.—A general scheme for distinguishing between the several classes of fibres has been proposed by R. Schlesinger in his "Leitfaden für die mikroskopische und mikrochemische Analyse der technisch verwendeten Rohstoffe der Textil-Industrie." It is in outline as follows:

TREAT WITH CAUSTIC SODA.		
The fibre does not dissolve in ten per cent. caustic soda solution, and in burning, which takes place readily, does not develop any burnt horn odor.	The fibre dissolves in concentrated caustic soda, and when treated with ammoniacal cupric oxide shows scales upon its surface.	The fibre does not dissolve in cold ten per cent. caustic soda, but dissolves perfectly in concentrated sulphuric acid; shows neither scales nor medullary substance.
[illegible]	Animal hairs or wool.	Silks.

The vegetable fibres are then to be studied by the aid of the iodine and dilute sulphuric acid reaction, and the several groups already noted in the classification on p. 303 are established.

The animal hairs are to be distinguished best by the microscopical characters and measurements.

The several varieties of silk are also to be distinguished by a comparison of the diameters of the fibre as measured under the microscope.

A scheme for distinguishing between the more important textile fibres, based upon their behavior to the two dyes malachite-green and Congo-red, and after examination under the microscope, has been proposed by Behrens ("Microchemische Analyse," 2te Heft, p. 51). The grouping thus established is as follows:

Group A. *Dyed fast to washing by malachite-green.*
  Here belong, of the textile fibres, silk, wool, and jute.
    Aa. Not capable of supplementary dyeing by aromatic amines: silk and wool.
    Ab. Capable of supplementary dyeing by aromatic amines: jute.
Group B. *Dyed partially fast only by malachite-green.*
  Hemp and manila.
    Ba. Strongly polarizing: hemp.
    Bb. Weak polarizing: manila.
Group C. *Fugitive dyeing with malachite-green; complete supplementary dyeing with benzidine dyes.*
  Here belong cotton and flax.
    Ca. Weak polarizing: cotton.
    Cb. Strongly polarizing: flax.

Several of the simpler differences between the vegetable and the animal fibres as groups have already been alluded to in classifying the fibres. (See p. 302.) Other special tests are as follows:

1. Millon's reagent (mercurous and mercuric nitrate) colors the animal fibres red, but not the vegetable fibres.

2. Liebermann gives the following test: Prepare a fuchsine solution, add potash solution drop by drop until it is decolorized, filter, and dip in the sample of goods. Wool or silk fibres are colored red, cotton remains colorless.

3. Ammoniacal cupric oxide solution dissolves cotton as well as silk. While cotton, however, is precipitated by certain salts as well as by sugar and gum, silk is only precipitated by acids.

4. As wool always contains sulphur, a sodium plumbate solution (made by boiling red lead with caustic soda solution and filtering) is at once blackened on contact with wool. This test may be interfered with in the presence of sulphur-treated silk.

5. Wool and silk may be distinguished by the use of hot hydrochloric acid. Silk dissolves easily in this, while wool merely swells up but does not dissolve.

6. According to Höhnel, wild silks behave differently from true silks with chromic acid. If a cold saturated solution of chromic acid be diluted with an equal bulk of water and then boiled for one minute with the sample of silk, the true silk dissolves up, while the wild silk remains unattacked even after two or three minutes' boiling. Wool behaves

A. Remont gives a process for determining wool, silk, and cotton when mixed in the same fabric. Four pieces of about two grammes' weight each are taken; three of these are boiled for a quarter of an hour in two hundred cubic centimetres of three per cent. hydrochloric acid, which is renewed if the liquid becomes strongly colored, and the samples are then well washed. The dressing is thus removed and the coloring matter in the case of the cotton, but only slightly in the case of wool and silk; the weighting of the silk with iron salts is also completely removed by the hydrochloric acid if the weighting does not exceed twenty-five per cent. of the weight of the silk, leaving the fibres chestnut-brown in color. Two of the samples thus treated are dipped for one to two minutes into a boiling solution of basic chloride of zinc of specific gravity 1.69; then thrown into water and washed first with acidified water and then with pure water. This removes the silk. The basic chloride of zinc solution is prepared by heating one thousand parts of zinc chloride, forty parts of zinc oxide, and eight hundred and fifty parts of water.

One of the two samples freed from silk is then boiled gently for a quarter of an hour with sixty to eighty cubic centimetres of caustic soda solution of specific gravity 1.02. This is best done with inverted condenser, so that an injurious concentration of the soda solution is avoided. Wash gently without too much rubbing and the wool is removed. All four samples are now washed for a quarter of an hour with distilled water, pressed out, dried in the air, and weighed. The first will weigh as before, two grammes or nearly, a slight difference of a few milligrammes being neglected; the difference in weight between the first and second samples gives the dressing; that between the second and third gives the silk; that between the third and fourth the wool present, and the weight of the fourth sample the vegetable fibre present. This is slightly attacked by the soda solution, and in the case of cotton it is usual to reckon five per cent. as the loss from this cause.

V. Bibliography and Statistics.

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STATISTICS.

Wool.—The following figures show the production, importation, and home consumption of wool for the United States in recent years:

Year.	Production. Pounds.	Importation. Pounds.	Home consumption. Pounds.
1905	295,488,428	249,135,746	542,062,536
1906	298,915,130	201,688,668	494,960,990
1907	298,294,750	203,847,545	498,695,547
1908	311,138,321	125,980,524	431,252,030
1909	328,110,749	266,409,304	590,996,078

(Statistical Abstract of U. S., 1909.)

The importations of wool during the last few years are thus classified:

	1908	1909	1910
Class I.—Clothing wool (lbs.)	45,798,303	142,580,993	111,592,978
Valued at	$10,278,199	$29,455,598	$27,231,052
Class II.—Combing wool (lbs.)	13,332,540	21,952,259	31,614,235
Valued at	$3,624,617	$4,591,559	$7,931,145
Class III.—Carpet wool (lbs.)	66,849,681	101,876,052	120,721,019
Valued at	$9,762,122	$11,124,837	$16,058,647

The world's production of raw wool in 1903 was estimated to be 2666 million pounds. The chief producing country, Australia, exported as follows:

	Raw wool.		Scoured wool.	
	Amount in 1000 lbs.	Value in 1000 pds. sterling	Amount in 1000 lbs.	Value in 1000 pds. sterling
1904	339,395	13,147	55,911	3,975
1905	380,420	15,574	56,775	4,247
1906	415,353	17,547	64,889	5,099
1907	512,757	22,928	72,318	5,964
1908	471,846	18,028	70,915	4,886

(Statistical Abstract, 1909.)

After the British Colonies of Australia, New Zealand, and Cape of Good Hope, the largest wool producing country is the Argentine Republic and La Plata. The exports in bales of one hundred and twenty-five kilos. were as follows:

1900	468,000 bales.
1905	403,821 bales.
1906	419,386 bales.

Silk.—The production of raw silk throughout the world at five-yea intervals, as given in the Census Report of 1905, was:

	1885.	1890.	1895.	1900.	1905.
Italy (kilos)	2,810,000	3,033,000	4,661,900	4,528,500	4,900,0
France (kilos)	483,000	618,000	896,000	500,000	625,0
Austria (kilos)	142,000	267,000	266,000	276,000	315,0
Spain (kilos)	85,000	65,000	90,000	78,000	77,0
The Levant (kilos)	730,000	707,000	1,244,000	1,760,000	2,186,0
Japan, exports (kilos) .	1,346,000	2,130,000	3,076,000	3,371,000	5,679,5
China, Shanghai (kilos).	2,695,000	2,914,000	3,358,000	4,756,000	2,950,0
China, Canton (kilos) .	774,000	1,529,000	1,394,000	2,253,000	2,137,7
India, Calcutta (kilos) .	861,000	210,000	199,000	350,000	180,
Total	9,926,000	11,473,000	15,184,900	17,932,000	19,050,

The same report thus gives the raw silk consumption of the wo by countries, taking an average of the years 1902, 1903, and 1904:

Country.	Kilograms.	Pounds.	Per cent. of total.
United States	6,128,000	13,512,240	31.0
France	4,327,000	9,541,035	21.9
Germany	2,846,000	6,275,430	14.4
Switzerland	1,595,000	3,516,975	8.1
Russia and Caucasus ..	1,271,000	2,802,555	6.4
Italy	966,000	2,130,030	4.9
Austria-Hungary	776,000	1,711,080	3.9
England	709,000	1,563,345	3.6
India	350,000	771,750	1.8
Egypt	200,000	441,000	1.0
Spain	183,000	403,515	0.9
Syria	110,000	242,500	0.6
Morocco	70,000	154,350	0.4
Algeria and Tunis	65,000	143,325	0.3
Other countries	152,000	335,160	0.8
	19,748,000	43,544,340	100.0

No data exist to show the consumption in China and Japan and are not included.

The importations of raw silk into the United States for the last years have been as follows:

1905	22,357,307	pounds, valued at	$61,040,053
1907	18,743,904	" "	71,411,899
1908	16,662,132	" "	64,546,903
1909	25,187,957	" "	79,903,586
1910	23,457,223	" "	67,129,603

(Commerce and Navigation of U. S., 1910.)

CHAPTER X.

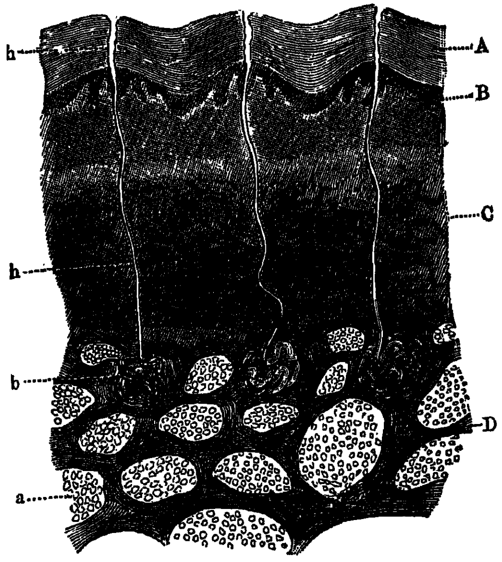
ANIMAL TISSUES AND THEIR PRODUCTS.

A. LEATHER INDUSTRY.

I. Raw Materials.

1. Animal Hides and Skins.—The moist animal skin undergoes decomposition very rapidly; if dried it becomes stiff and horny, or if boiled with water is changed into soluble glue. The object of tanning is to bring the animal skin into such a condition that decomposition is arrested, and after drying it no longer forms a stiff horny mass, but an opaque tissue insoluble in water, distinctly fibrous and pliable. The product known as leather has properties which at once distinguish it from the untanned hide, such as greater or less impermeability to water and toughness and strength. Nevertheless, the best authorities on the subject believe that in the main tanning is a physical rather than a chemical process, and that the function of the tanning material is chiefly to penetrate the pores of the skin and envelop the individual fibres so that in drying they are prevented from adhering and so stiffening the whole mass. The power of the skins to fix tanning materials upon the surface of its fibres varies considerably according to the nature of the material used, and in many grades of leather is undoubtedly supplemented by a chemical combination of the coriin of the skin with the tannin.

Fig. 93.



To understand the nature of the change wrought by tanning in the animal hide, it is necessary irst to refer briefly to its anatomical structure. Fig. 93 shows a section of ox-hide cut parallel with the hair, magnified about fifty diameters. It consists essentially of three layers: the *epidermis*, which is itself made up of two layers, the outer horny layer [illegible]

B, the *rete Malpighii*, a watery cellular layer, which rests upon the true skin and is continually renewing the outer layer; the *derma* or *corium*, th true skin, *C*, which alone is the leather-tissue; and the *fatty unde tissue*, shown in the illustration at *D*, in which the perspiratory an sebaceous glands are embedded. Both the epidermis and the unde tissue are removed in the preparatory processes of tanning, so that th corium alone remains to combine with the tanning materials to for leather. The hair of the animal is enclosed in hair-sheaths, which pas down through the epidermis and rest upon the corium, from which i life the hair-glands draw their nourishment. The corium, or tru leather-forming layer, is composed of bundles of interlacing fibre between which is found an albuminoid substance, *coriin*, which as t skin dries cements the fibres together and stiffens the hide. This is i soluble in water but soluble in lime-water, and hence removed in lar part by the process of liming to which the hides are submitted.

The animal skins which are utilized in the manufacture of leath are, first, those of the ox, cow, buffalo, horse, etc. These are known *hides*, or if from younger animals of the same kind as *kips*. Secon those of the calf, sheep, goat, deer, etc. These are known as *skins*. F special purposes the skins of crocodiles, alligators, porpoises, and sea are also made into leather.

The hides may come to the tannery according to the source when obtained either as *fresh* or *green* hides,—that is, direct from t slaughter-houses,—as *wet salted*, as *dry salted*, and as *dried* hides. addition to the domestic production, great numbers of hides are i ported into the United States from the Argentine Republic and t River Plate in South America. England imports from India, the Ca of Good Hope, and Australia as well as from South America. Go skins for the morocco trade are brought mainly from India and the Ea

2. TANNIN-CONTAINING MATERIALS.—The conversion of the hides i leather is usually accomplished by the action of an extract or infusi of tannin or tannic acid. This powerful astringent acid is very wid distributed in nature, being found in barks, roots, leaves, seed-po flowers, and fruits, and in excrescences on trees. More accurately spe ing, we find a number of varieties of tannic acid in these different ve table sources, of which some are more valuable for tanning than oth As a class they are readily soluble in water, amorphous, of slight a reaction, and astringent taste. They yield with iron salts bluish-bl or greenish precipitates, throw gelatine and albumen out of soluti and change hides into leather. In tanning it is not necessary to ext the acid in a pure state, but infusions are made from the powdered ba as needed, or concentrated extracts prepared for this purpose are u We will note briefly the more important tannin-containing mater used at the present time in leather manufactures.

Oak-bark.—The common English oak (*Quercus Robur*), which cludes the two varieties *Q. pedunculata* and *Q. sessiliflora*, is one of most important materials. It contains from twelve to fifteen bark, known as *coppice-oak*, is yellowish-brown in hue and very rich in tannin; *Quercus suber* (or cork-oak) and *Quercus Ilex* (or evergreen-oak), both of which are grown in Algiers, Italy, Spain, and the South of France. In the United States the most important varieties of oak are *Quercus prinus* or *castanea* (chestnut-oak); *Quercus rubra* (common red-oak); *Quercus alba* (or white-oak). The tannin of the several varieties of oak is known as *quercitannic acid.* According to the researches of Etti,* the main constituents of the oak-bark are *quercitannic acid,* with the formula $C_{17}H_{16}O_9$; its first anhydride, *phlobaphene,* $C_{34}H_{30}O_{17}$; its second anhydride, $C_{34}H_{28}O_{16}$; its third anhydride, *Oser's oak-red,* $C_{34}H_{26}O_{15}$; and its fourth anhydride, *Löwe's oak-red,* $C_{34}H_{24}O_{14}$. Of these, the quercitannic acid and the phlobaphene are specially concerned in the tanning process.

Hemlock-bark.—The bark of the hemlock (*Abies Canadensis*) of Canada and the United States contains nearly fourteen per cent. of tannin. This is extensively used, either jointly with oak-bark (union tanned leather) or as a substitute for it, in the manufacture of sole-leather. It is said to produce a harder leather than oak-bark, but less pliable and more pervious to water. A solid extract from the hemlock-bark containing from twenty-five to thirty-five per cent. of a deep red tannin is prepared in large quantities for export. The production of this solid extract is said to be at present considerably over ten thousand tons per annum. Liquid extracts with fifty per cent. of solid matter are also largely sold.

Pine-bark is much used in Austria, Bavaria, and Southern Germany. It contains from seven to ten per cent. of tannin and considerable resinous extractive matter. It does not yield so good a leather as oak-bark.

Closely related and somewhat used are the barks of the *White Spruce,* the *Larch,* and the *Fir.*

Willow-bark.—Several species of the willow, notably *Salix arenaria* and *S. caprœa,* are used in Russia and Denmark for the tanning of lighter skins, for the manufacture of glove leather and the so-called Russia leather. It is stated that the yearly consumption of willow-bark in Russia at present is some six and a half million kilos. against two and a half million kilos. of all other tanning barks. The percentage of tannin in the willow is usually given at from three to five per cent., although Eitner † found over twelve per cent. in several species.

Chestnut-wood.—The wood of the chestnut (*Castanea vesca*) contains from eight to ten per cent. of a tannin which closely resembles gallotannic acid. The extract, containing from fourteen to twenty per cent. of tannin, is used largely to modify the color produced by hemlock extract and for tanning and dyeing.

Horsechestnut-bark.—The bark of the horsechestnut (*Æsculus hippocastanum*) is also said to be used for the manufacture of an extract under the simple name of "chestnut extract," but such manufacture in the United States is very doubtful.

Catechu (or *Cutch*) is the name given the dried extract from *Acacia Catechu,* cultivated in India and Burmah, and containing forty-five to fifty-five per cent. of a special variety of tannic acid (catechu or mimotannic). The extract is evaporated until a semi-solid dark-brown product is obtained. This is exported in mats, bags, and boxes to European and American markets.

Gambier or Gambir (*Pale Catechu*) is the dried extract from the leaves of *Uncaria Gambier* and *U. acida.* It contains thirty-six to forty per cent. of a brown tannin which rapidly penetrates leather and tends to swell it, but taken alone produces a soft, porous tannage; it is largely used in conjunction with other materials for tanning both light and heavy leathers. It is exported from Singapore in pressed blocks and cubes. The catechutannic acids of cutch and gambier differ from gallotannic acid in giving a grayish-green precipitate with ferric salt and no reaction with ferrous salts; by giving a dense precipitate with cupric sulphate and none with tartar emetic. They also contain *catechin,* which is said to be an anhydride of catechutannic acid.

Kino is an extract somewhat resembling cutch, and is the dried juice from a variety of plants. Thus, the East Indian kino is obtained from *Pterocarpus marsupium,* the Bengal kino from *Butea frondosa,* the African from *Pterocarpus erinaceum,* and the Australian from the several species of *Eucalyptus.* It ordinarily forms small angular frag ments of black lustrous appearance, brittle, and crumbling to brown-re powder. It contains thirty to forty per cent. of a tannin (kinotanni acid) analogous to catechutannic acid, together with phlobaphene.

Sumach consists of the powdered leaves, peduncles, and youn branches of *Rhus coriaria, Rhus cotinus,* and other species of *Rhus* Thus, Sicilian sumach, the most esteemed variety, is from *R. coriaria* Spanish sumach is from several species of *Rhus,* and comes in thre varieties, Malaga, Molina, Valladolid; Tyrolean sumach from *R. cotinus* French from *Coriaria myrtifolia;* American from *R. glabra, R. Can dense,* and *R. copallina.* The leaves are collected while the shrub is i full foliage and cured by drying in the sun. They are then groun under millstones and the product baled. The sumach contains fro sixteen to twenty-four per cent. of a tannin which seems to be identic with gallotannic acid. The American variety contains usually six eight per cent. more than the European, but also contains more of dark coloring matter, which renders it inferior to the Sicilian suma for white leathers.

Myrobalans (or *Myrabolans*).—The fruit of several species of *Ter nalia* found in Hindostan, Ceylon, Burmah, etc. Myrobalans varies size from that of a small hazel-nut to that of the nutmeg. The tann occurs in the pulp which surrounds the kernel. It is generally used combination with other tanning materials to modify the objectiona color which some of the latter impart to the leather. By itself it p duces a soft and porous tannage.

Valonia is the commercial name for the acorn cups of several spe [illegible] *macrolepis* coming from A

Minor, Roumelia, and Greece. They are of a bright-drab color, and contain twenty-five to thirty-five per cent. of a tannin somewhat resembling that of oak-bark, but giving a browner color and heavier bloom. It is generally used in admixture with oak-bark, myrobalans, or mimosa-bark, because of itself it produces too brittle a leather.

Mimosa-bark (*Wattle*).—The bark of numerous species of *Acacia* (*A. decurrens* and *A. dealbata*) from Australia and Tasmania, contains from twenty-four to thirty per cent. of mimotannic acid. The bark comes into commerce chopped or ground and also in the form of an extract. It makes a red leather and is generally used in admixture.

Divi-divi.—The seed-pods of *Cæsalpinia Coriaria,* a small tree found in the neighborhood of Maracaibo, South America. The pods are about three inches long, brownish in color, and generally bent by drying into the shape of the letter S. It contains thirty to fifty per cent. of a peculiar tannin somewhat similar to that of valonia, but is liable to fermentation.

Quebracho.—This is the name applied to several South American trees possessing hard wood. They are *Aspidosperma Quebracho* (*Quebracho blanco*), *Loxopterygium Lorentzii* (*Quebracho colorado*). The wood and bark of the latter contain from fifteen to twenty-three per cent. of a bright red tannin. Both the wood and the extract are used in tanning.

Nutgalls is the term applied to the excrescences on plants produced by the punctures of insects for the purpose of depositing their eggs. The principal commercial kinds are oak-galls (or Aleppo galls) and Chinese galls. The first of these are the product of the female of an insect called *Cynips,* which pierces the buds on the young branches of the *Quercus infectoria* and other species of oak. In the centre of the gall thus produced the larva is hatched and undergoes its transformation, boring its way out as a winged insect in five to six months. If the galls are gathered while the insect is in the larval state they are known as "blue" or "green" galls; if the insect has cut its way out they are known as "white" galls, and are of inferior character and less astringent. The best oak-galls contain from sixty to seventy per cent. of gallotannic acid.

The Chinese gallnuts are the product from the *Rhus semialata,* the leaves of which are punctured by an insect, the *Aphis Chinensis.* The nuts are of irregular shape but are very rich in tannin, containing about seventy per cent.

Knoppern are galls from immature acorns of several species of oak largely used for tanning in Austria. They contain from twenty-eight to thirty-five per cent. of tannin.

II. Processes of Manufacture.

Leather may be manufactured from hides or skins by a number of methods, which may be summarized, however, under three heads,—viz., tanning by the use of tannin-containing barks or extracts; mineral tan

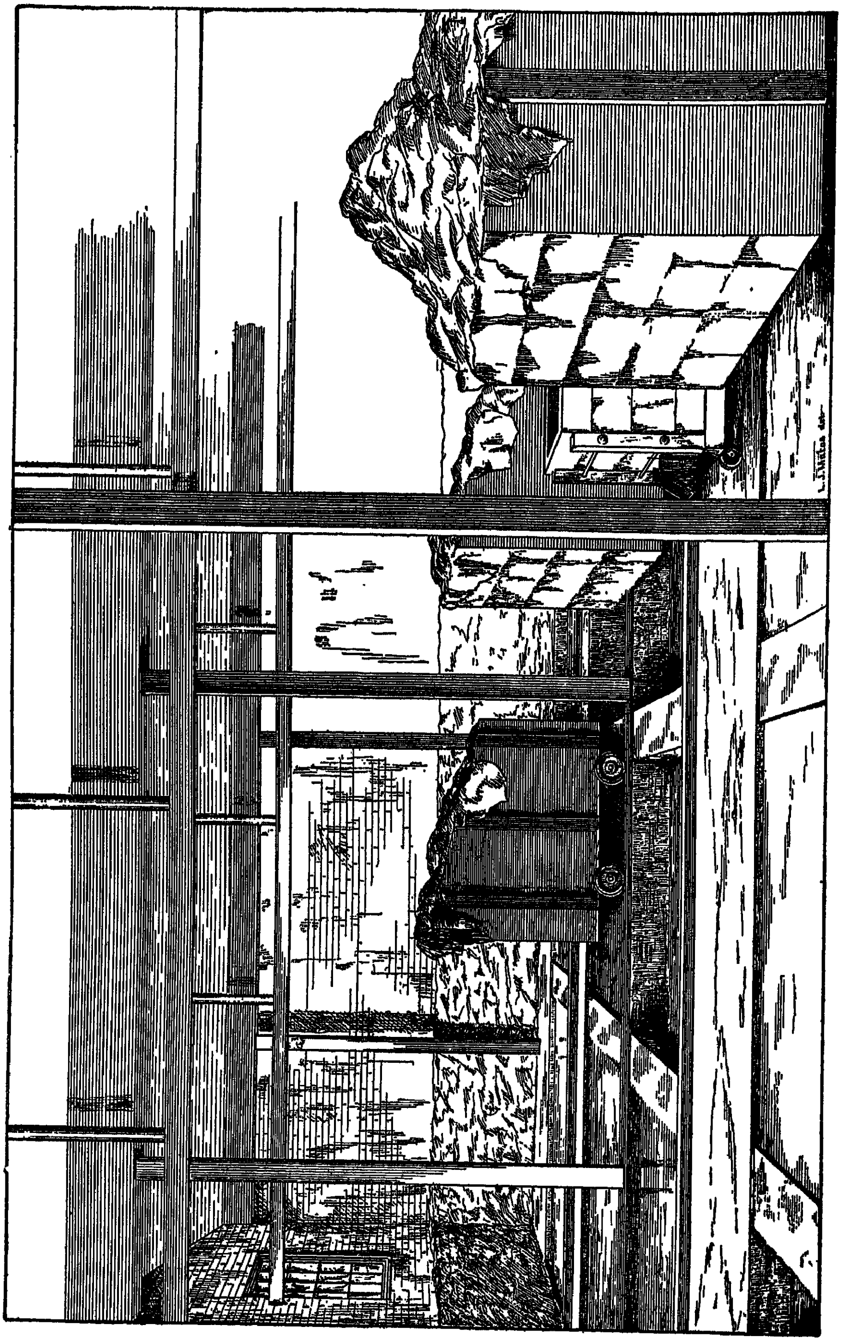
and salt, as in "tawing;" and the manufacture of soft leather by tr
ment of the skins with oils.

We will note first the methods involving the use of tannin-conta
ing materials, and these again differ somewhat according to the gr
of leather to be made and the character of the hides or skins used.

A. MANUFACTURE OF SOLE-LEATHER.—1. *Softening and Clean*
the Hides.—This process differs according as the hides are taken in
fresh or green state or are salted or dried. For fresh hides, a wasl
with pure water to cleanse them from dirt and blood is all that is ne
sary to prepare them for the next or "swelling" process. For sa
hides, a soaking in fresh water for from two to three days is necess
while for hard dried hides a longer treatment is necessary, first in w
which has been repeatedly used for softening and afterwards in f
water. This involves often a slight putrefaction of the coagulated a
men of the dry hide. To control this and prevent injury to the cor
of the hide a weak salt solution (five per cent.) is often used in this
longed softening. "Stocking" or kneading the hides with heavy
or breaking weights is also needed for heavy hides which have been d

2. *Unhairing and Swelling.*—These operations are carried out
gether. As the swelling proceeds the cells in which the roots of the
are embedded are softened, so that the hair is easily removed by mec
ical means. The horny epidermis is similarly softened, so that it ca
removed by the same means. The swelling may be effected by se
different methods: (1) by *sweating;* (2) by *treatment with acid*
liquor; (3) by *liming;* (4) by *treatment with sulphides of sodium*
calcium, etc. The sweating process now in use is the so-called "
sweating" method, and consists in hanging the hides in a moist c
ber kept at a uniform temperature of 60° to 70° F. (15° to 21° C.
that an incipient putrefaction ensues which attacks the soft parts o
epidermis and root-sheaths before materially injuring the coriu
leather-forming material. This method is that generally followe
sole-leather in this country and on the Continent of Europe, whi
England liming is more generally adopted. The swelling with acid
liquor depends upon the action of the acids which are present in
siderable quantity in old tan-liquors and their effect upon the conne
tissue. The swelling and unhairing by lime always adopted for
skins is also used for sole-leather hides in England. A view of the
pits and skins in process of softening by lime as carried out in mo
tanneries is shown in Fig. 94. The action of the lime upon the hi
in part a solvent one. The hair-sheaths are loosened and dissolve
the hardened epidermis swells up and softens, so that both come
more or less completely with the hair when scraped. The interce
substance, or coriin, as before stated, is also soluble in the lime-
and as this is removed the fibrous nature of the leather-forming
becomes more evident. The hides are generally put into several
pits in succession, in the first of which is old liquor with the w
alkaline reaction because of its partial saturation with organic ma

FIG. 94.



tion. The hides require to be turned and changed in position during this liming process as well as removed from one pit to the other. The swelling and unhairing by the use of alkaline sulphides largely used upon the Continent of Europe consists in taking a solution of sodium sulphide (made from alkali-waste by Schaffner and Helbig's process) and bringing it to a thin pasty condition with lime. This is then spread upon the hair side of the hides and they are packed together for five to twenty hours, when the loosened hair and sulphide paste are washed off and the hides left in water a time longer to "plump" or swell. Another process uses the sulphide in solution only. The hair having been loosened by one or the other of the means just described, it is to be removed by mechanical means. This is usually done on the "beam," a sloping frame of wood or metal, with a blunt two-handled knife, which pushes the hair downward and away from the workman. After the unhairing, the loose flesh and fat, the latter somewhat saponified by the lime, are next removed from the inner side of the hide by a sharp-edged knife. Hand "fleshing" is in many cases superseded by machine treatment, as the hide must not only be scraped but worked to force out the fat which remains in the loose tissue, as this would impede tanning. The hides after the fleshing are trimmed, and the inferior ends and edges are cut off with a sharp knife. They have still to be freed from the traces of lime which they have absorbed during the lime treatment before they can be put in the tan-liquors. This used to be done for sole-leathers, as it is still done for calf- and goat-skins, by means of "bate," or dung of animals, mixed with water, but that is now almost entirely replaced by the use of dilute acids which shall combine with the lime, when the lime salts so formed are to be washed out. Dilute sulphuric, phosphoric, and hydrochloric acids have been used (the latter being best because its lime salt is soluble), as well as the acid tan-liquors containing gallic, acetic, and lactic acids. The organic acids are considered to be safer for the hide than the inorganic.

3. *Tanning.*—The bark or other tanning material must be crushed and then ground to a state sufficiently fine to allow of the extraction of the tannic acid, and yet not so fine as to cause it to cake together in clayey masses. This is accomplished in bark-mills and disintegrators of various kinds, which need not be specially described here. The tan-house into which the cleansed and prepared hides or "butts" now come is provided with rows of pits running in parallel lines, which are to contain the butts during the treatment with the tan-liquor. The butts in most cases are first suspended in weak tanning infusions before they go into the first, or "handler," pits. The object of this is to insure the uniform absorption of tannin by the skins before subjecting them to the rough usage of "handling," which in the early stages of the process is liable to cause injury to the delicate structure of the skin. During this suspension the skins should be in continuous agitation to cause the tannin to be taken up evenly. Both the suspension and the agitation are accomplished generally by mechanical means. From the suspenders

OUTLINE OF TANNING PROCESS FOR SOLE-LEATHER.

s are taken either green, salted, or dried, and washed or soaked, as the case may be, with either water or weak brine to remove dirt and blood and to soften them, aided in the case of dried hides by "stocking," and useless ends trimmed off.

SOFTENED HIDES

ired generally either by sweating or by liming, and then worked on the beam.

UNHAIRED HIDES

raped or fleshed to remove flesh and fat, and then trimmed free from rough ends.

FLESHED AND TRIMMED HIDES

from lime by drench with "bate," or by washing with weak acids (acid tan-liquor).

CLEANSED HIDES READY FOR TANNING

aced first in suspender-pits, then in "handlers" with weak tan-liquors (15° to 20° bark), and finally in "layer"-pits with liquors increasing in strength from 35° to 70°, and stratified with bark.

ROUGH-TANNED HIDES READY FOR FINISHING

ushed, washed, and partially dried, sweated, and "struck." Again dried and rolled, and finally dried.

FINISHED SOLE-LEATHER SIDES.

SIDE-PRODUCTS:
- Spent tan and tan-liquors
- Waste liquors containing lime salts
- Scrap and skin for glue manufacture
- Hair sold for cheap blanket and cloth manufacture, or used with lime in plastering
- Scrap for glue manufacture, and refuse washings

the liquor. They are here treated with weak infusion of bark, commencing at about 15° to 20° by the barkometer, and are handled twice a day during the first two or three days. This may be done by taking them out, turning them over, and returning them to the same pit, or more generally by running them, fastened together, from one handler-pit into another. The treatment of the butts in the handlers generally occupies about six to eight weeks, by which time the coloring matter of the bark and the tannin should have "struck" through about one-third of the substance of the skin. Many of the butts will have become covered, moreover, with a peculiar "bloom" (ellagic acid) insoluble in water. They are now removed to the "layers," in which they receive the treatment of bark and "ooze," or tan-liquor, in progressive stages until the tanning is complete. Here the butts are stratified with ground oak-bark or valonia, which is spread upon each butt to the depth of about one inch, and a thicker layer finally on top. The pit is then filled up with ooze, which varies in strength from about 35° barkometer at the beginning to 70° at the end of the treatment. For heavy tannages six to eight layers are required, the duration of each ranging from ten days at the beginning to a month in the later stages. Each time the butts are raised they should be mopped on the grain to remove dirt and loose bloom.

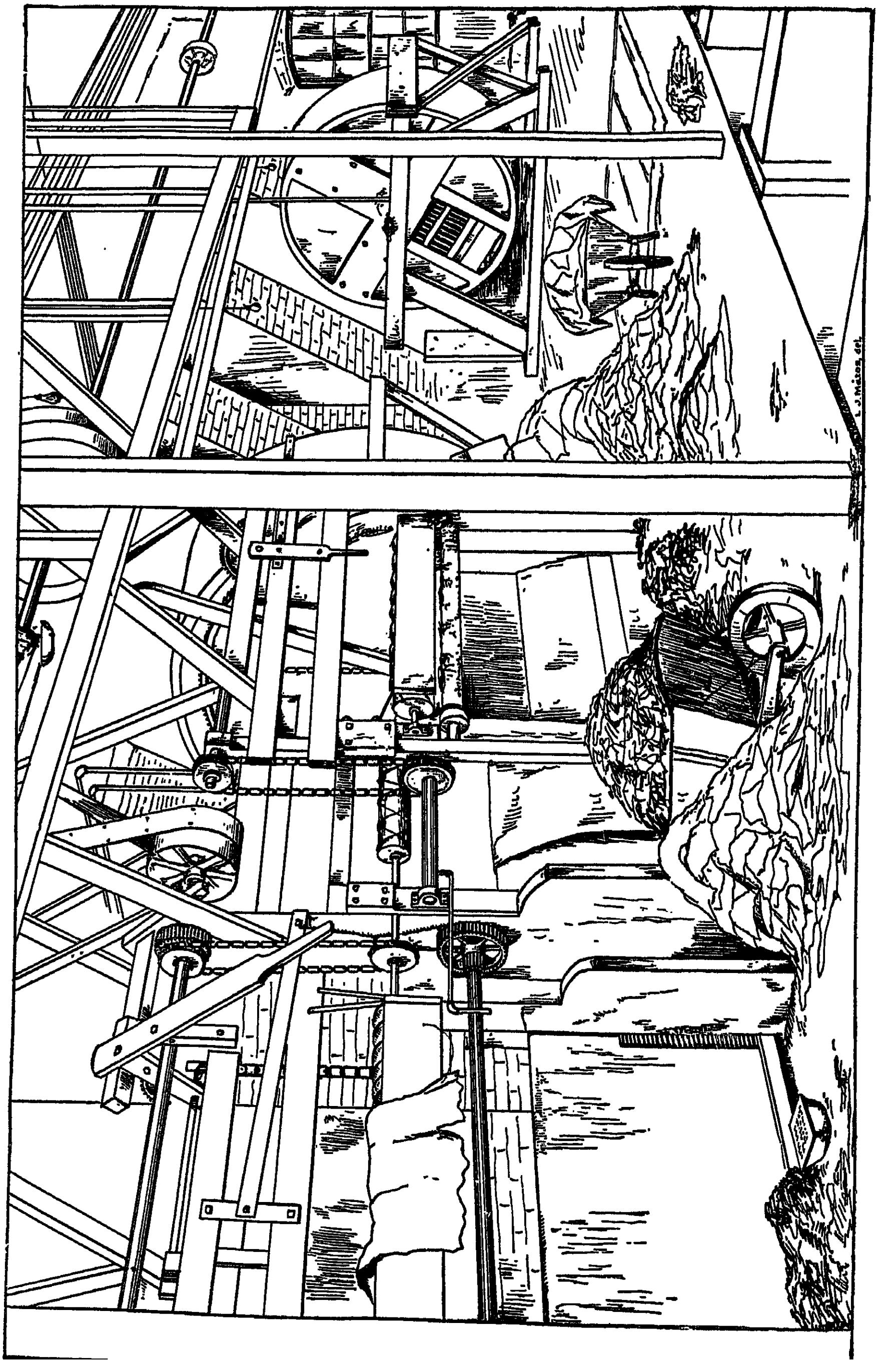
With the use of strong prepared extracts, especially with the aid of heat, the tanning process can be carried out in much shorter time than that just indicated, but the leather produced though hard is deficient in toughness and is liable to crack on bending sharply.

4. *Finishing.*—The butts after coming from the last layer are well brushed, washed in a clear liquor, and then thrown over a "horse" to drain before going to the drying-shed. They are then frequently oiled lightly on the grain so as to prevent too rapid drying out and hung on poles in the drying-loft. When about half dry, they are heaped upon the floor in piles and covered to sweat a little, which facilitates the operation of "striking," which next follows.

The "striking," which may be done by hand with a two-handled tool with triangular blunt edges or by machinery, is chiefly for the purpose of removing the deposit called bloom, although it somewhat flattens and stretches the leather. After a little further drying the butt is laid upon a flat bed of wood or metal and is rolled either by heavy hand-rollers or by the aid of machinery. The leather is then sometimes colored on the grain with a mixture of yellow ochre, with size and oil to give a gloss, and then brushed again, well rolled, and dried off gradually in a room slightly warmed by steam. The main outlines of sole-leather tanning are summarized on the accompanying diagram.

B. Upper and Harness Leathers.—For upper and harness leathers the hides of cows and smaller oxen are chosen. Fresh hides are, moreover, much better adapted for this class of leathers than dry salted or dry "flint" hides, as the utmost toughness and strength rather than

FIG. 95.



then "bated" in a bate of hen manure or treated with sour bran-liquor to completely remove the lime from the pores of the skin. The remaining portions of hair-sheaths and fat-glands are at the same time so loosened that they are easily worked out by a blunt knife on the beam. This final cleansing process is called "scudding." The action of the "bate" is considered by the best authorities to be a fermentative one, and the weak organic acids produced neutralize and remove the lime and at the same time soften the hide by dissolving out the coriin and probably also portions of the gelatinous fibre. "Stocking" is also used to assist in the softening and cleansing. These lighter tannages are also carried out very largely by the aid of gambier in combination with bark, valonia, mimosa, and myrobalans. The tanning liquors are often used at temperatures of from 110° to 140° F. (43° to 60° C.). The finishing of the light leathers requires much care in order to give them the proper softness and strength. They are alternately worked with a stretching-iron, or "sleeker," and rubbed with oil or with a mixture of dégras and tallow.

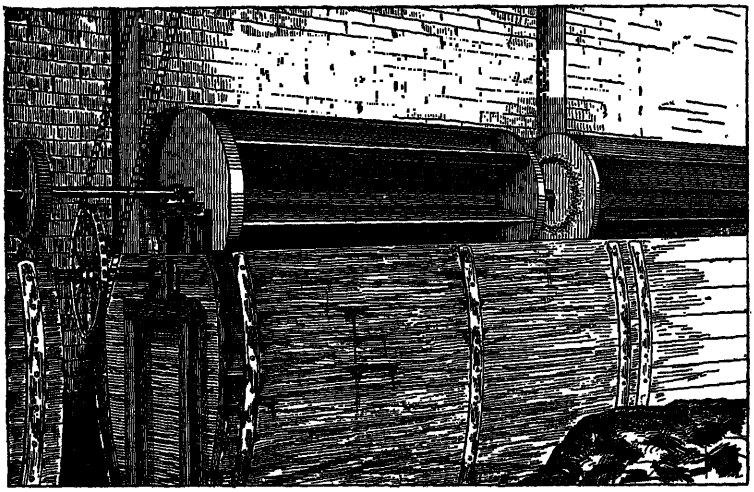
C. Morocco Leather.—This is generally made from goat-skins, although a cheaper variety is made from sheep-skins. The skins are softened and then unhaired by lime, to which a small quantity of arsenic sulphide is often added, whereby calcium sulphydrate and sulpharsenite are produced, which assist in softening the hair-sheaths and in giving the grain a higher gloss. A view of the unhairing machines and washing drums of a morocco tannery is given in Fig. 95. They are then bated with a mixture of dog's dung and water, known as the "puer." This is often followed by a treatment with bran to aid in removing the lime from the skins. A "scudding" or scraping with a blunt two-handled knife on both the grain and flesh sides then ensues to remove the last portions of lime salts and albuminoid matters. The tanning was formerly done with sumach and gambier, either in revolving paddle "tumblers," as shown in Fig. 96, or according to the English method, by sewing up the skins into bags partially filled with the sumach-liquor and then distended by air and floated in a large vessel of the same liquor. The bags are turned over constantly, and afterwards piled up in heaps. The sumach solution is thus forced through the pores of the skin, and the tanning is rapidly effected. The tanned skins are thoroughly washed and "struck," or scraped and rubbed, until smooth. After thorough drying they are again struck until thoroughly soft and smooth. This sumach tannage has been replaced in this country almost entirely by the chrome tanning, to be mentioned later.

D. Mineral Tanning or "Tawing."—Skins may be converted into a substance resembling leather, although in fact essentially different from it, by the action of alum and salt. There has been no chemical combination, however, analogous to that formed by the gelatine and tannic acid in the ordinary tanning processes, as the gelatine, alum, and salt can be again separated by treatment with water.

hairing, and fleshing, steeping in bran-water and working on the beam, are essentially the same as have been described already. The skins with the pores cleared of lime and sufficiently opened are then put into a kind of wooden drum or "tumbler," such as is used for washing skins and for treating morocco leather skins with sumach solution. For every two hundred skins some twelve pounds of alum and two and a half pounds of salt with twelve gallons of water are used.

The action is continued for a short time only,—about five minutes. They are then put into an emulsion of yolk of eggs with flour and water, and tramped and worked in this until it has been thoroughly absorbed. The skins are now hung upon poles to dry, after which they are stretched and softened by drawing them to and fro upon the "stake," a blunt steel blade set in upright position.

Fig. 96.



"Combination tanning," in which the joint action of gambier and alum is used, is also extensively followed.

Very different from this kind of mineral tanning is that introduced within the last few years under the name of "chrome tanning." It depends upon the power of chromium oxide (sesquioxide of chromium) of forming an insoluble compound with the gelatigenous fibre of the hide, furnishing a product which possesses in a high degree the waterproof character desirable for leather.

The process generally in use at present in this country involves treating the skins at first with a weak solution of bichromate of potash to which sufficient hydrochloric acid is added to liberate the chromic acid (of course pickled skins may be used without the necessity of adding free acid). After the skins have taken up a bright yellow color through their entire texture they are drained and transferred to a bath of sodium thiosulphate, to which some acid is added to liberate sulphurous acid, which reduces the further portion of sulphurous acid, until the whole of the chromic acid is reduced. Hydrogen sulphide liberated from alkaline sulphides has also been used as the reducing agent for bichromated skins, and still more recently electrolytic hydrogen developed upon the bichromated skin itself. In any case the reduction must take place rapidly, so that the potassium bichromate may be reduced superficially before it can "bleed" or diffuse out of the skins into the water of the reducing bath.

The leather so produced is of a pale bluish-green color, tough and flexible, and thoroughly resistant to water. Indeed, it is this latter property which distinguishes it from all other forms of leather, as the combination of the hide fibre or coriin with the chromium oxide is apparently more stable than its combination with tannin and yields less to boiling water, as has been shown in tests made by Professor Henry Procter, of Leeds. The leather can also be dyed and produced in a variety of colors, but the dyeing must be done before the leather dries, as its water-repellent character is such that once dried it cannot be wetted sufficiently to take up a full color.

Chrome-tanning processes involving the use of chrome alum and other salts of the sesquioxide of chromium as the basis of the tanning vat have been used, but apparently the combination does not take place so readily as where the chromium oxide is obtained in *statu nascendi* by reduction from the bichromate under the influence of reducing agents. Basic chromium salts, such as the basic chromium chloride, have also been proposed as mineral tanning agents, it being claimed that the dissolved chromium oxide is taken up by the hide-fibre at once and that a single bath only is necessary in this case. Such a basic salt is prepared by dissolving commercial chromium hydroxide (chrome green) in hydrochloric acid, adding sal soda until precipitation of the hydrate begins again. The solution is then nearly neutral, and contains an oxychloride or basic chloride in solution. Common salt is also added to prevent injury to the grain of the leather and to facilitate tanning. After the absorption of the chromium oxide is completed the skins are agitated in water containing suspended carbonate of lime to neutralize all traces of acid. They are then washed and are ready for the fat liquor. At the present time the bulk of the glazed kid made in the United States is chrome-tanned, two establishments in Philadelphia each turning out at present three thousand dozen chrome-tanned goat-skins daily.

Quite recently formaldehyde, applied either as gas or in aqueous solution, has been introduced as a tanning agent, the well-known coagulating power of the formaldehyde on animal tissue causing it to unite with the hide fibre to form an insoluble leather. All grades of leather, from sole leather to light morocco, it is asserted, can be made readily and very rapidly by this treatment. As yet, it is too early to judge conclusively of its quality and durability.

E. CHAMOIS AND OIL-TANNED LEATHER.—The skins tanned in this way are sheep- and calf-skins, and formerly chamois- and deer-skins.

shaved so that the oil can penetrate easily. The skins receive a thorough liming, so that the coriin is thoroughly removed from between the fibres, making them very soft. A bran-drench follows to remove the lime, and they are worked on the beam. The surplus water having been removed by pressing, while still moist they are oiled with fish, seal, or whale oil (to which some five per cent. of carbolic acid is often added). After being stocked for two to three hours, shaken out, and hung up for one-half of an hour to an hour to partially dry, they are again oiled and stocked, and this process is repeated until the skins lose their original smell of limed hide and acquire a peculiar mustard-like odor. The later dryings are frequently conducted in a heated room, and when the oiling is complete the skins are piled up, and the oxidation of the oil which has already commenced during the fulling and drying is completed by a sort of a fermentation, in which the skins heat considerably. This heating must be controlled so that the leather is not injured, and if necessary the pile of skins is turned. When the oxidation is complete the skins are of the yellow chamois leather color. To remove the surplus oil, the skins are again oiled, then thrown into hot water and wrung out. The semi-solid fat obtained this way is the dégras so much prized for currying purposes. Or the whole of the uncombined oil is removed by washing with soda or potash lye and then set free by neutralizing with sulphuric acid. The oil so obtained forms the "sod oil" of commerce. About half of the oil employed is retained by the skin, and cannot be removed even by boiling with alkalies. No gelatine is obtained by boiling with water, to which the chamoised skin is much more resistant than ordinary leather. The skins intended for gloves, etc., are bleached like linen, by sprinkling and exposure to the sun or with weak solution of potassium permanganate followed by sulphurous acid.

III. Products.

1. SOLE-LEATHER.—This is the heaviest and firmest variety of leather produced. It is made from the heaviest and thickest hides, and is valued for its fine grain and toughness. It retains the whole thickness of the hide, and no part is split off, so that it is not weakened by the loss of the flesh side. The tanning process is protracted until the whole hide is of uniform color throughout and shows the completed action of the tannin upon the interior of the hide.

2. UPPER AND HARNESS LEATHERS.—These are made from lighter hides, and are tanned for strength and flexibility rather than for weight, and are finished with care to give perfect pliability. They may be shaved or split leather. The black color and finish are put on upper leather by coating it with a mixture of lamp-black, linseed oil, and fish oil, to which tallow and wax and a little soap have been added. This is brushed on, allowed to dry, and then thoroughly rubbed in and the skin sized with a glue size.

3. MOROCCO LEATHER.—The true morocco leathers are manufactured

of the skins are fixed face to face with the flesh side inward, so that the dye acts upon one side of each skin only. After dyeing the skins are rinsed and drained, saturated with linseed oil to prevent too rapid drying, and then curried by repeated oiling or waxing and rubbing with a glass "slicker."

4. ENAMELLED OR PATENT LEATHERS.—These are leathers finished with a water-proof and bright varnished surface similar to lacquered woodwork. The name "enamelled" is generally applied when the leathers are finished with a roughened or grained surface, and "patent," or "japanned," when the finish is smooth. Thin and split hides are used. The skins after drying are prepared with a mixture of linseed oil and white lead and heated in closets to 160° F. (71° C.) or higher, then coated with a varnish of spirits of turpentine, linseed oil, thick copal varnish, and asphaltum, and heated again in closets or "stoves," as they are termed. This varnishing and heating are alternated, while the surface is meanwhile rubbed smooth with pumice, until the desired thickness is acquired.

5. RUSSIA LEATHER.—This variety is peculiar in its characteristic odor and ability to withstand dampness without any tendency to mould both of which qualities it owes to the currying with the empyreumatic oil of birch-bark. In Russia the skins are tanned with willow-bark, bu the imitation Russia leather made largely in Germany and England i tanned in the ordinary way with oak-bark. The birch-bark oil is rubbe into the flesh side of the tanned skins with cloths, care being taken no to apply so much as to cause it to pass through and stain the grain sid of the leather. The red color is given by dyeing with Brazil-wood o red saunders, and the diamond-shaped marking by rolling with groove rollers.

6. CHAMOIS LEATHER is a soft felt-like leather originally prepare from the skin of the chamois goat, but now made from other goat-skin and from the "flesh-splits" of sheep-skins. In these leathers the grai has practically been removed by scraping or "prizing" before the oil applied, so that it is uniformly porous and soft throughout. The acquire a yellow color and a peculiar odor, although they are ofte bleached whiter by subsequent treatment. (See preceding page.) T combination of oil with the hide makes chamois leather very resista to water and allows it to be washed without any change of nature.

7. WHITE-TANNED OR "TAWED" LEATHER.—Skins to be tanned wit the hair on, as sheep-skin rugs, etc., are always alum-tawed, as well light calf kid and glove leather. The glove leather obtained in th process has softness and considerable strength but is not thorough water-resistant, although the treatment with egg-yolk and flour-pas which follows the alum treatment tends to give it somewhat of th character.

8. CROWN LEATHER.—This is a variety which is intermediate betwe oil-tanned and tawed leather, being stronger than the first and mo water-resistant than the latter. The hides are first tawed with the alu

mixture of fat, ox-brain, barley-flour, and milk. They are then put into a revolving tumbler and rotated for a time, and again rubbed with the fat mixture and rotated if necessary. The leather readily becomes mouldy, but seems to be strong and specially adapted for belting.

9. PARCHMENT AND VELLUM.—The first of these is prepared from the skins of sheep and goats and the second from the skins of calves. The skins are washed, limed, unhaired, and fleshed, again well washed, and then stretched either upon hoops or upon a square wooden frame called the *herse.* On these the skin while wet and soft is stretched thoroughly. It is then scraped again free from the fleshy matters, the flesh side dusted over with sifted chalk or slaked lime and rubbed in all directions with a flat piece of pumice-stone. The grain side is also scraped with a blunt tool and rubbed with pumice. The skin is then allowed to dry on the frame in the shade, care being taken to avoid sunshine or frost. Very fine vellums are prepared with the finest pumice-stone.

10. DÉGRAS.—Among the side-products of the leather industry is one which is quite valuable for after-use. Dégras, originally obtained only as a side-product of the chamois-leather manufacture, is now also made specially on a large scale. The purest dégras is essentially an emulsion of oxidized fish oil produced by soluble albuminoids. That which is squeezed out of the skins after completion of the fermentation and heating, which makes the last stage of the chamois-leather manufacture (see p. 370), is the finest grade of dégras. That which is recovered by the aid of caustic alkalies and after-liberation with sulphuric acid is the second grade (sod oil). The great demand for dégras for currying purposes has led to the manufacture of it as a special industry. The skins employed for this purpose are treated exactly as are those in the normal chamois-leather manufacture, but are used over and over until no longer capable of taking up the oil. An artificial dégras has also been made from oleic acid, fat, and a little lime soap to which some tannic acid had been added.

Dégras is of semi-solid consistence and has a peculiar odor. Its specific gravity is higher than that of fish oil, and after dehydrating is from 0.945 to 0.955. Its characteristic constituent is the so-called dégras-former, which in a genuine dégras should range from twelve to twenty per cent. It is this which effects the ready emulsion with water. The dégras-former is a brown resinous saponifiable substance, fusing at from 65° C. to 67° C., and is distinguished from fats in that it is not precipitated when in alkaline solution by salt and is not soluble in petroleum-ether. According to Fahrion, the dégras-former is a mixture of oxy-fatty acids.

IV. Analytical Tests and Methods.

1. QUALITATIVE TESTS FOR THE SEVERAL TANNING MATERIALS.—H. R. Procter * has constructed the following table (see p. 373) showing the reactions of the several tanning materials.

2. ANALYSIS OF LIQUID AND SOLID TANNING EXTRACTS.—The method

REAGENT.	Myrobalans.	Divi-divi.	Valonia.	Oak-bark.	Chestnut-wood. (Extract.)	Hungarian larch. (Extract.)	Hemlock. (Extract.)	Mimosa-bark.	(Pegu.)	(Cuba.)	one per ce
Boiled with equal volume of sulphuric acid (1:9 water).	Pale deposit on cooling (ellagic acid).	Pale deposit on cooling (ellagic acid).	Slight pale deposit.	Slight pale deposit or turbidity on cooling.	Slight red deposit on cooling.	Yellow flocculent deposit, separates quickly.	Abundant red flocculent deposit.	Heavy red deposit on cooling.	Light-red deposit on cooling.	Reddish deposit on cooling.	Usually some pal deposit.
Bromine-water.	No precipitate.	No precipitate.	No precipitate.	Pale precipitate.	No precipitate.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	No preci tate.
Dilute ferric chloride.	Blue-black precipitate.	Dark-blue precipitate.	Blue-black precipitate.	Bluish-black precipitate.	Blue-black precipitate.	Dull-brown precipitate.	Dirty-green precipitate.	Full-brown precipitate.	Green-black precipitate.	Intense green color.	Blue-blac precipit
Add ammonia.	Brown precipitate.	Dark-red precipitate.	Red-brown precipitate.	Red-brown precipitate.	Dull-red precipitate.	Dull-red precipitate.	Reddened precipitate.	Purple color.	Dark-red precipitate.	Reddened.	Reddenec precipit
Solution of tartar emetic.	No precipitate.	Faint clouding.	No precipitate.	No precipitate.	Slight clouding.	No precipitate.	No precipitate.	White precipitate.	No precipitate.	No precipitate.	No precip tate.
Add ammonic chloride.	Light precipitate.	Dense precipitate.	Pale precipitate.	Whitish precipitate.	Pale precipitate.	Pale precipitate.	Slight pale precipitate.	Dense white precipitate.	Pale precipitate.	Faint clouding.	White pr cipitate.
Copper sulphate.	Faint clouding.	Slight green precipitate.	No precipitate.	Slight precipitate.	No precipitate.	Slight clouding.	Pale precipitate.	Slight precipitate.	Dense precipitate.	No precipitate.	No prec tate.
Add ammonia.	Dense dark precipitate.	Dense dark precipitate.	Dark-reddish precipitate.	Brown precipitate.	Dark-brown precipitate.	Deep-blue coloration.	Dark-green coloration.	Deep-red precipitate.	Deep violet coloration.	Dark-green color.	Brown cipitate
Lime-water.	Yellow precipitate turning greenish.	Yellow precipitate turning purple.	Yellow precipitate turning red-purple.	Brown precipitate.	Purplish-brown precipitate.	Dirty-brown precipitate.	Brown precipitate.	Slight reddish precipitate.	Slight clouding, soluble in excess.	No precipitate.	Pale prec tate, tu blue.
Ammonic molybdate in nitric acid.	Dirty-yellow precipitate.	Dark-greenish precipitate.	Dark-greenish precipitate.	Greenish precipitate.	Dirty-green precipitate.	Slight clouding.	Slight precipitate.	Brown precipitate.	Slight clouding, soluble in excess.	No precipitate.	Yellow color.
With sodic sulphide exposed to air on a tile.	Yellow color.	Yellow color.	Turns purplish-red.	Turns red.	Reddish precipitate.	No change.	No change.	Turns red.	Slight reddening.	No change.	No chan
Add concentrated sulphuric acid to one drop of infusion.	Yellow color.	Intense crimson.	Deep yellow.	Deep-red precipitate on dilution.	Dark brown.	Dark-brown or crimson.	Intense crimson.	Intense purple-red.	Deep red, no precipitate on dilution.	Dark brown or crimson.	Yellow.
Lead nitrate.	Light-yellow precipitate.	Dark-yellow precipitate.	Pale precipitate.	Brown precipitate.	Brown precipitate.	Pale precipitate.	Pale precipitate.	Clouding.	No precipitate.	Faint clouding.	White p cipitat
Cobalt acetate.	Buff precipitate.	Buff-pink precipitate.	Dirty-pink precipitate.	Brown precipitate.	Dirty-yellow precipitate.	Purplish precipitate.	Purple precipitate.	Brown precipitate.	Brown precipitate.	No precipitate.	Purple cipitat
Manganese acetate.	Yellow precipitate.	Yellow precipitate.	Dirty-yellow precipitate.	Brown precipitate.	Gray precipitate.	Slight clouding.	Slight precipitate.	No precipitate.	No precipitate.	No precipitate.	White p cipitat
Uranium acetate.	Dark-red color.	Dark-red color.	Dark-red color.	Dark-brown precipitate.	Dark-red color.	Slight darkening.	Light-brown precipitate.	Dark-red color.	Dark-red color.	Dark-red color.	Crimson color.
Ammoniacal picric acid solution.	No precipitate.	No precipitate.	Brown precipitate.	No precipitate.	No precipitate.	No precipitate.	Clouding.	No precipitate.	No precipitate.	No precipitate.	No pre tate.
Potassium dichromate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	Brown precipitate.	No precipitate.	Brown precipitate slowly formed.	Brown precipitate.	Brown color.	Brown precipitate slowly formed.	Brown cipitat

prescribed by the "Official and Provisional Methods of Analysis" of the U. S. Department of Agriculture is as follows: Dissolve in nine hundred cubic centimetres of water at 80° C. such a quantity of the extract as will give from 0.35 to 0.45 gramme of tannin in one hundred cubic centimetres of solution. Allow to cool slowly for from twelve to twenty hours at a temperature not below 20° C. and dilute to one litre.

a. Thoroughly mix the solution, immediately pipette one hundred cubic centimetres into a tared dish, evaporate and dry for sixteen hours in a combined evaporator and dryer at from 98° to 100° C. The result is the *total solids.*

b. Add seventy-five cubic centimetres of solution (kept at from 20° to 25° C. during filtration) to two grammes of kaolin (free from soluble salts), stir, let stand fifteen minutes, decant, and discard as much as possible of the supernatant liquid and again add seventy-five cubic centimetres of the tannin solution to the kaolin. Stir and pour immediately on a fifteen centimetre folded filter. Keep the filter full and the funnel and receiving vessel covered. Reject the first one hundred and fifty cubic centimetres of filtrate, evaporate and dry the next one hundred cubic centimetres (which must be as clean as practicable) as before under total solids. The residue is the *soluble solids.*

c. *Non-tannins.*—Prepare a sufficient quantity of hide powder in the following manner: Digest with twenty-five times its weight of water until thoroughly soaked; add three per cent. of chrome alum in solution, agitate occasionally for several hours and allow to stand over night. Wash by squeezing through linen, until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press if necessary, so that it contains from seventy to seventy-five per cent. of water and determine moisture (twenty grammes is a convenient quantity).

Add to two hundred cubic centimetres of the tannic solution such a quantity of the cut hide as contains from twelve to thirteen grammes of dry hide, shake for ten minutes in a shaker and squeeze immediately through linen, add two grammes of kaolin to the filtrate, stir and filter through a folded filter, returning until clear. Evaporate and dry one hundred cubic centimetres as in previous section. Correct the weight of the residue for dilution caused by the water contained in the cut hide powder. This non-tannin filtrate must not give a precipitate with a gelatine salt solution (one per cent. of gelatine and ten per cent. of salt).

d. The difference between the weight of the soluble solids and the corrected non-tannin residue is the weight of tannin in one hundred cubic centimetres of solution.

3. Quantitative Estimation of Tannin.—Of the numerous processes that have been described for this purpose, the only one generally accepted as capable of sufficient accuracy is Löwenthal's permanganate method. This depends upon the oxidation of the tannin, etc., by permanganate of potash in acid solution in the presence of indigo, which

matters besides tannins, it is necessary to separate these and titrate a second time in order to ascertain the volume of permanganate actually required by the tannin present. This separation may be effected by digestion with hide-raspings, or more conveniently by a solution of gelatine. In practice, a mixed solution of gelatine and common salt is used to which a small quantity of sulphuric or hydrochloric acid is added. Procter has also improved the process by adding kaolin, after the gelatine and salt have removed the tannin, for the purpose of facilitating filtration.

The special precautions and details of the process as generally practised and as modified by the Commission of German Technical Chemists are given in Allen.* The results are always stated in terms of crystallized oxalic acid to which the tannin is equivalent in reducing power upon the permanganate solution, and are gotten by the aid of the proportion $c : (a - b) : : 63 : x$, in which c represents the volume of permanganate needed for ten cubic centimetres of decinormal oxalic acid, a and b the volume of permanganate needed for the tanning infusion before and after precipitation of the tannin. The shaking method with chromed hide-powder, as given on the preceding page, is that generally used by American leather chemists. It is objected to, however, by European chemists, that the shaking introduces abnormal conditions so that some of the non-tannins are absorbed and that the result will vary somewhat with the degree of chroming of the hide-powder. Many workers, therefore, prefer the bell, as proposed by Procter, which is packed with the chromed hide-powder and the shaking is dispensed with. The most recent method adopted by the International Association of Leather Trade Chemists and officially promulgated by them is found in Trotman's Leather Trades Chemistry, p. 146.†

4. DETERMINATION OF ACIDITY OF TAN-LIQUORS.—A method for the determination of volatile and non-volatile organic acids and the sulphuric acid present in acid tan-liquors has been given by Kohnstein and Simand.‡ One hundred cubic centimetres of the tanning liquor are taken and eighty cubic centimetres distilled off, the residue diluted and again distilled with steam. The acidity of the distillate is determined and the result is the *volatile organic acids* reckoned in terms of acetic acid. To determine the non-volatile organic acids, eighty cubic centimetres of the tanning infusion is treated with three to four grammes of freshly-ignited magnesium oxide and the mixture left for some hours with frequent agitation, when the filtered liquid will be nearly colorles and perfectly free from tannin. The magnesia in solution is determined in an aliquot part of the filtered solution, and will be equivalent to th *total free acids* of the liquor exclusive of the tannic acid. Anothe portion of the filtrate is evaporated to dryness, the residue gently ignited moistened with carbonic acid water, and dried. It is then boiled wit distilled water and the solution filtered. The carbonate of magnesi

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* Allen, Commercial Organic Analysis, 2d ed., vol. iii, Part i, pp. 109-116.

† Leather Trades Chemistry, S. R. Trotman, 1908, J. B. Lippincott Co., Phila.

remaining insoluble represents the *total organic acids,* and can be more accurately determined by converting the magnesia into pyrophosphate and weighing. If these total organic acids be calculated in terms of acetic acid, and the previously found volatile acids, reckoned as acetic, be deducted, the difference represents the *non-volatile organic acids.* The magnesia remaining in the filtrate from the carbonate of magnesia is combined as sulphate, and when determined gives the *sulphuric acid* of the original liquors.

5. ANALYSIS OF LEATHER.—It is possible in the case of a leather to determine the percentage of moisture, total fats, water-soluble matter, insoluble fibre, and ash. In the case of mineral tannages, the quantitative determination of the chief constituents of the ash is of special importance. The fats are determined by extraction in a Soxhlet apparatus, as described in a previous chapter, carbon disulphide or petroleum-ether being used as solvent. The dry leather residue remaining after this extraction is digested for some hours with distilled water at 40° C. and then thoroughly extracted by fresh water at the same temperature. The washings are then brought to fixed volume and the residue determined in an aliquot portion. Uncombined tannin may also be determined in this aqueous extract by means of the hide-powder or Löwenthal method. The total ash is obtained by igniting a separate quantity of the leather. This is chipped in small fragments and ignited gradually in small portions in a platinum dish. After the leather swells and carbonizes, it can be burned completely at a dull-red heat without loss of the mineral salts.

B. GLUE AND GELATINE MANUFACTURE.

Glue is a decomposition product of many nitrogenous animal tissues. These lose on heating with water (analogous to starch-granules) their organized structure, swell up, and gradually go into solution. The solutions, even when very dilute, gelatinize on cooling, forming a jelly, which dries to a horny translucent mass. This mass is glue or gelatine, as the finer grades are termed. It dissolves in hot water to a liquid possessing notable cementing power. Neither the original solution obtained from the nitrogenous tissues nor the jelly formed from it on cooling have any cementing power. This is only acquired when the jelly has dried to the hard mass known as the glue. Two proximate principles seem to be present as characteristic in all preparations of glue: *glutin,* obtained chiefly from the hide and larger bones, and *chondrin,* from the young bones while yet in the soft state and the cartilage of the ribs, and joints. Of these, the former much exceeds the latter in adhesive power, and is therefore sought to be obtained predominantly in the glue manufacture.

I. Raw Materials.

1. HIDES AND LEATHER.—The corium of the animal hides (see p. 356) is the most important glue-yielding material to be had. Neither the epidermis nor the underlying fat-tissue contribute to the glue produc-

as "glue-stock" is made up of the trimmings from the ox, sheep, and calf-skins, the refuse of the beam-house, and scraps of parchment, which have been softened and unhaired by liming and are in condition for immediate boiling. Of still greater value are the so-called calves' heads which after liming and drying form a special article of commerce. The amount of glue obtainable from these various materials varies fron fifteen to sixty per cent. According to Fleck,* the scraps from the alum-tawing process yield forty-five per cent., those from the ox-hide thirty per cent., hare- and rabbit-skins and parchment trimmings fifty to sixty per cent., foot and tail pieces of oxen fifteen to eighteen per cent., other scraps from the tanneries, such as ear-laps of sheep and cows, sheep's feet, étc., thirty-eight to forty-two per cent. Scraps o bark-tanned leather, such as shoemaker's and saddler's trimmings, ar also available after a special treatment for the removal of the tannin (See p. 379.)

2. Bones.—The bones contain on an average nearly one-third (32. per cent.) of their weight of organic constituents, extracted by boiling and converted into glue, which, however, is inferior in adhesive powe to that prepared from animal skins. The soft bones of the head, shoulders, ribs, legs, and breast, and especially deer's horns and the bony cor of the horns of horned cattle, yield a larger quantity of glue than th hard thigh-bones and the thick parts of the vertebra, which are principally composed of calcium phosphate and require a more prolonged treatment to extract the glue-making constituents.

3. Fish-bladder.—The inner skin of the air-bladders of the severa varieties of sturgeon and cod furnishes a very pure glue substance, which on account of its purity is preferably used for culinary and medicina purposes, and is known as "isinglass." It is inferior in adhesive powe to hide-glue, but on account of its freedom from color, taste, and odor and its almost perfect solubility in hot water, commands a higher price It is used for food preparations, for clarifying wine, beer, and othe liquids. The chief production of isinglass is from the sturgeon in Russia, on the borders of the Caspian and the Black Sea.

4. Vegetable Glue.—Certain species of algæ (*Plocaria tenax* an others) found in Chinese and Japanese waters when cleansed and boile yield a product known under the several names of "Chinese isinglass and "agar-agar." Of similar character is no doubt the "algin" obtaine from Scotch algæ by E. C. C. Stanford.†

II. Processes of Manufacture.

1. Manufacture of Glue from Hides.—The hide trimmings an offal, if in the fresh state, must first of all be well limed,—that is, treate with milk of lime in pits for a period varying from ten to forty day according to the character and source of the hides, the lime being fr quently renewed. The lime softens and swells the hide-tissue, saponifi

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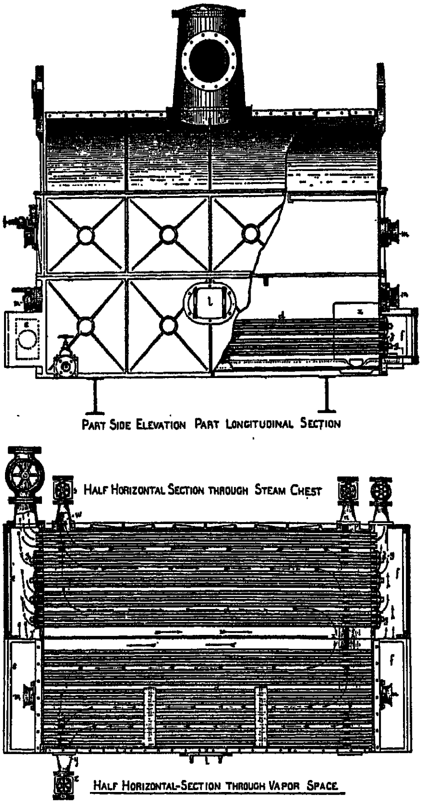
* Die Fabrikation Chemischer Producte, etc., p. 60.

the fats, and dissolves in large part the coriin, blood, and flesh-particles which do not form glue. The glue-stock is then thoroughly washed free from the lime, lime salts, and dirt, usually by putting it in nets or wicker baskets which are suspended in running water. The liming also serves to preserve the glue-stock in case it is not to be immediately worked up. After washing it is spread out to dry. The lime scum from the pits is often utilized in fertilizer manufacture. Caustic soda has also been used instead of milk of lime for this treatment. A short treatment with chloride of lime immediately after taking the stock out of the lime-pits has also been found to give the glue a bright color and excellent adhesive power. In recent years sulphurous acid has been used with advantage to cleanse and prepare the glue-stock, as it bleaches and at the same time swells the hide, at least as well as can be done by the lime.

FIG. 97.



PART SIDE ELEVATION PART LONGITUDINAL SECTION

HALF HORIZONTAL SECTION THROUGH STEAM CHEST

HALF HORIZONTAL-SECTION THROUGH VAPOR SPACE

The boiling and conversion of the glue-stock into solution may be effected by heating with water or with steam. The use of steam, either from closed pipes or direct steam from perforated pipes, greatly improves the extraction, shortening the time required and improving the quality of the product. Direct high-pressure steam blown into closed vessels has been found to be quite effective in rapidly melting down the glue-stock and producing a concentrated solution.

The use of vacuum-pans and the extraction by steam under reduced pressure and at lower temperatures has also been found very satisfactory in giving a good product in which the adhesive qualities of the gluten are in no way impaired. A form of vacuum pan designed for the evaporation of thin glue extraction liquors is shown in Fig. 97. The solution must be freed from any melted fat and lime soaps by skimming and from suspended impurities by settling, by filtering through linen bags, or clarifying by the use of bone-black. The addition of alum as sometimes practised has an injurious effect upon the adhesive power of the product. The residue of the glue-stock left unextracted is pressed nitrogen. The clarified glue solution is poured into shallow wooden moulds some six inches in depth, in which as it cools it gelatinizes to a brownish-yellow jelly containing from eighty to ninety per cent. of water. The block of jelly is then turned out upon a smooth table, previously moistened to prevent adherence, and sawed by horizontal wires into thin slabs, which are again cut by vertical wires into strips of the proper width.

The drying of the jelly is one of the most troublesome parts of the whole process, as it must take place rapidly so that the glue-making material may not spoil, as it is very prone to do while in the jelly form, and, on the other hand, the heat should not exceed 20° C. (68° F.). It may take place with this limitation of temperature in the open air, if the air is not too moist or too dry, both of which conditions are unfavorable. It is now generally effected in drying-rooms in which a current of warm dry air at the right temperature is made to circulate. As the surface of the cakes after drying is generally rough and dull, it is improved in appearance by moistening with warm water, brushing with a soft brush, and again drying.

2. Manufacture of Glue from Leather-waste.—Before attempting to boil the leather-waste to glue, the removal of all traces of tannic acid becomes absolutely necessary, since the retention of the smallest quantity prevents the animal tissue from dissolving in water. The waste must therefore be comminuted as thoroughly as possible to facilitate the complete removal of the tannic acid. This is done frequently in the "hollander" used for paper-pulp, and the washed and ground leather-waste then heated in a pressure-boiler under a pressure of two atmospheres with fifteen per cent. of its weight of slaked lime. After thorough washing, the residue is ready for use as glue-stock.

3. Manufacture of Glue or Gelatine from Bones.—Two methods have been followed for the extraction of gelatine, as the product is generally called in this case, from bones. The bones are either boiled under pressure, or they are treated with hydrochloric acid to remove the calcium phosphate and afterwards boiled for the extraction of the gelatine. The bones in either case are with advantage deprived of their fat first, which is done either by heating them with water and steam in boiler-shaped vessels, when the fat rises and can be skimmed off from the water, or in closed vessels with volatile solvents like petroleum benzine and carbon disulphide. The older process of extracting th gelatine by boiling the powdered bones with water under pressur decomposes a portion of the valuable material, and is now generally replaced by the method of treatment with hydrochloric acid for th removal of the calcium phosphate. The crushed bones are placed in wooden vats with dilute hydrochloric acid of specific gravity 1.05 (fort litres of acid to ten kilos. of bones) and allowed to remain for severa days. They are then placed in lime-water for a time, well washed, an boiled eight to ten hours with a large excess of water, or converted mor rapidly into gelatine solution by the aid of steam. The resulting solu

into forms to gelatinize. The manufacture of bone gelatine is frequently combined with the fertilizer manufacture, as the calcium phosphate extracted by the hydrochloric acid treatment contains from eighteen to twenty per cent. of phosphoric acid. The newer method of extracting the fat by volatile solvents yields five to six per cent. of fat without injury to the gelatine of the bones, while the older method of boiling out the fat yields from three to four per cent. only and tends to lessen the yield of gelatine.

4. Manufacture of Fish Gelatine.—The swimming-bladders of the fish are taken and thoroughly washed in water from all fatty and bloody particles. They are then removed and cut longitudinally into sheets, which are exposed to the sun and air to dry, with the outer face turned down upon boards of linden or bass-wood. The inner face of the bladders is pure isinglass, which when partially dried can with care be removed from the outer muscular layer. The isinglass layer, possessing a silvery white lustre, is taken either in sheets, rings, or horseshoe-shaped strips, etc., bleached with sulphurous acid, and then thoroughly dried.

A product distinct from isinglass and known as fish glue is prepared by boiling the skin and muscular tissue of fish, and more resembles ordinary hide glue in its adhesive properties, but is offensive in odor. It is prepared from the scales and skins of large fish like the carp by acting on them with hydrochloric acid as upon bones and then extracting with water.

III. Products.

1. Hide Glue is the variety which shows most strongly the adhesive property, and hence is that manufactured for joiner's and carpenter's use. Its color may vary considerably without any impairing of its adhesive power. It is rarely perfectly colorless or transparent. A gray to umber or brown-yellow color and translucent or partially opaque appearance is more usual. It should be clear, dry, and hard, and possess a glassy fracture. It should swell up but not dissolve in cold water, but dissolve in water at 62.5° C. (144.5° F.). Inorganic substances such as white lead) are intentionally introduced into some varieties, uch as the Russian glue, without injury to their adhesive power.

The variety known as "Cologne glue" is manufactured from scrap ide, which after liming is carefully bleached in a chloride of lime ath and then thoroughly washed.

"Russian glue," as stated, contains some inorganic admixture. It is f a dirty-white color, and contains from four to eight per cent. of white ead, chalk, zinc-white, or barytes.

"Size glue" and "Parchment glue" are both skin glues prepared ith special care.

2. Bone Glue (or Bone Gelatine).—Bones yield a product of less dhesive power than the glue of skins and tendons, but when carefully

therefore much used for culinary purposes and for medicinal appli tions, and for fining or clarifying beer, wine, and other liquids it largely superseded isinglass. The gelatine thus used must, however, absolutely tasteless and free from odor.

Bone gelatine is now made use of very largely in the manufact of gelatine capsules, etc., for medicinal uses, of court-plaster for app ing to wounds, and of gelatine emulsions with bromide and chloride silver for coating the photographic dry plates. Mixed with glycer it makes an elastic mass used for printers' rollers, for hectographs,

"Patent Glue" is a very pure variety of bone glue of deep da brown color. It is very glossy and swells up very much in water.

3. Isinglass (or Fish Gelatine).—This is the finest and best animal glues. The best isinglass should be pure white, nearly tra parent, dry and horny in texture, and free from smell. It dissol in water at from 35° to 50° C. (95° to 122° F.) without any resid and in cooling should produce an almost colorless jelly. The c mercial varieties of isinglass are the *Russian* (the best coming f Astrachan), *North American* (or *New York*), *East Indian, Huds Bay*, *Brazilian*, and *German* (or *Hamburg*).

4. Liquid Glue.—By the action of nitric or acetic acid upon a s tion of glue its power to gelatinize may be completely arrested w its adhesive power is not at all interfered with. Thus, if one kilo glue is dissolved in one litre of water and .2 kilo. of nitric acid of 36 be added, after the escape of the nitrous fumes we have a solution will not gelatinize on cooling, although it has the full adhesive po of the glue. Four parts of transparent gelatine, four parts of str vinegar, one part of alcohol, and a small amount of alum will yield an excellent liquid glue.

IV. Analytical Tests and Methods.

The nature of glue makes it rather a question of physical mechanical tests as to quality of a given sample than of chemical t

1. Absorption of Water.—Thus the relative amount of water a given sample will take up when laid in cold water is regarded moderately fair criterion of its quality. A weighed sample is laid twenty-four hours in cold water (not exceeding 12° C. (53.4° F. temperature), and at the expiration of that time the excess of w having been poured off, the jelly is weighed. Very good varieties (v gelatine prepared from bones) will take up thirteen times the qua of water in gelatinizing, second quality glue ten times, and inf grades only about six times the amount of water. At the same tim *consistency* of the jelly formed must also be taken into considera A firm jelly produced by the absorption of a large quantity of indicates a glue of the best quality.

Two observations are of value in this connection: first, glue dissolved and again dried is capable of drying out more thoroughly than glue obtained by a single drying; and, second, that hide glue on taking up smaller quantities of water becomes very soft and more difficult to weigh accurately than bone glue, which, with larger amounts of absorbed water, still forms a firm jelly. This difference in behavior alone is capable of giving an indication of the source of the glue.

2. Inorganic Impurities.—The presence of inorganic salts, as in the case of Russian glue, can be determined by the use of the appropriate reagents, and the amount also quantitatively determined.

3. Adulteration of Isinglass with Glue.—Isinglass is sometimes adulterated by rolling up sheets of gelatine (bone gelatine) between the layers of true isinglass and drying them in this condition.

Redwood and Letheby have observed that the ash of pure isinglass does not exceed .9 per cent., while glue contains from two to four per cent. of ash. An adulterated sample of isinglass gave Letheby 1.5 per cent. of ash.

On heating with water, true isinglass gives only a peculiar fish or algæ odor, while the adulterated isinglass gave a strong glue-like odor at once recognizable.

V. Bibliography and Statistics.

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STATISTICS.

1. IMPORTATIONS OF TANNING MATERIALS INTO THE UNITED STATES.–

	1908.	1909.	1910.
Gambier or terra Japonica (pounds)	26,681,791	30,992,245	25,572,6
Valued at	$894,752	$1,313,997	$1,255,2
Quebracho extract (pounds)	98,186,787	102,004,981	95,183,0
Valued at	$2,260,304	$2,740,530	$3,021,9
Quebracho-wood (tons)	48,871	66,113	80,2
Valued at	$612,971	$731,795	$1,058,6
Sumac (pounds)	8,576,091	10,974,613	13,632,8
Valued at	$227,611	$293,299	$299,1

2. IMPORTATION OF SKINS AND HIDES INTO THE UNITED STATES.—

	1908.	1909.	1910.
Goat-skins (pounds)	63,640,758	104,048,244	115,844,758
Valued at	$17,325,126	$26,023,914	$30,837,590
Sheep-skins (pounds)		48,906,326	67,406,131
Valued at		$8,276,637	$11,289,158
Calf-skins (pounds)		....	75,503,451
Valued at		....	$17,922,051
Cattle-hides (pounds)	98,353,249	192,252,083	285,468,821
Valued at	$12,044,435	$23,795,602	$42,306,943
Horse-skins (pounds)		....	19,512,397
Valued at		....	$3,080,484
All others (pounds)	120,770,918	99,347,672	12,258.753
Valued at	$25,400,575	$20,319,171	$2,418,414
Total (pounds)	282,764,925	444.554.325	608,619,028
	$54,770,136	$78,487,324	$112.247.836

3. Leather Industry According to Census of 1905.—

Raw materials used—	Number.	Value.
Hides and skins of all kinds	17,581,613	$89,126,593
Tanning materials—		
Hemlock bark (cords)	1,000,328	8,471,292
Oak bark (cords)	422,269	3,765,559
Gambier (bales)	80,610	752,347
Hemlock extract (barrels)	21,766	265,665
Oak-bark extract (barrels)	214,391	2,300,395
Quebracho		2,490,487
Sumac (tons)	7,958	338,614
Chemicals		2,847,441
All other materials used in tanning		3,798,244
Oil, dĕgras, tallow, etc., used in currying		3,807,186
Aggregate value of products		252,620,986

4. United States Exports of Leather.—

	1908.	1909.	1910.
Sole-leather (pounds)	31,189,897	33,002,746	38,332,247
Value	$6,593,950	$6,887,298	$8,307,880
Upper leather—			
Kid, glazed—value	2,879,969	3,593,909	10,926,255
Patent or enamelled—value	131,154	168,825	367,601
Splits, buff, grain, and other upper leathers—value	15,342,497	17,623,525	15,620,336
All other leather	2,004,022	2,159,542	2,192,103

5. Production of Glue and Gelatine in Different Countries.—

United States (Census of 1905), 50,000 tons, valued at $10,034,685.
Germany (1901) 32,000 tons, including 2000 tons of fine gelatine.
England (1907), 30,850 tons, valued at $2,530,000.

6. Exports of Glue and Gelatine from the United States.—

	1908.	1909.	1910.
Glue (pounds)	2,917,173	2,340,426	2,488,205
Valued at	$289,441	$244,751	$261,756

7. Imports of Glue and Gelatine into the United States.—

	1908.	1909.	1910.
Glue and gelatine (pounds)	6,731,943	6,610,894	8,821,554
Valued at	$629,032	$655,127	$861,888

CHAPTER XI.

INDUSTRIES BASED UPON DESTRUCTIVE DISTILLATION.

DESTRUCTIVE distillation has been defined as "the decomposition of a substance in a close vessel in such a manner as to obtain liquid products." It must be observed here that the word product is used to indicate something not originally present in the substance distilled. A body may be obtained in the liquid distillate which has merely been driven over by heat and which already existed in the original material in physical or mechanical admixture. Such a body is, to speak exactly, an *educt* and not a *product.*

The substances which are submitted to destructive distillation are in the main solids, as most classes of liquids are capable when heated with care of volatilization without decomposition, although such liquids as fatty oils, glycerine, etc., are decomposed if distilled under normal atmospheric pressure. (The cracking of petroleum is another illustration of destructive distillation of a liquid purposely brought about.) With solids, on the other hand, it is the exception rather than the rule to find one capable of melting and vaporizing unchanged in composition when distilled under normal atmospheric pressure. The same solid, moreover, if of at all complex molecular composition, may decompose quite differently and yield different sets of products according to the conditions which govern the distillation. The most important of these modifying conditions is that of temperature. "Low temperature" distillation and "high temperature" distillation as practised upon the same material (wood or coal, for example) may yield quite different results. The physical condition or mechanical subdivision of the substance also has an influence, although a subordinate one, upon the nature of the products. Solids, upon the destructive distillation of which important industries are founded, are wood, coal, shales, bones, and animal refuse. The distillation of shale has already been considered in connection with the mineral oil industry. (See p. 28.) The other industries will now be noted in succession.

A. DESTRUCTIVE DISTILLATION OF WOOD.

I. Raw Materials.

1. COMPOSITION OF WOOD.—The wood which is to be destructively distilled is composed, we may say in general terms, of woody fibre and plant-juice or sap, which is an aqueous solution of the substances, both nitrogenous and non-nitrogenous, which serve as the food for the living plant. The woody fibre is made up primarily of cellulose, which is in part changed into "lignin," as the incrusting substance is called. In

this latter substance differs from the pure cellu lose in containing more carbon and less oxygen and hydrogen. The amount of incrusting material varies, being more abundant in hard and heavy varieties than in light and soft kinds, and wood which contains it in the largest proportion gives the most acid and naphtha on distillation. The amount of water present in wood also varies not only according to the season of the year, but also quite widely in different woods cut at the same season. Thus, the following table of Schübler and Hartig shows the percentage of water of different trees taken at the period of minimum amount:

	Per cent. of water.		Per cent. of water.
Beech	18.6	Horsechestnut	38.2
Willow	26.0	Pine	39.7
Maple	27.0	Alder	41.6
Elder	28.3	Elm	44.5
Ash	28.7	Lime	47.1
Birch	30.8	Lombardy poplar	48.2
White hawthorn	32.3	Larch	48.6
Oak	34.7	White poplar	50.6
White fir	37.1	Black poplar	51.8

2. Effect of Heat upon Wood.—The effect of heat upon wood in the absence of air is a matter which is to be carefully noted as throwing light upon the results obtained in destructive distillation. It of course differs radically from the result of heating with free contact of air. Violette[*] found that when wood was carefully and slowly heated no decomposition occurred under 150° C., water only being given off; between 150° and 160° C. the loss was two per cent. of weight of the water-free wood; between 160° and 170° C., 5.5 per cent.; between 170° and 180° C., 11.4 per cent., and so on until at 280° C. 63.8 per cent. of volatile products had been driven off and 36.2 per cent. only of the water-free wood remained in the retort. The products given off in this period of heating between 150° and 280° are the valuable liquid products known as pyroligneous acid (acetic acid and its homologues), wood-naphtha or methyl alcohol, methyl acetate, acetone, furfurol, the mixture of phenols known collectively as "wood-creosote," and all other bodies of empyreumatic and tarry odor. Above 280° C., the decomposition proceeds somewhat differently, hydrocarbons, both gaseous and liquid, being formed. The additional percentage of loss by weight between 280° and 350° C. is only 6.5 per cent. of the water-free wood, but it makes from eighty to ninety volumes of gas. The decomposition continues from 350° to 430° C., when the total loss by weight amounts to eighty-one per cent. of the water-free wood. The products obtained within these limits of temperature are largely solid hydrocarbons like paraffin and high temperature products like benzene and toluene, naphthalene, phenol and cresol. From 430° to 1500° C. the additional loss of weight is only 1.7 per cent. We may sum up these results by saying that three periods may be distinguished broadly for this decomposition of wood by heat: first, from 150° to 280° C., the period of watery acid products; second,

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from 280° to 350° C., the period of gaseous products; and, third fro 350° to 430° C., the period of liquid and solid hydrocarbons. Violet found also great difference in the results according as the temperatu was slowly raised or as the wood was rapidly brought up to a high heat. Thus, one hundred parts by weight of wood slowly heated so th the temperature of 432° C. was only reached after six hours left 18. parts of charcoal, while one hundred parts of the same wood put into retort previously heated to 432° C. left only 8.96 parts by weight charcoal.

II. Processes of Manufacture.

1. DISTILLATION OF THE WOOD.—The primitive method of distilli wood devised by the charcoal-burners, in which the wood was piled up large heaps covered in by clay and turf so as to form a circular don shaped mound, is still followed in some heavily-wooded districts. course the charcoal is the only product sought in this case, and the ga ous and liquid products of the distillation are allowed to escape. Russia and Sweden the charcoal-burning in mounds is now frequen combined with the collection of tar, which as it condenses is made flow through inclined troughs, and is drawn off from below. In t way the valuable birch-bark tar (see p. 371) and kienoel (Russian tı pentine oil) are obtained. For a proper collection of all the produ of the destructive distillation of wood, however, it is essential that distillation be carried out in retorts provided with proper condensat apparatus. These retorts may be either set in horizontal or verti position, and may be either fixed or capable of removal for empty and recharging. It is found convenient in large works where it desirable to carry on the distillation continuously to have a series retorts connected with one and the same condensation apparatus heated by the same flues. This arrangement allows of the removal re-charging of a single retort without interrupting the working of others. In recent years the American and Canadian wood distill plants have been built with large horizontal retorts of such size t material in wagons of light skeleton construction can be run in o track prepared for them and the wood distilled without having to han it until completely changed to charcoal. Several such wagons, each taining one cord of wood cut to suitable length, are run in one back the other, and the doors of the horizontal retort closed and locked ti when the heating is begun. When the distillation is finished these containing the glowing charcoal are pushed from the farther end of retort into large cooling chambers of boiler iron, where they ren until cooled sufficiently to allow of their being brought into the without ignition. The heating should be conducted slowly at firs that the maximum yield of the low temperature products, acetic and methyl alcohol, may be obtained, then increased until the gas co off freely, and at the end of this stage of the decomposition a strengthened to drive over the high temperature products character

is beyond the record of the mercury thermometer, a pyrometer can be used or a small bar of metallic antimony which melts at 432° C. taken as indicator. Superheated steam has also been used as a means of accurately controlling the application of heat in the distillation, and it is said that the majority of European works manufacturing charcoal for gunpowder purposes use this method of distillation. The liquid which runs off from the condenser is at first wax-yellow in color, but becomes dark-colored, reddish-brown, and eventually nearly black and quite turbid. When allowed to stand at rest it soon separates in two sharply distinct layers,—the lower one of a thick tar, dark or perfectly black in color, and the upper one, which is much the larger in amount, is the crude pyroligneous acid and is reddish-yellow or reddish-brown in color. A light film of oil often covers, in part at least, this watery layer and represents the benzene hydrocarbons produced. We have already noted the fact that the yield of liquid products is affected greatly by the temperature used for distillation. Different varieties of wood also vary somewhat in the results obtained, even when distilled under the same conditions of temperature. This is illustrated in the following few examples: *

		Charcoal.	Tar.	Crude pyroligneous acid.	Containing actual acid.	Gases.
Red beech	slowly heated	26.7	5.9	45.8	5.2	21.7
	rapidly heated	21.9	4.9	39.5	3.9	33.8
Birch	slowly heated	29.2	5.5	45.6	5.6	19.7
	rapidly heated	21.5	3.2	39.7	4.4	35.6
Oak	slowly heated	34.7	3.7	44.5	4.1	17.2
	rapidly heated	27.7	3.2	42.0	3.4	27.0
Pine	slowly heated	30.3	4.4	41.0	2.7	24.4
	rapidly heated	24.2	9.8	42.0	2.4	24.1

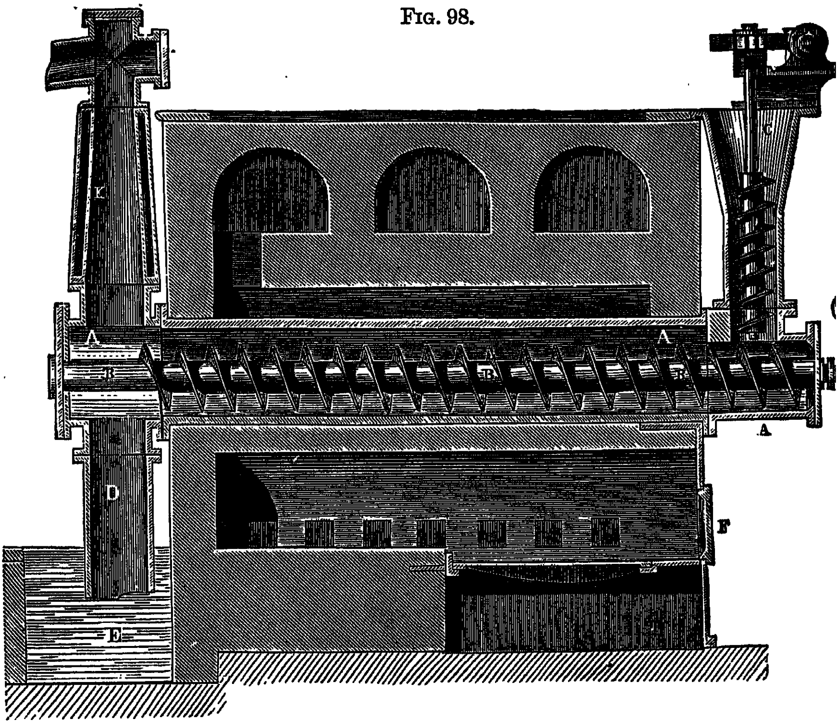
Beech-wood and foliage trees in general yield distinctly more acid than coniferous trees, but the latter yield more tar of terebinthinate character. The figures given above, it must be remembered, however, were gotten in experiments with small portions. In practice, working with larger quantities, the yield of several of the products is notably larger. The yield of wood-spirit, or methyl alcohol, varies from five-tenths to one per cent. of the weight of the dry wood.

The emptying of the retorts, if done as intended while the charcoal is yet glowing, involves the use of air-tight pits into which the charcoal can be emptied from the retorts and immediately covered with moist charcoal-powder to prevent loss by combustion. A form of apparatus for distilling the sawdust so abundantly produced in wood-working processes has been devised by Halliday, of Salford, England, and is said to work satisfactorily in practice. It is shown in Fig. 98. It consists of a horizontally placed cylindrical retort, *A*, within which revolves an endless screw, *B*. The sawdust is regularly fed in through the vertical pipe *C*, and falling upon the screw is kept moving at a uniform speed along the entire length of the heated retort. At the farther e the vapors and gaseous products of the distillation escape through a ascending pipe, *K*, leading to the condenser, while the powdered charco drops through the pipe *D* into water, where it is at once quenched.

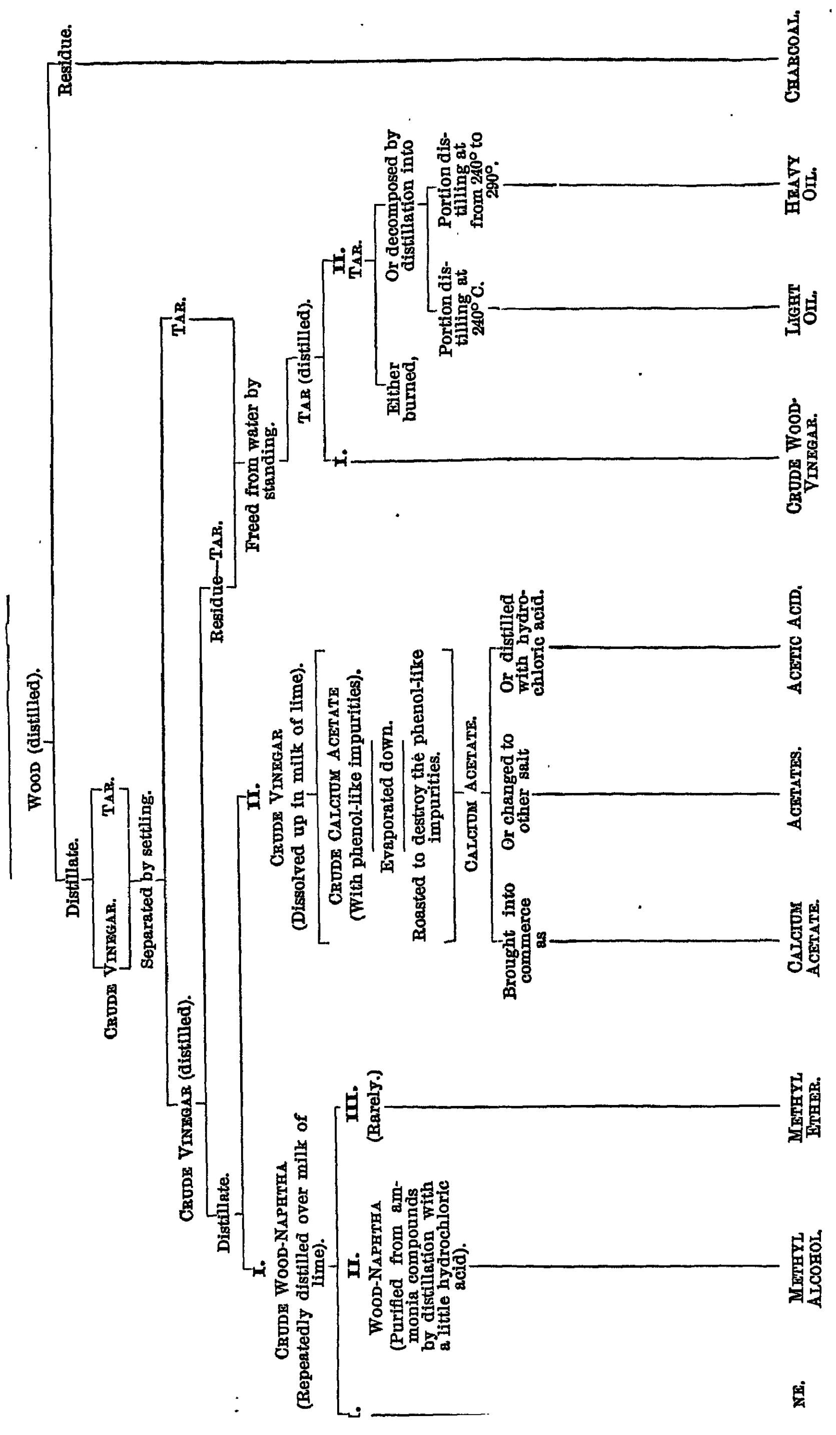
A general view of the products of the distillation of wood and the subsequent treatment is given in the accompanying diagram taken fro Post.*

2. TREATMENT AND PURIFICATION OF THE CRUDE WOOD-VINEGAR.- The brown aqueous solution poured off from the tarry layer (see abov has a strong empyreumatic odor, and contains, besides the acetic aci

FIG. 98.



methyl alcohol, acetone, and homologous ketones, allyl alcohol, ho logues of acetic acid (such as formic, propionic, butyric, and valeria acids), methyl acetate, acetate of ammonia and of methylamine, al hyde, furfurol, phenols, and other empyreumatic and tarry bodies. is not used in its crude condition except in the preparation of the cr pyrolignite of iron (*iron-liquor*) or in limited amount for impregnat wood. The first step towards purification is to separate the *wo naphtha* (the fraction containing the methyl alcohol, acetone, and met acetate) from the *wood-vinegar* (crude acetic acid), which is done distillation. Two procedures are possible here. Either to neutra the crude pyroligneous acid with milk of lime and then distil off volatile constituents only, using an iron still, or to distil the crude p


Wood (distilled).
Residue.
Distillate.
Crude Vinegar.
Tar.
Separated by settling.
Tar.
Crude Vinegar (distilled).
Residue—Tar.
Freed from water by standing.
Tar (distilled).
I.
II.
Tar.
Either burned,
Or decomposed by distillation into
Portion distilling at 240°C.
Portion distilling at from 240° to 290°.
Distillate.
I.
Crude Wood-Naphtha
(Repeatedly distilled over milk of lime).
II.
Crude Vinegar
(Dissolved up in milk of lime).
Crude Calcium Acetate
(With phenol-like impurities).
Evaporated down.
Roasted to destroy the phenol-like impurities.
Calcium Acetate.
Brought into commerce as
Or changed to other salt
Or distilled with hydrochloric acid.
I.
II.
Wood-Naphtha
(Purified from ammonia compounds by distillation with a little hydrochloric acid).
III.
(Rarely.)
NE.
Methyl Alcohol.
Methyl Ether.
Calcium Acetate.
Acetates.
Acetic Acid.
Crude Wood-Vinegar.
Light Oil.
Heavy Oil.
Charcoal.

ligneous acid from a copper still without neutralizing with lime. In the former case, while the wood-naphtha distils off, the tarry impurities of the crude pyroligneous acid remain with the lime salt in the still, and on evaporation a dark mass is obtained known as "brown acetate of lime.' In the latter case, after catching the wood-naphtha distillate, the receiver is changed and the crude acetic acid is also collected freed to a considerable extent from the tarry matter, so that on neutralizing with mill of lime and evaporating the product is a lighter salt known as "gray acetate of lime." The latter process is now more generally in use. The solution of the calcium acetate is evaporated in iron pans; the phenols and tarry products which volatilized with the acetic acid separate largely as scum and may be skimmed off, so that the residue of the evaporation is much purer than the product of the other method mentioned above.

If the brown acetate of lime has been obtained and is to be furthe worked for acetic acid, it is found necessary to roast it at a temperatur not exceeding 250° C. so as to drive off as much of the tarry impurity as possible without decomposing any of the acetate. If, on the othe hand, the gray acetate is taken, it is distilled from copper retorts with concentrated aqueous hydrochloric acid, taking care to avoid an excess The acetic acid distils over between 100° and 120° C., is clear in colo and has only a slight empyreumatic odor. Its specific gravity usuall ranges from 1.058 to 1.061, and it contains about fifty per cent. of pur acetic acid. If some water is added with the hydrochloric acid so tha the distilled acetic acid is more dilute, it tends to give a purer product as the liberated acetic acid cannot decompose any of the calcium chlorid before coming over. A good proportion is said to be one hundred part of acetate of lime, ninety to ninety-five of hydrochloric acid of 1.16 specific gravity, and twenty-five parts of water. The acetic acid s obtained has a slight empyreumatic odor. It may be freed from this b distilling with from two to three per cent. of potassium bichromate, o by filtration through freshly ignited wood charcoal.

The brown acetate of lime usually contains about sixty-eight sixty-nine per cent. of pure acetate, while the gray acetate contains fro eighty-five to eighty-six per cent. of true acetate.

In recent years it has been found practicable to prepare pure acet acid from the crude pyroligneous acid by making the sodium salt i stead of the lime salt. The sodium salt allows of purifying by recry tallization, and can also be fused without decomposition. Glacial acet acid is generally made by distilling the anhydrous and fused sodiu acetate with concentrated sulphuric acid.

Rohrmann has recently developed a process by which it is possib to make ninety per cent. or even glacial acetic acid direct from the cru acetate of lime in one operation. He uses a column still provided w Lunge-Rohrmann plates, over which concentrated sulphuric acid is ma to trickle. This meets the ascending acetic vapors and dehydrates the They pass over into a condenser, while the empyreumatic vapors a drawn off by a warm-air current which connects with the column. Wh acid can be brought to eighty per cent.; when sulphuric acid is used, one hundred per cent. acid can be obtained.

3. PURIFICATION OF THE CRUDE WOOD-SPIRIT.—The wood-spirit forms the first fraction when the crude pyroligneous acid is distilled, and amounts to perhaps one-sixth of the latter in bulk. It is usual to collect, however, until the hydrometer reading of the distillate, which begins at about .900, has risen to 1.000 or a little beyond. This distillate forms a greenish-yellow liquid of unpleasant odor and contains many impurities besides the acetone and methyl acetate, the chief substances which are present with the methyl alcohol. Milk of lime is first added and allowed to stand with the liquid for several hours. The mixture heats up quite distinctly as the lime combines with any free acid and begins to decompose the methyl acetate and other ethereal compounds of acetic acid, small quantities of ammonia often being given off. It is then distilled by connecting it with a column rectifying apparatus. (See p. 244.) The distillate thus obtained, of about .816 specific gravity, is colorless at first but gradually darkens in color, and if diluted with water becomes milky from separated oily hydrocarbons and ketones. It is therefore diluted down with water to about .935 specific gravity and allowed to stand until this oily impurity rises to the top in a distinct layer. The diluted spirit is again distilled over lime once or twice with a rectifying column and so brought to ninety-eight or ninety-nine per cent. strength. The acetone impurity, however, is not removed by any of these rectifications, as the boiling-points of acetone (56.4° C.) and methyl alcohol (55.1° C.) do not allow of their separation in this way. To remove the acetone a number of methods have been proposed. The methyl alcohol may be converted into the solid chloride of calcium compound, or the oxalate of methyl and the acetone having been removed by careful heating, the methyl compound is decomposed by water or alkali. Or the methyl alcohol is distilled over chloride of lime, which reacts with the acetone to form chloroform. The passing in of chlorine in order to convert the acetone into high-boiling chloracetones, which are then separated from the methyl alcohol by distillation, has also been proposed.

4. TREATMENT OF THE WOOD-TAR.—The tar which has separated from the crude pyroligneous acid by settling, and that which has risen and been skimmed off in the neutralizing of the acid, are united and submitted to distillation in horizontally-placed iron retorts, which are set at a slight inclination. At first acid-water comes over, then light oils, and finally heavy oils until no more will distil. The pitchy residue is run out while hot, so that it does not adhere to the walls of the retort. The relative amounts of the several fractions from the tar depend upon the nature of the wood used in the original distillation and upon the way that distillation has been carried out. Hard woods usually give a tar which, according to Vincent, when redistilled yields as follows:

Aqueous distillate (wood-spirit and pyroligneous acid)	10 to 20	per	cent.
Lighter oily distillate (specific gravity .966 to .977	10 to 15	"	"
Heavy oily distillate (specific gravity 1.014 to 1.021)	15	"	"
Pitch	50 to 65	"	"

The oily distillates are washed with weak soda to remove adherin acid and then carefully rectified, when the oils coming over under 150° C are collected for solvent and varnish-making purposes, those betwee 150° and 250° C. collected as creosote oils, and those above 250° C. use for burnings oils.

The creosote oil, which is the most valuable part, is thoroughly agitated with strong caustic soda solution, the aqueous layer drawn off mixed with sulphuric acid, and allowed to stand for a time at rest, whe the creosote oil separates out. This is best driven off by steam distillation and again rectified finally from glass retorts.

Stockholm tar, so largely used in ship-building, is the product of rude distillation of the resinous wood of the pine.

North Carolina pine-tar is also the product of a distillation of th pine. The billets of pine-wood are piled in heaps like a charcoal-burner' mound, though not so large, covered in with clay and turf, and lighte from the top. The resin or tar distils downward and runs off throug inclined troughs previously fixed for it. It is obvious that the composition of both the Stockholm and the North Carolina tar differs notabl from that of wood-tar distilled in retorts from hard woods. This composition will be referred to later.

III. Products.

1. Pyroligneous Acid and Products therefrom.—The crude aci as obtained in the distillation is a clear liquid of reddish-brown colo and strong acid taste, with a peculiar penetrating odor described a empyreumatic, and now known to be due largely to the furfurol it contains. It possesses a specific gravity of from 1.018 to 1.030 and contain from four to seven per cent. of real acetic acid. *Pyrolignite of iron* (iro or black liquor) is a solution of ferrous acetate with some ferric acetate prepared by acting upon scrap-iron with crude pyroligneous acid. I forms a deep-black liquid, and is concentrated by boiling to 1.120 specifi gravity, when it contains about ten per cent. of iron. It is extensivel used by calico-printers. *Brown and gray acetate of lime* have bee already referred to. Other technically important acetates are *lead acetate* (sugar of lead), used in the preparation of the alum mordants an the lead pigments; *copper acetate,* the basic salt of which is known a "verdigris;" *aluminum acetate,* the solution of which is used in calicoprinting under the name of "red liquor."

Pure acetic acid is a colorless acid liquid with pungent smell an taste. It crystallizes when chilled in large transparent tablets, meltin at 16.7° C., whence the name "glacial acetic acid." Its specific gravit at 15° C. is 1.0553, and it boils under normal pressure at 119° C.

2. Methyl Alcohol and Wood-spirit.—As before stated, crude wood spirit is a complex liquid and contains many impurities. The percentage of real methyl alcohol may rise to ninety-five per cent., but mor generally ranges from seventy-five to ninety per cent. Some impur

varnish-making, but does interfere with its use in the aniline-color industry, where a very pure methyl alcohol is needed for the manufacture of dimethyl aniline. The methods of freeing methyl alcohol from the two chief impurities, methyl acetate and acetone, have already been referred to. Pure methyl alcohol has a purely spiritous odor, a specific gravity of .7995 at 15° C., and boils at 55.1° C. It is miscible in all proportions with water, ordinary alcohol, and ether.

3. ACETONE.—This substance is of interest as always produced in the distillation of wood, and hence present in the crude wood-spirit. The acetates yield it as the chief product when submitted to dry distillation, and the vapors of acetic acid distilled over porous baryta at a temperature of from 350° C. to 400° C., it has been found by Dr. Squibb, will also readily yield acetone. One hundred kilos. of forty per cent. acid will give from twelve to thirteen kilos. of acetone. At present it is made on a large scale by distilling the gray acetate of lime in iron stills provided with mechanical agitation at a temperature of about 290° C. When purified, it is a colorless liquid of peculiar ethereal odor and burning taste, and, like methyl alcohol, is miscible in all proportions with ether, alcohol, and water. It is an excellent solvent for resins, gums, camphors, fats, and pyroxyline, or gun-cotton. It does not form a compound with dry calcium chloride and can thus be separated from methyl alcohol when in admixture with this latter. Chlorine and iodine in the presence of an alkali react with acetone to form chloroform and iodoform.

4. CREOSOTE.—Wood-tar creosote is a strongly refracting liquid, which is colorless when freshly distilled but gradually acquires a yellow or brown color. It has a smoky aromatic odor, which is very persistent and is quite distinct from that of carbolic acid. It has a specific gravity ranging from 1.030 to 1.080, and boils between 205° and 220° C. It is a powerful antiseptic, and is largely used to preserve meats, etc. It differs from coal-tar creosote in containing relatively little common phenol (carbolic acid) and relatively large amounts of higher phenols, such as phlorol, $C_8H_9.OH$, guaiacol, $C_7H_7O.OH$, and creosol, $C_8H_9O.OH$.

5. PARAFFIN.—This mixture of solid hydrocarbons, as already said, occurs in the higher boiling distillate gotten from wood. It is of interest o recall that paraffin was first discovered by Reichenbach in beech-wood ar. At present, however, the extraction of paraffin from wood-tar is not to be thought of because of the cheapness of its production from petroleum and bituminous shales. It has been already described under he chapter on Petroleum. (See p. 33.)

6. CHARCOAL.—We have already shown in the table of results of low and rapid distillation of wood (see p. 388) that the relative amount of charcoal depends upon the manner of heating, being larger with gradual application of heat and smaller with rapid heating. The properies and chemical composition of the charcoal are similarly dependent upon the temperature to which the wood is heated. Wood is stated to become brown at 220° C., at 280° C. it becomes a deep brownish-black nd begins to be friable, and at 310° C. forms an easily friable black

with a metallic sound when struck. The accompanying table from Violette shows the gradual change in the composition of charcoal prepared at different temperatures from the same kind of wood (buckthorn):

	Heated to	Carbon, per cent.	Hydrogen, per cent.	Oxygen, nitrogen, and loss.	Ash, per cent.
Dry wood	150° C.	47.51	6.12	46.29	0.08
Charred wood	260° C.	67.85	5.04	26.49	0.56
Red charcoal	280° C.	72.64	4.70	22.10	0.57
Brown charcoal	320° C.	73.57	4.83	21.09	0.52
Dull black charcoal . . .	340° C.	75.20	4.41	19.96	0.48
Lustrous black charcoal .	432° C.	81.64	1.96	15.25	1.16
Extreme white heat . .	1500° C.	96.52	0.62	0.94	1.95

IV. Analytical Tests and Methods.

1. Assay of Pyroligneous Acid and Crude Acetates.—The crude pyroligneous acid, as before stated, contains from four to seven per cent. of real acetic acid. Its strength may be ascertained by titration with standard alkali, using phenol-phthalëin as an indicator. If the liquid is too dark to allow of the end reaction being readily seen, it can be diluted sufficiently, as the reaction will still be sufficiently delicate. In the absence of sulphates in the sample, the acetic acid can be determined by adding excess of pure precipitated barium carbonate to the solution, filtering, and determining the barium in the filtrate by the aid of sulphuric acid.

As the pyroligneous acid is largely converted into calcium acetate in the process of purifying, the analysis of the brown or gray acetate of lime as a common cemmercial product becomes of some importance. This commercial acetate may contain from sixty-five to eighty per cent. of true acetate of lime, with carbonate of lime, so-called "tar-lime," and empyreumatic matter as chief impurities. The acetic acid determination may be made by different methods, but the most accurate according to the experience of the author is the distillation method, as suggested by Stillwell and Gladding. One gramme of the sample of acetate of lime is placed in a small distillation bulb or flask with a long neck, a little distilled water added, and then a solution of five grammes of glacial phosphoric acid dissolved in ten cubic centimetres of water. The flask is then heated to distil off the acetic acid, care being taken to avoid spurting and mechanical carrying over of any of the phosphoric acid. When the contents have nearly gone to dryness, some twenty-five cubic centimetres of distilled water are introduced and the distillation repeated. If this is done some three or four times, the distillate will be found to be free from acid reaction. The combined distillate is then brought to definite volume and titrated with decinormal soda solution, using phenol-phthalëin as indicator.

2. Determination of Methyl Alcohol in Commercial Wood-

of wood-spirit are allowed to drop slowly upon fifteen grammes of phosphorus di-iodide placed in a small flask of some thirty cubic centimetres capacity. This is connected with an inverted condenser and cooled externally while the reaction takes place. Five cubic centimetres of a solution of one part iodine in one part of hydrogen iodide of 1.7 specific gravity is then added and the mixture gently digested for a quarter of an hour, when the condenser having been turned downward the iodide of methyl formed is distilled off. It is collected in a graduated tube divided into one-tenth cubic centimetres, washed with some fifteen cubic centimetres of water with vigorous agitation, allowed to settle, and the volume read off. Five cubic centimetres of pure and perfectly dry methyl alcohol should give 7.45 cubic centimetres of iodide of methyl.

3. DETERMINATION OF THE ACETONE IN COMMERCIAL WOOD-SPIRIT.—This may be done by either the Kraemer and Grodzki gravimetric method or the Messinger volumetric method, both of which depend upon its quantitative conversion in the presence of iodine and caustic alkali into iodoform. In the former case, one cubic centimetre of the sample of wood-spirit is mixed with ten cubic centimetres of a double normal solution of caustic soda (eighty grammes to the litre), and to the mixture, after thorough agitation, is added five cubic centimetres of a solution containing two hundred and fifty-four grammes of iodine and three hundred and thirty-two grammes of potassium iodide to the litre. The iodoform which separates on agitation is dissolved by the addition of ten cubic centimetres of ether free from alcohol. An aliquot portion of the ethereal layer is then pipetted off into a tared watch-crystal, and the iodoform remaining after evaporation is weighed. Three hundred and ninety-four parts of iodoform correspond to fifty-eight parts of acetone. More accurate is the Messinger volumetric process. In this, twenty cubic centimetres (or thirty cubic centimetres in samples rich in acetone) of normal potash solution and one or two cubic centimetres of the wood-spirit in question are shaken together in a stoppered 250-cubic-centimetre flask and a known quantity (twenty or thirty cubic centimetres) of a one-fifth normal iodine solution added. The mixture is shaken until the supernatant liquid clears perfectly on momentary standing, hydrochloric acid of 1.025 specific gravity is added in amount equal to the potash solution before used, and excess of decinormal sodium thiosulphate run in. Starch paste is then added, and the excess of sodium thiosulphate titrated with one-fifth normal iodine solution. If r be the volume in cubic centimetres of the iodine solution required to combine with the acetone, and n the volume in cubic centimetres of the methyl alcohol taken, then the quantity of acetone by weight in one hundred cubic centimetres of the sample is equal to $\frac{r \times .193345}{n}$.

4. QUALITATIVE TESTS FOR WOOD-TAR CREOSOTE.—The U. S. Pharmacopœia gives the following tests as enabling one to distinguish between wood-tar creosote and coal-tar creosote:

1. On stirring together

2. If one volume of creosote be mixed with one volume of ninety-five per cent. glycerine, a clear mixture will result from which a creosotic layer equal to or greater in volume than the creosote employed will separate on the addition of one-fourth volume of water.

3. On adding to ten cubic centimetres of a saturated aqueous solution of creosote one drop of ferric chloride test solution, the liquid develops a clear violet-blue color, which is very transient; it then clouds almost instantly, the color passing rapidly from a grayish-green into a muddy-brown, with finally the formation of a brown precipitate.

4. If one cubic centimetre of creosote be cautiously and gently shaken with two cubic centimetres of petroleum benzine and two cubic centimetres of freshly-prepared barium hydroxide solution until a uniform mixture is produced, upon complete separation three distinct layers are visible, the middle one of which contains the creosote, unaltered in appearance; while the petroleum benzine should not be blue or muddy and the aqueous layer should not have acquired a red tint (absence of cœrulignol and other high-boiling constituents of wood-tar).

B. DESTRUCTIVE DISTILLATION OF COAL.

I. Raw Materials.

Probably the most important industry involving the destructive distillation of coal is the manufacture of illuminating gas. The classes of coals employed for the purpose are confined to those varieties which are bituminous in their nature, yielding when distilled volatile hydrocarbons in varying quantity. The uncombined or "fixed carbon," with the mineral constituents originally present in the coal, remaining after the distillation comprise coke.

Bituminous Coals have the property, not possessed by the anthracites, of softening and apparently fusing when subjected to a temperature below that at which combustion would take place. This fusion indicates the commencement of destructive distillation, when both solid, liquid, and gaseous carbon compounds are formed. Bituminous coal is essentially a coking coal, and as such is, to a very great extent, employed in the coking regions of Western Pennsylvania. It is black or grayish-black in color, of a resinous lustre, and somewhat friable, being easily broken into cubical fragments of more or less regularity; upon ignition it burns with a yellow flame. When it is heated to bright redness in retorts or ovens, free from the access of air, the volatile matter, before mentioned, carbon compounds of hydrogen and of oxygen, with water pass off. Coals having a large percentage of hydrogen will yield more volatile substances at the temperature of distillation and less carbonaceous residue than others which may contain less hydrogen and more carbon,—approaching anthracite in composition.

Coking and Non-coking Coals are quite similar in chemical composition; the coking varieties contain less volatile matter, however, than th non-coking; the latter do not possess the property of fusing to a com has no commercial value unless it is obtained from large pieces of the coal.

Cannel Coal is much more compact than gas or coking coals, duller in appearance, possessing a grayish-black to brown color, and burning with a clean candle-like flame. It does not soil the hands, and is not readily fractured. It is capable of taking a high polish, and can be cut or turned into articles for use or ornamentation. Cannel coal occurs in large quantities in West Virginia, and near Glasgow, Scotland, in Lancashire, England, and at other localities. Destructively distilled, it yields a larger amount of volatile matter and ash, with much less coke, than the bituminous coals.

Brown Coal, or Lignite, appears to occupy an intermediate position between the bituminous coals and wood. It retains the ligneous structure of the material from which it is formed,—hence the name *Lignite.* The vegetable remains in a great many cases are quite distinct. The color varies from yellowish-brown in the earthy, to black in the more compact, coal-like varieties. The percentage of carbon contained is low, fifty to eighty per cent., though rarely exceeding seventy per cent., while the hydrogen is from 4 to 6.85 per cent. Oxygen and nitrogen are present in variable quantities from 7.59 to 36.1 per cent. The ash in good qualities is low, in earthy specimens is high, in many cases exceeding fifty per cent. Lignite does not yield coke. Aside from being utilized as fuel in the several localities where it is found, for both domestic and industrial purposes, it has been distilled for volatile constituents in Saxony.

Peat, or Turf, occurring in large areas in Ireland and in some parts of Europe, consists of the decayed remains of certain forms of plants. It has been, according to Mills, destructively distilled for tarry products, the industry, however, being no longer profitable.

The following tables, taken from the Reports of the Second Geological Survey of Pennsylvania, show the analyses of some of the more important varieties of American gas coals, coking coals, and non-coking, or block coals.

I. Gas Coals.

	WESTMORELAND COAL COMPANY.			PENNSYLVANIA GAS COAL COMPANY.		
	South Side Mine.	Foster Mine.	Larrimer, No. 2.	Irwin, No. 1.	Irwin, No. 2.	Sewickley.
Water at 225° . .	1.410	1.310	1.560	1.780	1.280	1.490
Volatile matter .	37.655	37.100	39.185	35.360	38.105	37.153
Fixed carbon. .	54.439	55.004	54.352	59.290	54.383	58.193
Sulphur	0.636	0.636	0.643	0.680	0.792	0.658
Ash.	5.860	5.950	4.260	2.890	5.440	2.506
Total	100.000	100.000	100.000	100.000	100.000	100.000
Coke, per cent. .	60.935	61.590	59.255	62.860	60.615	61.357
Fuel ratio . . .	1:1.47	1:1.48	1:1.38	1:1.67	1:1.42	1:1.56
	McCreath	McCreath	McCreath			

II. *Coking Coals.*

	Connellsville, Frick & Co.	Bennington, Cambria Iron Company.	Broad Top, Barnet.	Broad Top, Kelley.	Cumberland.	Huntingdon County, [illegible] Colliery.
Moisture	1.260	1.400	. . .	. . .	1.10	0.250
Volatile matter.	30.107	27.225	16.00	19.68	15.30	14.510
Fixed carbon .	59.616	61.843	74.65	71.12	73.28	77.042
Sulphur	0.784	2.602	1.85	1.70	1.23	1.338
Ash	8.233	6.930	7.50	7.50	9.08	6.860
Total	100.000	100.000	100.00	100.00	100.00	100.000
Coke, per cent. .	68.63	71.375	81.00	71.00	83.59	85.24
Fuel ratio . . .	1:1.98	1:2.27	. . .	. .	1:4.78	1:5.30
	McCreath.	McCreath.	T. T. Morrell.	T. T. Morrell.	McCreath.	McCreath.

III. *Non-coking Coals (Block Coal).*

	Mercer County, Pa., Sharon Coal.	Youngstown, Ohio.	Mercer County, Pa.	Straitsville, Ohio.	Brazil, Ind.
Moisture	3.79	3.60	3.80	. . .	. . .
Volatile matter . .	35.30	32.58	25.49	36.50	40.15
Fixed carbon . .	53.875	62.66	68.03	55.60	57.20
Sulphur	0.675	(0.85)	1.04	0.96	0.75
Ash	6.36	1.16	1.70	6.94	1.90
Total	100.000	100.00	100.06	100.00	100.00
Coke, per cent. . .	60.91	. . .	. . .	61.00	58.00
	McCreath.	Wormley.	Jno. Fulton.	Wormley.	Prof. Cox.

Effects of High or Low Temperature in the Distillation of Coal.—Coal when distilled at a low temperature yields products of a very dif ferent nature from those obtained if the temperature employed had bee high. On this subject Professor Edmund T. Mills, of Glasgow, in hi little manual on "Destructive Distillation" (3d ed., p. 9), states tha "at a very high temperature the products from coal and shales ar carbon and carbonized gases of low illuminating power, with but littl liquid distillate; at a low temperature there is much liquid product an gas of high illuminating power. The greatest amount of liquid produ of low boiling-point is found in American and Russian petroleums, whic have probably been produced by the long-continued application of very gentle natural heat.

"When coal is slowly heated (as must be to a great extent the ca when it is broken fine, or when a large retort is used), its oxygen chiefly converted into water; when rapidly heated, the oxygen is e pelled as carbonic oxides."

To show the verification of these principles in practice, the results high and low temperature distillation upon three different coals may

Yield of Gas, Oil, etc., from Shales and Coals at High and Low Heats.

		GOOD SHALES.		BOGHEAD COAL.		GAS COAL.	
		High heats.	Low heats.	High heats.	Low heats.	High heats.	Low heats.
Volatile matter.	Gas	13.65	2.54	37.32	4.83	20.49	6.49
	Ammonia-water	3.65	6.47	2.43	3.28	3.09	7.24
	Tar or oil	11.04	17.65	20.65	50.29	17.08	26.45
	Sulphur	0.99	...	0.18	...	0.29	...
	Water at 212°	2.82	...	0.80	...	4.15	...
		32.15	26.66	61.38	58.35	45.10	40.18
Coke	Fixed carbon	4.16	10.81	9.01	12.40	45.00	49.93
	Sulphur	1.05	...	0.06	...	0.34	...
	Ash	62.64	62.53	29.55	29.25	9.56	9.89
		67.85	73.34	38.62	41.65	54.90	59.82
		100.00	100.00	100.00	100.00	100.00	100.00
Coke (dry) per ton of shale or coal		1,520 lbs.	1,642.2 lbs.	865 lbs.	934 lbs.	1,230 lbs.	1,340 lbs.
Specific gravity of shale or coal		1.818		1.224		1.296	

NOTE.—The low heat results were gotten by distilling the sample in a two-inch iron tube in a gas-furnace.

Lunge (Coal-Tar and Ammonia, 2d ed., p. 17) states that "The quantity, and to a much greater extent the quality, of the tar are influenced by the *temperature* at which the decomposition of the case is carried on. Low temperatures, with nine thousand cubic feet of gas per ton of coal, will yield, with some coals, sixteen gallons of tar; whilst at high temperatures the yield will be but nine gallons, with about eleven thousand cubic feet of gas, from the same coal."* If the temperature be a comparatively low one, mostly such hydrocarbons are formed as belong to a paraffin (methane) series, having the general formula C_nH_{2n+2}, along with the olefins, C_nH_{2n}. The lower members of this series are liquid, and, furnished in the pure state, are lighting and lubricating oils; the higher ones are solid and form commercial paraffin. They are always accompanied by oxygenized derivatives of the benzene series (phenols); but of these the more complicated ones predominate, in some of which methyl occurs in the benzene nucleus, in others replacing the hydrogen of hydroxyl,—*e.g.*, cresol, $C_6H_4(CH_3)(OH)$; guaiacol, $C_6H_4(OH)(OCH_3)$; creosol, $C_6H_3(CH_3)(OH)(OCH_3)$, etc. Liquid products prevail; and among the watery ones acetic acid (which is again a compound of the fatty series) is paramount. Of course also permanent gases are always given off, though in comparatively small quantity.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. Whilst the olefins and members of the acetylene series still occur more or less, the hydrocarbons of the paraffin series disappear almost entirely; and from them are formed on the one hand compounds much richer in carbon, on the other hand more hydrogenized bodies. The latter always occur in the gaseous state; hence the gas so produced contains methane, or marsh-gas, CH_4, and free hydrogen as principal constituents, and is ve much increased in quantity. The carbon thus set free is partly deposit in the retorts themselves, and then occurs in a very compact graphiti form; another portion of the free carbon occurs in a state of extreme fine division in the tar, and forms a constituent of the pitch or co remaining behind from tar-distilling; another portion contributes to t formation of compounds richer in carbon, belonging to the "aromati series, all of which are derived from benzene, C_6H_6. At the same ti the action of heat effects further molecular "condensations," usual with separation of hydrogen, by which process compounds of a high molecular weight are formed, as naphthalene, anthracene, phenanthre chrysene, etc. The never absent oxygen must also in this case cause t formation of phenols; but here phenol proper, or carbolic acid C_6H_5(OH predominates, whilst cresol and the other homologues are diminished quantity, and the dioxy-benzenes, as well as their methylated derivativ disappear altogether. The above will be better illustrated by the sta ment (from Stohmann-Kerl's "Chemie," 3d ed., vi. p. 1162) th Zwickau glance coal yielded the following quite different products, cording to whether it was put into a cold retort and gradually broug to a red heat (*a*), or distilled quickly from a very hot retort (*b*):

	a.	*b.*
Coke	60.0	50.0
Water	10.7	7.7
Tar	12.0	10.0
Gas and loss	17.1	32.1

The tar from (*a*) consisted of photogen, paraffin oil, lubricating c paraffin, and creosote; that from (*b*), of benzene, toluene, naphthale anthracene (together with heavy oils corresponding to the paraffin a lubricating oil), and much creosote.

The annexed diagram, constructed by S. B. Boulton, and publish in the Society of Chem. Ind. Journal, 1885, p. 471, represents the wh process of the destructive distillation of coal, including the subseque treatment of the main fractions, and exhibits in their proper order t various products obtained therefrom.

II. Processes of Treatment.

1. Gas-retort Distillation of Coal.—The distillation of coal carried out in retorts differs from distillations of other substances mai in the apparatus employed and in the nature of the substances to recovered. For gas purposes, retorts, wherein the decomposition of t coal used takes place, are made use of, which were originally construc of cast iron, about one inch in thickness, twelve to fifteen inches width, and about seven feet in length, closed at the rear end, and p vided at the front or mouth with a heavy shoulder or rim supplied w studs to which is attached a cast-iron extension, technically termed "neck," which carries on its upper side a flange to which are secu

The front of the neck is provided with a screw clamp to retain the lid or cap of the retort in position. Iron retorts are destroyed with great rapidity; the destruction being caused by the heat of combustion of the fuel used, the sulphur in the gas coal (an impurity always present in more or less quantity), which acts, forming sulphide of iron, and the carbon, which, as a carbide of iron, graphitic in appearance, forms layers within the retort from one to two inches in thickness. The oxygen of the air also has a very deleterious influence, especially upon retorts when heated to redness.

In later years fire-clay retorts have been substituted for those made of cast iron, for the reason that they are more durable. These retorts are made of a mixture of clay and sand, and are furnished to the gas-works in several shapes, the semi-cylindrical being the one most generally employed. The sizes vary, six to nine feet in length, fifteen to twenty inches in width, and from ten to fifteen inches in height being the average, and take a charge of one hundred and fifty to two hundred pounds of coal. Retorts have been made up to nineteen feet in length, being charged from both ends.

The retorts, varying in number from five to seven, or even nine and more, are mounted in brick furnaces of special construction, in such a manner that the gases of combustion of the coal will pass around and over the retorts and out through a main flue leading to the chimney. The fuel employed can be either coal, coke, or a mixture of both. Gas as a means of firing has been used for the purpose, the method being based upon the well-known regenerative system of Sir William Siemens.

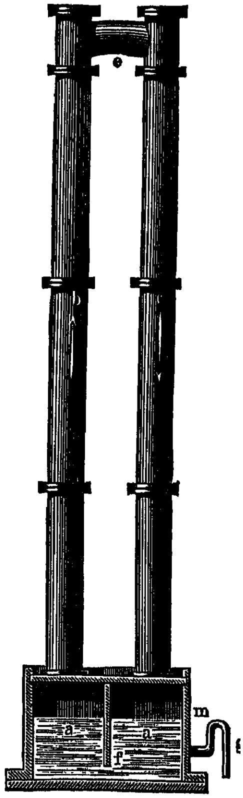
The retorts are charged by hand, care being taken to evenly distribute the coal over the *sole,* or bottom, and to close it quickly. Various attempts have been made to perform this laborious work with mechanical means, but at present no entirely satisfactory substitute has been found.

The products of distillation pass from the retorts proper through the neck, and upward through cast-iron *stand-pipes,* which are provided with *goose*-neck outlets, dipping below the surface of water in what is termed the *hydraulic main.*

It is in this part of the process that the main bulk of the tar is obtained, together with the ammonia-liquor. The hydraulic main is provided with an overflow-pipe through which all the tarry matters pass, This overflow-pipe leads to the tar-well, wherein the liquid products collect.

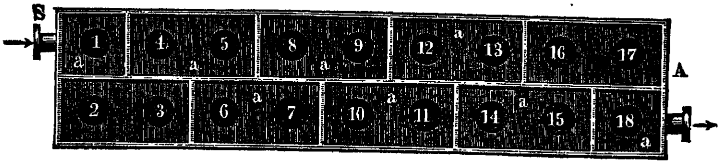
The gas having been freed from the tarry matters, etc., contained, passes from the hydraulic main with a considerably elevated temperature, carrying in a vaporized state hydrocarbons that would separate as its temperature is lowered. It is necessarily very important to remove these volatile and condensable products, which is effected by causing the gas to pass through a series of pipes, which reduces its temperature very close to that of the atmosphere. The older form of condenser was a series of pipes completely covered with water, similar to the worms as employed, and known as the atmospheric condensers, consisting of vertical pipes connected in pairs near the top by straight or curved pieces the lower end of the upright pipes being connected to a box or trough containing water, divided by partitions, causing the gas to pass up and down alternately, as shown in Figs. 99 and 100. Tarry matters and more ammoniacal liquor are again obtained, which find their way to the tar-well.

FIG. 99.



The gas after circulating through the condensers still contains impurities, which are removed by passing it through an apparatus known as the *scrubber,* consisting essentially of cylindrical wrought-iron towers filled with coke, over and through which trickles a light flow of water, or better, weak ammoniacal liquor; the gas passing upward meets this downward flow of liquid, and to it gives up the hydrogen sulphide contained, with the formation of ammonium sulphide, etc. Tarry matters again are separated, and in time cause the coke to become somewhat clogged. This apparent drawback has led to the introduction of perforated iron plates in place of the coke, or, what has also proved equally efficient, wooden lattice screens. Anderson's rotating scrubber consists of brushes, which while rotating dip in a trough of ammoniacal liquor, and thereby perform functions similar to the means above mentioned. Another form of scrubber consists of a tower containing cast-iron plates provided with perforations, through which ammoniacal liquor passes in its downward course, meeting the gas. The liquid is continuously pumped to the top, when it again passes down, coming in contact with fresh gas. This is repeated until the liquor has taken up sufficient ammonia to make it available to the ammonia sulphate manufacturer. From the scrubber the gas passes on to the *purifiers,* where the hydrogen sulphide still remaining, carbon-disulphide

FIG. 100.

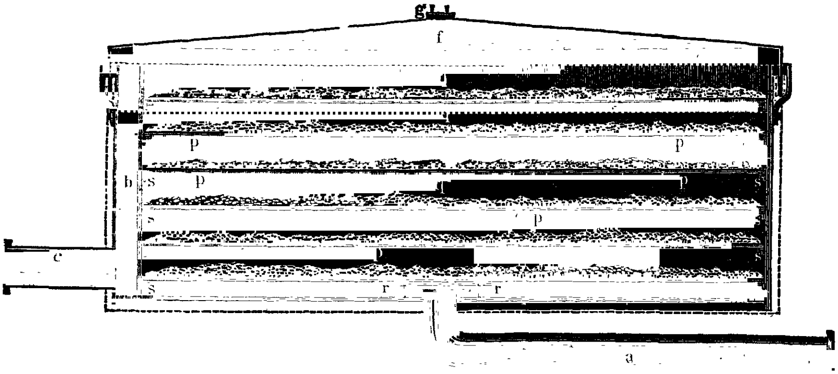


vapor, and the carbonic acid are removed. The purifiers ordinarily used consist of a large shallow box, constructed of cast iron in sections top of the box, acting as a seal and preventing the escape of gas at that point, as shown in Fig. 101. The purifying agent first employed was slaked lime, which was spread upon wood screens, within the box, from four to six in number, one above the other, and supported by ledges. Hydrogen sulphide and carbon dioxide are absorbed by the lime, while compounds of cyanogen are at the same time decomposed.

Four purifiers are generally used, three being in service, while the fourth is reserved charged with fresh lime. Gas enters the one containing the oldest lime, and when it is noticed that lead-acetate paper is discolored by some of the gas acting upon it, it is known that the purifying material is saturated; this purifier is discontinued, and the freshly-charged one placed in service. In this manner they are continually rotated.

Ferric hydroxide (hydrated ferric oxide) is now largely employed in gas purification,—Laming process. Gas charged with hydrogen sulphide coming in contact with the above causes a reduction to ferrous sulphide, at the same time some sulphur is deposited, with the formation of water. This process does not absorb the carbon dioxide from the gas; for this purpose lime is mixed with the ferric hydroxide, together with some cinders or sawdust, in order that the whole may be porous, and resist as little as possible the passage of the gas. When the purifying action has ceased, simply exposing the inert mixture to the action of the air for a while restores its properties, until after repeated use it becomes so charged with separated sulphur that it is no longer available.

FIG. 101.



The introduction of free oxygen into the gas, previous to it entering the purifiers, has been found to lengthen the time during which the oxide of iron can remain without being changed, thereby saving much handling. It has also improved the illuminating power of the gas. (Journ. Soc. Chem. Ind., vol. viii, pp. 84 and 694.)

From the purifiers the gas passes through the meter of the works, where the volume is registered, then on to the gas-holders, where it is stored and from which it is distributed.

The following table illustrates the composition of illuminating g
taken from various stages of manufacture:

	Entering the air-condenser.	Entering the scrubber.	Entering the Laming's purifier.	Entering the lime-purifier.	Enterin the gas-holder.
Hydrogen	37.97	37.97	37.97	37.97	37.97
Marsh-gas	39.78	38.81	38.48	40.29	39.37
Carbonic oxide	7.21	7.15	7.11	3.93	3.97
Heavy hydrocarbons	4 19	4.66	4.46	4.66	4.29
Nitrogen	4.81	4.99	6.89	7.86	9.99
Oxygen	0.31	0.47	0.15	0.48	0.61
Carbon dioxide	3.72	3.87	3.39	3.33	0.41
Hydrogen sulphide	1.06	1.47	0.56	0.36	. .
Ammonia	0.95	0.54	. .	. .	. .

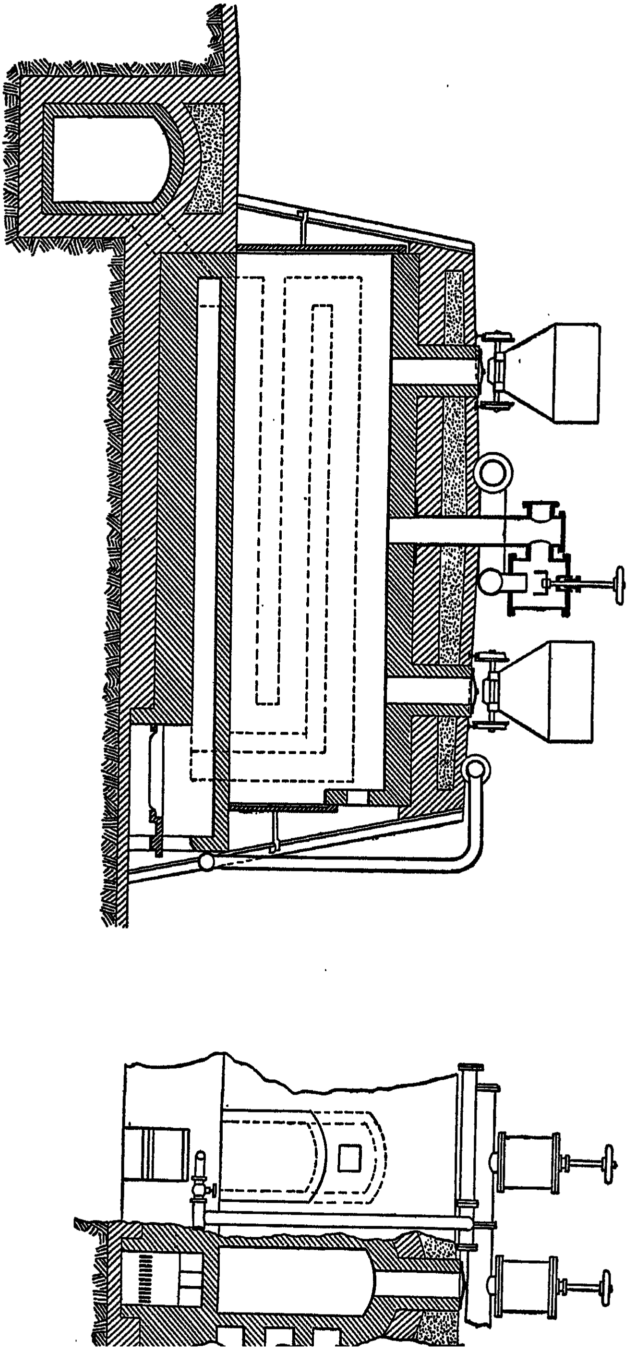
2. Coke-oven Distillation of Coal.—The burning of coke in pi
"meilers," or mounds, represents the first rough and wasteful meth
of converting bituminous coal into coke; involving, at the same tim
the total loss of all the volatile matter of the coal. It allows, howeve
of the smothering the finished coke with fine dust, instead of requiring
to be quenched with water, as in other methods. The so-called "be
hive" ovens allow of the volatilizing of a much greater amount
sulphur in the coal, and give a decidedly increased yield of coke ov
the pit-burning method. The charge can be run through, too, in le
than half the time. Some air is admitted in both cases, with conseque
loss of coke, and no attempt is made to save the residuals in either cas

The distillation of coal in ovens differs materially from the old
methods of production in piles or kilns in that the inflammable gas
given off are to some extent utilized.

Among the earlier forms of ovens planned for the collection of resi
uals (gas, tar, and ammonia) were the Appolt, which was a vertic
oven surrounded by air spaces in which combustion took place, and t
Coppée, which was a horizontal oven with vertical side canals for t
combustion of gas and air. One of the most successful forms based up
the Coppée principle but using the Siemens regenerative firing is t
Otto-Hoffmann oven, which has been extensively adopted in this countr

The Simon-Carvés oven, illustrated in Fig. 102, on the other han
has horizontal heating chambers for gas combustion. Mr. Henry Simo
C.E., in an address before the British Iron and Steel Institute (Jour
Iron and Steel Inst., No. 1, 1880), states: "According to our syste
the coal is rapidly carbonized by subjecting a comparatively thin lay
of it to a high temperature in a closed retort-like vessel, and, whilst
the bee-hive ovens the volatile products are burned inside, we burn the
around and outside of this retort-like vessel, and only after they a
deprived of the tar and ammoniacal liquor. Each oven is in the for
of a long, high, narrow chamber of brick-work, and a number of the

Fig. 102.



of each oven, and at one end of these is a small fireplace, consisting of a fire-grate and ash-pit, with suitable door, the fire-door having fitted above it a nozzle, through which gas produced from the coking is admitted to form a flame over some fuel burning on the grate. Only a very trifling amount of such fuel, consisting exclusively of the smal refuse coke, is used here, its function being really more that of igniting the gas than that of giving off heat. These grates are not charged with fue more than twice in each twenty-four hours when in regular work. The products of combustion pass from the fireplace along a flue under the oven floor to the end farthest from the fire. They return along another flue under the floor to the fire end; they then ascend by a flue in th partition-wall to the uppermost of several horizontal flues formed therein, and *descend* in a zig-zag direction along these flues, finally passing into a horizontal channel leading to a chimney. The oven in consequence is evenly heated at the bottom and sides, and the coal contained is rapidly and completely coked. No air enters the chambers, the only openings being for the escape of the volatile products. The improved ovens are fed with coal by openings in the roof, over which coal trucks are run on rails; and the coal is evenly distributed by rakes introduced at end openings, provided with doors faced with refractory material, which doors are closed and kept tightly luted while the oven is in operation. The feed-holes in the roof are also provided with covers Through the middle of the roof rises a gas-pipe provided with a hydraulic valve, which closes the passage by a lip projecting down from i into an annular cavity surrounding its seating, in which it is immersed in a quantity of tar and ammoniacal liquor, lodged there during previou distillations. The volatile products of the coal distillation rise by the gas-pipe, and are led through a range of pipes kept cool by externa wetting, so that the tar and ammoniacal liquor become condensed and separated from the combustible gas." When the charge of coal has been converted to coke, it is removed from the ovens by means of a piston worked by an engine traversing rails in front of the battery. The yield of coke has been stated to be from seventy-five to seventy-seven per cent of the coal. During a run of two hundred and fifteen days, the yield of residuals averaged 27.70 gallons of ammoniacal liquors per ton of coal carbonized, and 6.12 gallons of tar per ton of coal carbonized.

An improved form of oven analogous to the Simon-Carvés but with improved utilization of heat and greater yield of residuals is the Semet-Solvay, which has practically divided the field in this country with the Otto-Hoffmann oven. While the regenerative heating is not used in the Semet-Solvay oven, the air for combustion and sometimes the gas is heated by the waste gases of combustion. It is claimed that by the horizontal flue for the burning of the fuel gas a more uniform and higher temperature is obtained.

Considerable difference exists between the tars obtained from the different coking processes above referred to. The Simon-Carvés tar has a specific gravity of 1.106, and closely resembles, chemically, the tar at a high temperature. The Simon-Carvés tar is rich in naphthalene and anthracene, but low in naphtha, benzene, phenols, etc. Analogous to this, as might be expected, is the Semet-Solvay tar. A sample from Glassport, Pa., gave 3.7 per cent. light oils, 9.8 per cent. middle oils, 12 per cent. heavy oils and 4.3 per cent. anthracene oil, and had a specific gravity 1.170. On the other hand, a sample of Otto oven oil (Lunge, Die Industrie des Steinkohlentheers und Ammoniaks, 4te Auf., p. 87) gave light oil 3.4, creosote oil 14.5 per cent., crude naphthalene 6.7 per cent., and 27.3 per cent. anthracene oil. Much of the gas produced in the by-product coke oven contains benzol vapor and this is washed out of it, so that much more is obtained than the percentage of light oils in the tar would indicate.

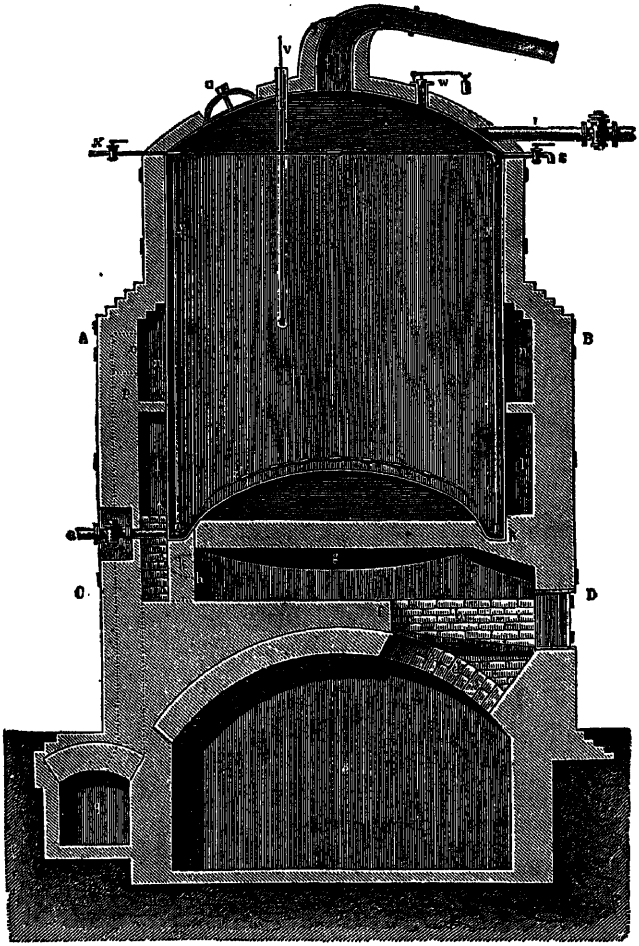
The following comparison of Otto-Hoffmann coke oven tar with gas retort tar from Dammer's Chemische Technologie der Neuzeit, vol. ii, p. 98, 1910) is instructive:

		Tar from Otto-Hoffmann oven.			Gas-tar.		
	Distillation temperature.	Dominion coal. Everett, Mass.	Dominion coal. Sidney, N. S.	Westphalian coal.	Germany.	Germany.	United States.
Light oil	80°–170°C.	1.26	1.38	6.55	3.0	2.5	1.65
Middle oil	170°–230°	14.76	11.46	10.54	7.5	2.5	10.66
Heavy oil	230°–270°	7.07	8.56	7.62	33.5	25.0	8.18
Anthracene oil . .	Above 270°	21.38	20.63	44.35	10.5	10.0	14.05
Pitch	. . . . . .	53.03	53.68	30.55	45.5	60.0	61.16
Water	. . . . . .	1.52	1.93	trace	. .	. .	1.81
Loss	. . . . . .	1.01	2.36	0.39	. .	. .	2.49
		100.00	100.00	100.00	100.00	100.00	100.00
Specific gravity		1.188	1.140	1.155	1.155	1.155	

3. Fractional Separation of Crude Coal-tar.—Following gas retort distillation, in point of technical importance is certainly the distillation of the coal-tar obtained from the former processes and the separation therefrom of certain constituents which have a wide application in several industries. The same general mechanical arrangement, though somewhat simplified, is employed, consisting of a still, a condenser, and a receiver. The still should be constructed entirely of wrought iron, and can be either horizontal or vertical. Horizontal stills are, according to Lunge, far less economical than the vertical. Fig. 103 is a vertical section of a tar-still showing the construction and fittings. The heat from the fire on the grate *b* is prevented from impinging against the concave bottom of the still by means of the arch *g*, but passes through the openings *h* in the circular wall *k* into vertical flues *i*, from which it enters the annular space *l* and through flues in the front of the still

chimney. The supply pipe *r* is for feeding the still, the pipe *s* is a overflow, and serves to indicate when the tank is full. The cock *a* i for drawing off the pitch. The still-head *t* is for conducting the vapors and is connected with the condenser. The system of pipes *x y z* indicated is for conducting superheated steam into the still for finishing th distillation; the pipes conforming to the shape of the bottom, are pro

Fig. 103.



vided with a number of jets for a more equal distribution of the stea The remaining attachments require no further mention.

The *condenser* consists of a coil of pipe immersed in water containe in an iron tank. In England, the pipe used is from six to nine feet i length, and from four to six inches in diameter; the total length for on the pipe from the still must be continued below the surface of the water in the condenser and join the worm there, in order to obviate the possibility of it being melted), made of two-inch pipe, and mounted in circular tanks provided with a steam-pipe for heating the water, and also with a small pipe connected with the worm for blowing in steam whenever it is necessary to clean it.

Connected with the condenser, and located at a safe distance from the still, is the *receiver,* which can be of any convenient shape, and of such a size as to contain the whole of one fraction; or a number can be employed, each acting as a store-tank and receiver. For the receivers to contain the volatile fractions, tight-closing covers must be supplied to guard against evaporation and fire, and the one containing the first fraction must have means for separating the oily from the watery layer. The receivers for the oils which deposit crystalline matter must be so arranged that they can be easily cleaned.

Coal-tar (Allen, Commercial Organic Analysis, 3d ed., vol. ii, Part ii, p. 47), "as obtained as a by-product in the manufacture of illuminating gas, is a black viscid fluid of a characteristic and disagreeable odor. The specific gravity ranges from 1.10 to 1.20, being usually between 1.12 and 1.15.

"As coal-tar is always more or less mixed with ammoniacal liquor, the consituents of the latter liquid are present in addition to those of the tar proper, and the constituents of the illuminating gas itself are also present in a state of solution.

"The first treatment of coal-tar on a large scale consists in distilling it in iron retorts and collecting the distillate in three or four fractions. The temperatures at which the receivers are charged vary considerably with the practice of different works, and hence the products are far from being strictly parallel."

The annexed table indicates the three most important methods of fractionation:

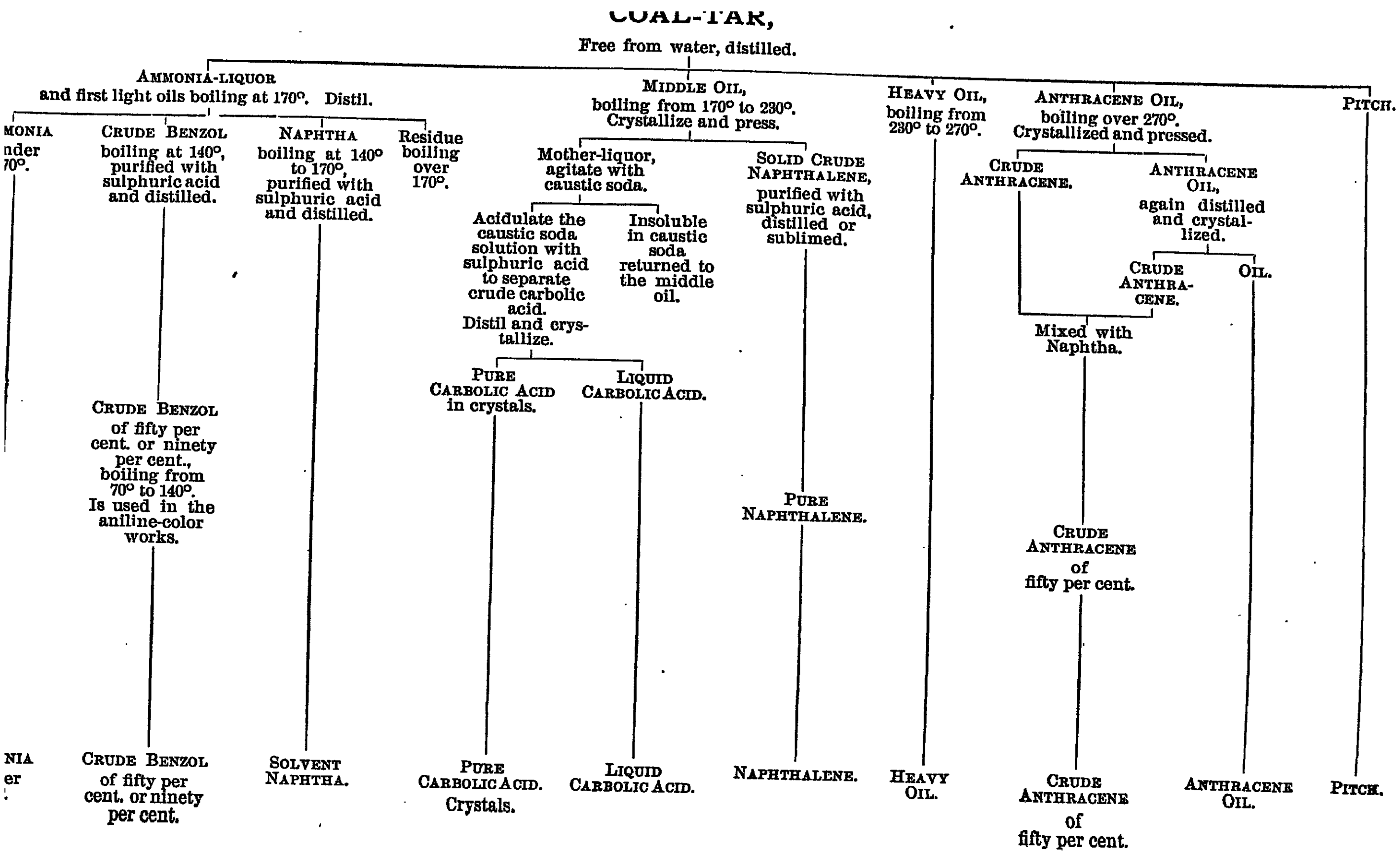
A.		B.		C.	
Product.	Distilling-point ° C.	Product.	Distilling-point ° C.	Product.	Distilling-point ° C.
Crude naphtha, or light oils .	0 to 170	First runnings, or first light oils	0 to 110	Light naphtha	0 to 110
Heavy oils, dead oils, or creosote oils . . .	170 to 270	Second light oils	110 to 210	Light oils. . .	110 to 170
Anthracene oils .	above 270	Carbolic oils .	210 to 240	Carbolic oils .	170 to 225
Pitch	. . . . .	Creosote oils .	240 to 270	Creosote oils .	225 to 270
		Anthracene oils	above 270	Anthracene oils	270 to 360
		Pitch	. . . . .	Pitch	. . . . .

The principal constituents of coal-tar are separated, one from the other, by means of fractional distillation, a process depending upon the fact that, if a mixture of liquids, each having a different boiling-point, be heated, the one having the lowest will pass over first, and if the temperature is not increased beyond that point at which the distillation of this fraction takes place, no other constituent will come over; if the temperature be gradually increased the others will follow in the order of their boiling-points. In cases where the boiling-points are close, and even in others where they are widely differing, the action of one substance upon another often prevents exact separations.

The hot stills (from the previous working) are charged with fresh tar, all the openings are then closed, and the fire carefully watched in order that no undue rise in temperature, and consequent boiling over of the contents, may take place. Gases, ammonia-liquor, and light oils distil over at 170°, the whole being designated "first runnings." This fraction is collected and allowed to stand, when the watery portion separates more or less completely from the oils, which are redistilled, yielding *ammonia* boiling under 70°, *crude benzol* at 140°, which is subsequently purified with sulphuric acid and distilled, *naphtha,* 140° to 170°, treated as the benzol, yielding "solvent naphtha." This whole fraction has a specific gravity nearly equal to that of water. The second fraction —"middle oil," or "carbolic oil"—distils over from 170° to 230°, and contains the impure phenols or carbolic acid and naphthalene. It is crystallized and pressed; the mother-liquor is agitated with caustic soda in an iron tank, the alkaline liquor (carbolate of soda) decomposed with sulphuric acid, separating crude carbolic acid, which is distilled and crystallized, yielding liquid and pure carbolic acid in crystals. The unchanged oil from the soda treatment is returned to the second fraction for re-working. The press-cake from the first treatment of this fraction is purified with sulphuric acid, distilled, and yields naphthalene. The *third fraction* constitutes the *heavy* or *dead oil,* so called from the fact that the specific gravity is greater than water, and boils from 230° to 270°, occupying a position between middle oil and the anthracene fraction. It is subjected to no further treatment, but is employed chiefly for preserving timber, varnish manufacture, burning for lamp-black, etc. The fourth fraction, or *anthracene oil,* boiling over 270°, constitutes the green oil or green grease, from which, upon subsequent treatment, the commercial anthracene is obtained. This fraction is allowed to stand for some time, in order to cool and to separate the crystallizable substances, when the mass is drained from the excess of oil and pressed. The press-cake is crude anthracene, which is dissolved in naphtha and known as *fifty per cent. anthracene.* The mother-liquor *from* the first pressing and the drainings are redistilled, crystallized and pressed, yielding crude anthracene, treated as above, and anthracene oil. The residue in the still constitutes *pitch,* which is withdrawn and employed for making pavements, varnish, etc.

The annexed diagram from Ost's "Lehrbuch der Technischen Chemie" graphically represents the preceding outline of the tar distillation process.

4. Treatment of Ammoniacal Liquor.—The ammoniacal liquor of the gas-works is that which passes out continuously from the scrubbers


COAL-TAR,
Free from water, distilled.
AMMONIA-LIQUOR and first light oils boiling at 170°. Distil.
MIDDLE OIL, boiling from 170° to 230°. Crystallize and press.
HEAVY OIL, boiling from 230° to 270°.
ANTHRACENE OIL, boiling over 270°. Crystallized and pressed.
PITCH.
MONIA nder 70°.
CRUDE BENZOL boiling at 140°, purified with sulphuric acid and distilled.
NAPHTHA boiling at 140° to 170°, purified with sulphuric acid and distilled.
Residue boiling over 170°.
Mother-liquor, agitate with caustic soda.
SOLID CRUDE NAPHTHALENE, purified with sulphuric acid, distilled or sublimed.
CRUDE ANTHRACENE.
ANTHRACENE OIL, again distilled and crystallized.
Acidulate the caustic soda solution with sulphuric acid to separate crude carbolic acid. Distil and crystallize.
Insoluble in caustic soda returned to the middle oil.
CRUDE ANTHRACENE.
OIL.
Mixed with Naphtha.
PURE CARBOLIC ACID in crystals.
LIQUID CARBOLIC ACID.
CRUDE BENZOL of fifty per cent. or ninety per cent., boiling from 70° to 140°. Is used in the aniline-color works.
PURE NAPHTHALENE.
CRUDE ANTHRACENE of fifty per cent.
NIA er
CRUDE BENZOL of fifty per cent. or ninety per cent.
SOLVENT NAPHTHA.
PURE CARBOLIC ACID. Crystals.
LIQUID CARBOLIC ACID.
NAPHTHALENE.
HEAVY OIL.
CRUDE ANTHRACENE of fifty per cent.
ANTHRACENE OIL.
PITCH.

ammonia of commerce. According to Lunge, ordinary gas-liquor contains the following:

(*a*) *Volatile at ordinary temperatures.*
  Ammonium carbonates (mono-, sesqui-, and bi-).
  Ammonium sulphide $(NH_4)_2S$.
  Ammonium hydrosulphide, $NH_4.HS$.
  Ammonium cyanide.
  Ammonium acetate (?).
  Free ammonia.
(*b*) *Fixed at ordinary temperatures.*
  Ammonium sulphate.
  Ammonium sulphite.
  Ammonium thiosulphate (hyposulphite).
  Ammonium thiocarbonate.
  Ammonium chloride.
  Ammonium thiocyanate (sulphocyanide).
  Ammonium ferrocyanide.

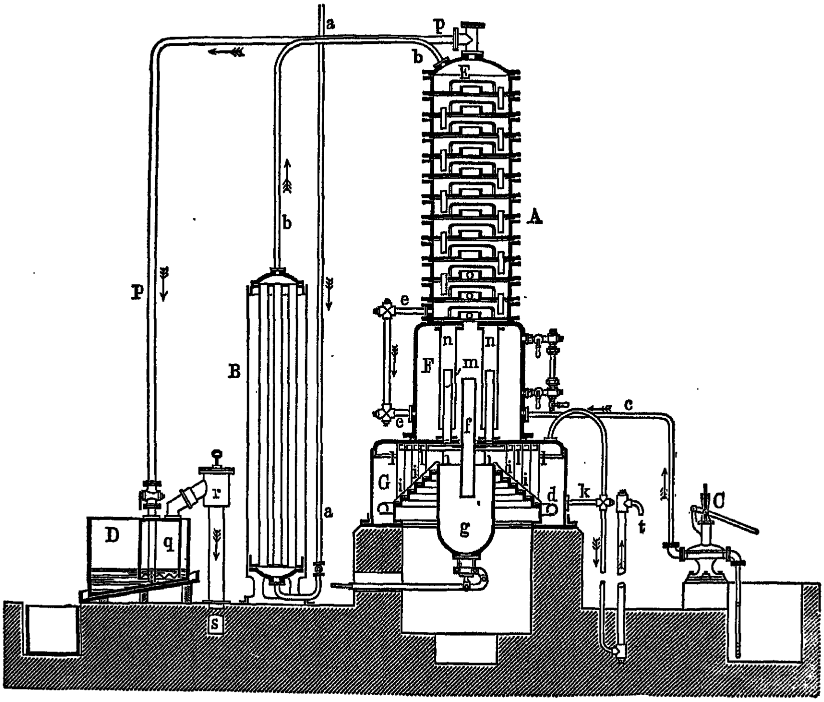
The salts of ammonia that are volatile are readily removed from the gas-liquor upon simply boiling, or by the aid of steam. The fixed ammonia salts require the addition of chemical agents—*e.g.*, lime—to break up the combination and liberate the ammonia which is eventually recovered. The greater the amount of volatile ammonia and less the amount of the non-volatile compounds, the greater the value the liquor has for treatment.

The method of recovering ammonia at a London works, where one hundred thousand gallons of liquor are treated daily, is briefly outlined as follows: The liquor is pumped into a large settling-tank, where, after remaining for a day or more, it is pumped into a "Coffey" still, thirty feet high, into which steam at two atmospheres pressure is blown. By this treatment the volatile ammonium compounds are separated from the water and the non-volatile compounds. Carried along with the steam, the volatile compounds pass from the still through a worm, provided with half-inch holes, into a sheet-lead saturator filled two-thirds with 140° Twaddle sulphuric acid in water. This water so dilutes the acid that it prevents the ammonium sulphate from crystallizing within the saturator. After saturation, steam is blown through the solution to remove hydrogen sulphide, which, after passing through a condenser, is burned; the heat generated being partly utilized in the production of steam for the operation. The saturated liquid is run off into leaden pans placed over a fire, and evaporated to such a point that the sulphate will crystallize out. The residual mother-liquor is made use of in the dilution of the sulphuric acid in the saturator.

Without going into the details of construction of the many improvements made in the apparatus employed for the recovery of ammonia, it may be well to mention the apparatus of Grüneberg and Blum, Fig. 104. *A* is the column, *B* the economizer through which the gas-liquor passes

C is the pump which introduces the lime into the lime-vessel *F*. *D* is the acid-tank or saturator. The gas-liquor enters the still at the top and descends from chamber to chamber, meeting the upward current of steam, till it reaches the lime-decomposition-tank *F*, and finally the boiler *G*. In this is a peculiar truncated cone, *l*, over which flows the liquor from step to step, and owing to the increased area of each step the liquor becomes thinner and thinner, permitting the steam to act very thoroughly. The ammonia generated passes from the still through the pipe *P* to the saturator *D*. Waste gases collect in the bell *q*, from which they are led to the economizer *B*, and finally burned.

FIG. 104.



Feldmann's apparatus is a steam still, capable of recovering both the olatile and fixed ammonia, and occupies very little space. It consists f a chambered column, lime-tank, and an auxiliary column, in connecion with feed-tanks, economizer, lime-pump, and saturator. The liquor lows from the feed-tanks through the economizer, where it is heated, o the top of the main column, down which it flows successively through he chambers in which it is boiled into the decomposing-tank, which ontains lime, where it is thoroughly agitated with steam. The liquor ows from this tank to the auxiliary column, similar to the first one, here the little ammonia found is driven out. The spent liquor collects n the lower compartment, from which it constantly flows away. Lunge liquor daily occupies a space of seventeen feet by thirteen feet by te feet.

The sulphate of ammonia as it is fished from the saturators is allowed to drain, sometimes slightly washed with water, and sold without drying.

III. Products.

Under this head will be considered the more important products that are obtained by the subsequent treatment of the main fractions of the distillation process as indicated on previous pages.

1. First Light Oil is the fraction distilling at a temperature up to 170° C. It includes a small percentage of ammonia-liquor which is mechanically contained in the tar, and is separated from the tar oils by being allowed to stand and settle out, when it is drawn off. The specific gravity of the fraction is about .975, and is made up of benzene, toluene, and higher homologues, with phenol, cresol, naphthalene, etc. The products obtained from it are separated by redistilling the whole fraction in a small still of the same general type as the large tar-still. The separate distillates are generally as follows:

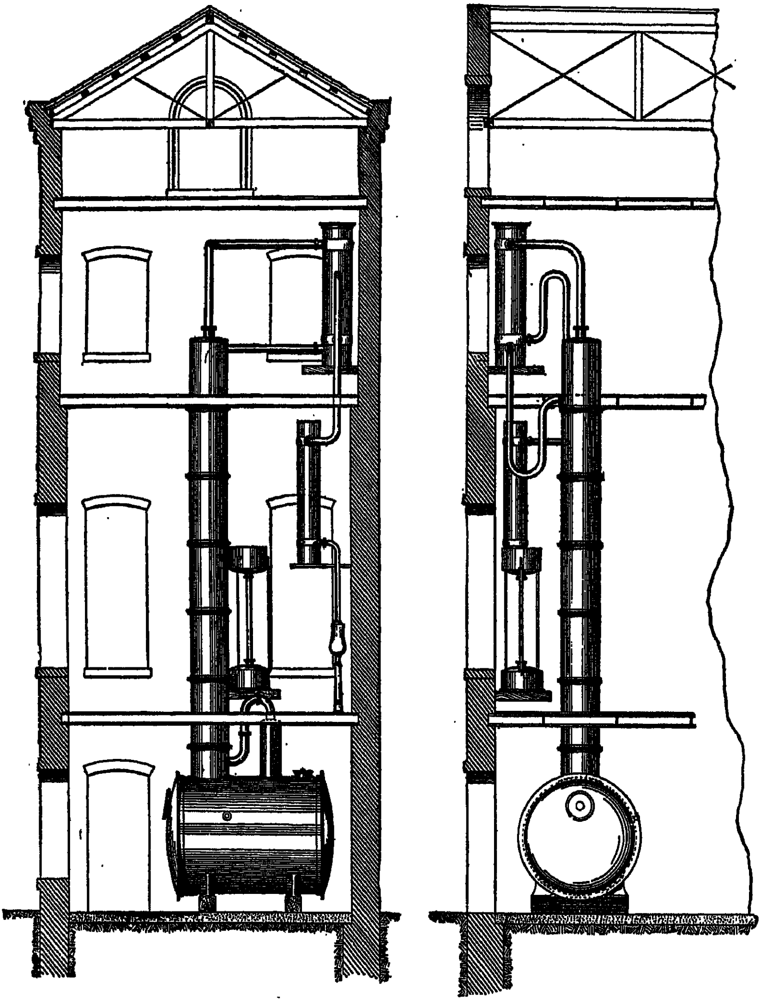
First Light Oil up to 170° yields

(*a*) To 110°	"90 per cent. benzol."
(*b*) 110° to 140°	"50 per cent. benzol."
(*c*) 140° to 170°	solvent naphtha.

The fraction obtained up to 110° is chemically washed, being agitated with sulphuric acid of 1.84 specific gravity in the proportion of one pound to one gallon of oil, which combines with the bases, dissolves resins, etc. The agitation is carried out in cast-iron or lead-lined wooden tanks securely covered to prevent loss of the volatile bodies, and provided with mechanical means for mixing. This is completed in ten or fifteen minutes, when the whole is allowed to stand at rest for an hour or more, and then the spent acid is completely removed. The oil is now thoroughly washed four or five times with water, until no color is imparted to the washings, which should have but a slight acid reaction. Agitation is again continued, but with a ten per cent. caustic soda solution, afterwards allowed to separate, when the alkaline solution is removed, and the oil is finally washed with water and distilled, either by means of fire or steam.

(*a*) "*Ninety per Cent. Benzol.*"—The product coming over at 110° is designated "ninety per cent. benzol," from the fact that ninety per cent. by volume of it distils before the thermometer rises above 100° C. A. H. Allen (Commercial Organic Analysis, 2d ed., p. 489) states: "A good sample should not begin to distil under 80° C., and should not yield more than twenty to thirty per cent. at 85°, or much more than ninety per cent. at 100°. It should distil below 120°. . . . . The actual percentage composition of a ninety per cent. benzol of good quality is a little xylene, and four to six per cent. of bisulphide of carbon and light hydrocarbons. The proportion of real benzene may fall as low as sixty or rise as high as seventy per cent. Ninety per cent. benzol should be free from opalescence and colorless ('water white'). The specific gravity is between .88 and .888 at 15.5° C. (= 60° F.), but this is not a true guide as to the quality, from the fact that bisulphide of carbon (specific gravity 1.27) and light hydrocarbons (specific gravity .86) sensibly affect the specific gravity of the benzol."

FIG. 105.



(*b*) "*Fifty per Cent. Benzol*" is a product of the fraction boiling from 110° C. up to 140° C., and is subjected to the same treatment as the previous one. The specific gravity of this benzol varies from .867

free from bisulphide of carbon, and contains little hydrocarbons, while the per cent. of toluene and xylene are greater than in the ninety per cent. benzol.

The "benzols" on the American market at present are: Benzol pure, boiling at 80°–83° C., and gravity .881 to .884; benzol one hundred per cent., gravity .875 to .884; benzol ninety per cent., gravity .875 to .882; benzol fifty per cent., gravity .871 to .875; benzol 160° (ninety per cent. at 160° C.), gravity .864 to .870; benzol straw color (crude, ninety per cent. benzol), gravity .862 to .870.

(*c*) *Solvent Naphtha*—so-called from the use to which it is put,—dissolving caoutchouc in the manufacture of water-proof materials, etc.,—follows the benzols, boiling over 140°, and consists of xylene, pseudocumene, and mesitylene. In some works the distillation of this fraction is not driven to the end, but stopped when the product yields ninety per cent. at 150° C., the residue being distilled as *burning naphtha* with a specific gravity of .90. Lunge states: "From the product distilled up to 140° may be extracted sixty or seventy per cent. of fifty per cent. benzol, twenty to twenty-five per cent. of carburetting and solvent naphtha, five to eight per cent. of burning naphtha. The product distilled between 140° and 170° yields twenty-five to fifty per cent. best naphtha, fifty to twenty-five per cent. burning naphtha, and twenty-five per cent. residue in the still." The separation of the preceding into benzene, toluene, xylene, etc., for the use of the color manufacturer, is not ordinarily carried out in the tar-distillery, but at the color-works, in especially constructed column stills. The appearance of such a benzene rectification still is shown in Fig. 105. For details of construction of such a column still, see Chapter VI, p. 247.

The following table (Lunge, "Coal-Tar and Ammonia," 2d ed., p. 476) shows the yield in percentage volumes of the products from the light tar oils:

COMMERCIAL PRODUCTS.	Initial boiling points.	° C. 88.	° C. 98.	° C. 100.	° C. 110.	° C. 120.	° C. 130.	° C. 138.	° C. 149.	° C. 160.	°C. 171.
	° C.										
"Ninety per cent. benzol"	82	30	65	90							
"Fifty per cent. benzol"	88	. .	13	54	74	90					
Toluol	100	. .	. .	. .	56	90					
Carburetting naphtha . .	108	. .	. .	. .	1	35	71	84	97		
Solvent naphtha	110	. .	. .	. .	. .	17	57	71	90		
Burning naphtha	138	. .	. .	. .	. .	. .	. .	. .	30	71.5	89

2. MIDDLE OIL.—This constitutes the second main fraction in the tar distillation process, and is collected between 170° and 230° C., yielding upon further treatment two very important and valuable products: liquid and solid *carbolic acid* and *naphthalene*, both of which find their widest application in the artificial-color industry, although large quantities are employed for many other purposes.

While this fraction is coming over from the still no cold water is of temperature to the point at which solid naphthalene would form in the condenser is to be avoided; a steam-pipe is generally led into the tank, and the water brought to 50° or 60°, thereby keeping crystallizable matter in a fluid condition and continually flowing.

This distillate is allowed to become cold, when nearly all of the naphthalene separates in leaflets, which are drained and pressed to expel the remaining portions of the non-crystallizable oil, which is the source of the carbolic acid.

1. *Carbolic Acid.*—The above oils are thoroughly mixed with a solution of caustic soda (specific gravity 1.26) in a tank provided with mechanical agitators, or with means for forcing air through the liquids. The mixing is performed at a temperature of from 40° to 50°, and is completed in one to one and a half hours, when, after standing to allow the alkaline liquors to subside, they are drawn off and cautiously decomposed by adding sulphuric acid till the liquor has an acid reaction, when it is at once removed to avoid the crystals of sodium sulphate forming in the tank; the carbolic acid is allowed to stand for a few days in order that any sodium sulphate solution remaining may separate out, when it is washed with water and finally distilled in small retorts, yielding, in the first fraction, *water and oil;* in the second, *crystallizable oil,* from which is obtained the *crystal carbolic acid* of commerce; and in the third fraction, the *non-crystallizable phenols,* or *liquid carbolic acid.*

That part of the mother-liquor from the naphthalene which is not acted upon by the caustic soda solution added to remove the phenols is returned to the main middle-oil fraction and again re-worked.

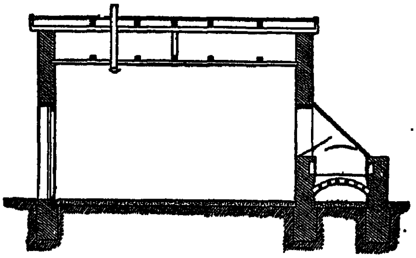
Carbolic Acid, or Phenol, C_6H_6O (or C_6H_5OH).—All compounds containing the group OH in place of one or more of the hydrogen atoms of benzene (C_6H_6) or its homologues, are designated *Phenols.* Carbolic acid has a very peculiar and characteristic odor, burning taste, is poisonous, and has preservative properties; the odor, however, is not so pronounced in pure as in impure specimens. The specific gravity at 0° is 1.084; it crystallizes in colorless rhombic needles which melt at 42°, boiling at 182°, and is not decomposed upon distillation. At ordinary temperature it dissolves in water with difficulty (1:15), but is soluble in alcohol, ether, glacial acetic acid, and glycerine in all proportions. Upon exposure to light and air it deliquesces, and acquires a pinkish color. The most extensive use made of it is as a raw material in the manufacture of many of the artificial coloring matters,—picric acid, used as a yellow dye, and which finds considerable application in the manufacture of a number of high explosives. Large quantities of various qualities of carbolic acid are consumed annually for antiseptic purposes, both for domestic use and in surgery.

2. *Naphthalene.*—The crude crystals which were obtained when the middle-oil fraction was allowed to cool, and also from the treatment by distillation of the unchanged oil from the carbolic acid separation, are purified by fusing and mixing thoroughly with caustic alkali, if impure, followed by a washing with hot water, and afterwards with sulphuric

line treatment may be dispensed with, and the refining commenced with the acid, which is of 1.453 specific gravity; Lunge states, however, that this is too weak, and recommends an acid of 1.70 specific gravity, 1.84 specific gravity being still better. The amount of acid used varies from five to ten per cent.; the mixing being performed in lead-lined tanks, after which it is washed with water several times, and to remove the remaining traces of acid weak caustic liquor is used. The naphthalene thus purified is sublimed in barrels hung over melting-pots suitably mounted, or in frame or brick chambers connected by proper openings with an iron melting-pan, the general construction of which is shown in Fig. 106. The best naphthalene is produced by distillation from stills, which are made shallow, with a very high dome. Larger quantities are handled by this method than by subliming.

Naphthalene, $C_{10}H_8$, is one of the principal constituents of coal-tar, occurring in it in various proportions from five to ten per cent.; it is also formed when the vapors of organic substances are passed through tubes heated to redness. The specific gravity of naphthalene when solid is 1.158, at its melting point (79.2°) it is 0.978; it boils at 216.6° C. The odor is pleasant, though characteristic; volatilizes to some extent at ordinary temperature, but readily in the vapor of boiling water. Crystallizes in large, silvery-brilliant, thin rhombic plates, which are faintly soluble in hot, but insoluble in cold water, though easily in methyl and ethyl alcohols, chloroform, ether, benzene, etc. The commercially sublimed naphthalene is from seventy to ninety-nine per cent. pure. Industrially, it is employed in the manufacture of a large series of coloring matters; as an enricher ("carburetter") of illuminating gas; and when specially refined, as a substitute for ordinary camphor in preventing the ravages of insects, etc., in woollen goods.

FIG. 106.



3. CREOSOTE OIL, OR HEAVY OIL, constitutes the third main fraction, and is generally collected from 230° to 270° C., or until it is *noticed* that solid matters begin to crystallize, which indicates that the *anthracene* is commencing to distil. In order to prevent any cresols from contaminating the phenol and naphthalene of the previous fraction, that fraction is not driven to completeness, which precludes the possibility of any of the heavy oil passing over. Any naphthalene contained in this fraction is recovered by crystallizing and pressing, the residual oil not being subjected to further treatment but employed directly.

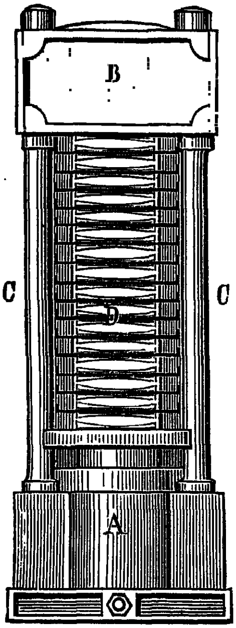
The oil has a greenish-yellow color, and is very fluorescent, which increases in intensity upon exposure to light and air. By transmitted light it is dark red, and by reflected light the appearance is bottle-green. The odor is unpleasant and extremely characteristic. It is heavier than gravity as 1.10. Creosote oil has been found to contain naphthalene, anthracene, phenanthrene, phenol, cresol, etc., with many other bodies but little known. It finds its widest application in the *creosoting* or *preservation of timber;* although, to a limited extent, it has been employed as a fuel, and for the production of illuminating gas, softening hard pitch, as a lubricant, for lamp-black production, etc.

The process of impregnating timber with coal-tar oils, with the view of preserving it against decay, dates from 1838, when a patent was granted to John Bethell. This process consists essentially of exhausting the already seasoned timber of air and moisture in a vacuum maintained by means of an air-pump; when the exhaustion is complete, the tar oil is allowed to enter the vessel, when it is at once absorbed by the pores of the wood. Various processes have been suggested from time to time, but those which have given the most complete satisfaction are nearly all based upon the one above mentioned. In the experimental work of the Forest Service of the U. S. Department of Agriculture on tie preservation a simpler and from many points of view a better process has been used in recent years. The ties are put into open tanks containing creosote oil, in which they are completely immersed, and the contents of the tank are gradually heated by closed coils carrying steam under pressure to a point at which moisture is eliminated as steam. After the lapse of sufficient time to allow the moisture and air from the pores of the wood to escape in this way, the hot ties are quickly transferred to tanks containing cold creosote oil, in which they remain until entirely cooled. In this way the oil is drawn into the pores of the wood as they contract and the wood fibre is not weakened by steaming and vacuum treatment.

Until recently in choosing a creosote oil for wood preservation most experts valued the tar acids and naphthalene as the important constituents, and demanded definite percentages of each. Now the weight of opinion is in favor of the heavy oils, which come over after naphthalene in the distillation, and considers the naphthalene as of small value. This is because naphthalene is volatile at all temperatures, and will entirely disappear from the wood in course of time. As an illustration of this may be quoted from Circular 141 of the Forest Service, U. S. Department of Agriculture, entitled "Wood Paving in the United States," the specifications of the City of Minneapolis for creosote oil for wooden block impregnation. These state "the specific gravity of the oil at 20° C. shall be at least 1.09; the oil shall be completely liquid at 25° C., and show no deposit on cooling to 22° C.; it shall not contain more than two per cent. of water nor more than three per cent. of matter insoluble in absolute alcohol or benzene; on distillation up to 150° C. nothing must come off, up to 170° C. two per cent., up to 210° from six to eight per cent., up to 235° from twenty to thirty per cent., up to 315° from forty to fifty per cent., up to 355° from sixty to eighty per cent." It will be seen that this calls for a relatively heavy oil containing high boiling fractions.

Prof. Gellert Alleman also, in discussing the results of the extraction of oil from ties and paving blocks which had been in use for a term of years, says: "Perhaps the most striking thing is the disappearance of the tar acids. It is certainly conservative to place the original tar acid content at five per cent., yet the extracted oil showed but a tenth of this amount. . . . It appears therefore that light oils boiling below 205° C. will not remain in timber but that heavy oils containing a high percentage of anthracene oil will remain almost indefinitely and protect the wood from decay and boring animals. It is probable that naphthalene stays in wood for many years, but whether it is as valuable as anthracene oil is open to question. The value of the tar acids has apparently been overestimated by many persons, for although it has not been proved that they are valueless, they have been shown to possess poor staying qualities."

FIG. 107.



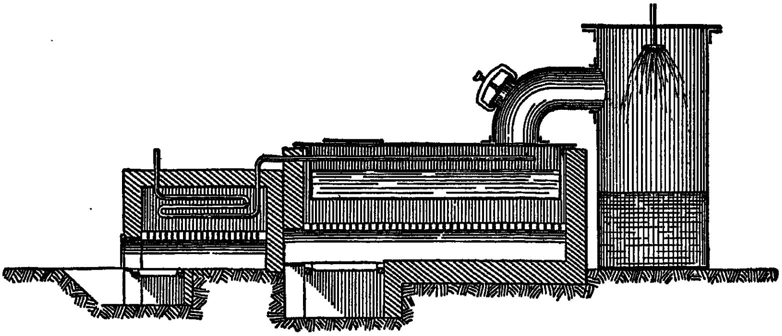
4. ANTHRACENE OIL.—The fraction distilling from 270° C. and over consists of that portion of the tar which is made up of bodies possessing the highest boiling points, and is distinguished from the heavy oil fraction by a separation, on cooling, of solid matters. In it have been found *naphthalene, methyl-naphthalene, anthracene, phenanthrene, methyl-anthracene, pyrene, carbazol,* etc. With the exception of methyl-naphthalene, which is a liquid, all the others are solids at ordinary temperature, but which have high melting points.

The separation of the crude anthracene from the distillate is accomplished by cooling or crystallizing, and pressing. The cooling takes place in large, shallow iron pans, either spontaneously or by refrigeration, when the semi-solid mass is transferred to bag filters, closed at the lower end, and connected by means of nipples at the upper end to a pipe for conducting compressed air, which acts in driving the liquid or non-solidifying portion out, and leaving the mass nearly dry. By using filter-presses instead of the above, a large and better yield can be obtained in a shorter time. The crude anthracene is placed in cloths and subjected to a gradually-increasing pressure in a vertical or horizontal hydraulic press, the plates of which are so constructed as to be heated by steam, or the whole press may be enclosed in a chest to which steam can be admitted. Fig. 107 illustrates the general arrangement of a press suited to the purpose. The use of heat in the pressing is to cause those bodies which have a lower melting point than that of the anthracene to be easily removed. The yield of anthracene by hot-pressing only comes up to about thirty to thirty-two per cent. of the oil in winter, and thirty-three to thirty-six per cent. in summer (Lunge). The pressed anthracene is ground to a fine powder and washed with solvent naphtha tight boiler, fitted with a steam coil, and provided with a mechanical agitator. The mixing requires several hours with gentle heat, when the whole is forced by compressed air to a closed filter, which separates the now washed anthracene from the naphtha.

A still purer anthracene is obtained by submitting this product to sublimation with the aid of steam. For this purpose the apparatus shown in Fig. 108 is employed. The anthracene is melted in an iron pan, and over the surface of the melted mass superheated steam is blown. The anthracene vapors are carried by the steam into a cooling chamber, where they are condensed by coming in contact with a spray of cold water.

The anthracene oils from the first draining of crude material are usually re-distilled in order that the anthracene contained in them may be recovered. Graham's process (Chem. News, xxxiii, pp. 99, 168) for this is to distil about fifteen hundred gallons of the filtered oils from a clean tar-still until crystals of anthracene are noticed, when a sample of the distillate is allowed to cool, at which point the operation is stopped, and the residue in the still is run out and allowed to become cold, when the product separates out. This is filtered and pressed in the manner above described for the first crystallization.

FIG. 108.



The oils which yield no more anthracene when subjected to further treatment are added to the creosote oils, or else employed to soften pitch, etc.

Anthracene, $C_{14}H_{10}$, is found under similar conditions to those giving rise to naphthalene, and was discovered in 1832 by *Dumas* and *Laurent,* while *Fritzsche* was the first to find it in coal-tar, in which it occurs as a characteristic constituent. When pure, it crystallizes in white, lustrous, rhombic plates, which exhibit a beautiful violet fluorescence. Melts from 210° to 213° C., subliming at about the same temperature in small scales. It is insoluble in water, sparingly in alcohol, while benzene, essential oils, light tar oils, and hot alcohol dissolve varying quantities. When oxidized it yields *anthraquinone,* which is further treated in the processes for the production of the valuable alizarine and other coal-t

5. Pitch.—By *pitch* is understood the residue remaining in the sti after nearly all the volatile constituents have been driven off. Fo merly, what remained in the still after the light oils were distilled wa called *asphalt,* and was equivalent to about eighty per cent. of the ta consequently it contained those constituents mentioned in the middl oil and creosote oil fractions, with the anthracene. This method o fractionation, however, is not followed, but the distillation is generall carried to that point when the distillate shows a specific gravity of 1.0 when soft pitch will result. If the distillation is carried further, o until it has a specific gravity of 1.12, hard pitch is obtained. In som cases the distillation is pushed as far as the still will stand with safet in which case no more volatile bodies remain and a coke virtually r mains. As a rule, a moderately hard pitch is made, which is run int casks or barrels directly from the still.

The utilization of the pitch is carried out in several ways: in th manufacture of *patent fuel* (*briquettes*) when incorporated with coa dust or coke-refuse. This industry, which has had an extensive deve opment in Europe, has in the last few years assumed importance in th United States. Briquettes contain from six to eight per cent. of pitc according to the amount of pressure employed in their manufacture.

In deciding the value of a given pitch or tar for briquetting purpose three points may be noted:* 1. The pitch or tar is distilled and a oils coming over below 270° C. are rejected as of no value for brique ting. 2. The flowing point of the portion to be used in briquetting determined. This should generally be not less than 70° C. 3. The pitc is extracted with carbon disulphide. The smaller the amount of resi ual carbon the more satisfactory the pitch.

IV. Analytical Tests and Methods.

1. Valuation of Tar Samples.—Practically, the most efficie method to follow for the determination of the value of tar samples to distil twenty or thirty gallons from a small still, in the same mann and under, as far as possible, the same conditions as is practised in t distillation of tar on a large scale. The products are weighed and mea ured. When a small still is not accessible, recourse must be had, f laboratory purposes, to the following method, which gives excellent sults if carefully attended:† "Two hundred and fifty cubic centimetr or ten ounces measure, of the tar is placed in a retort which it only o third fills, so as not to spoil the distillate if there is much frothing duri distillation. The retort should be supported on a cup-shaped piece coarse wire gauze, placed in an aperture in a sheet-iron plate. Over t retort is placed a dome, made by removing the bottom from a tin can bottle, and cutting out a piece of the side to allow the neck of the ret to pass through. This contrivance confines the heat, and prevents distillate or heavy vapor from falling back." . . . "The produ

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* U. S. Geological Survey Bulletin 343 p. 41 1908

obtained by the distillation are: (1) Ammoniacal liquor; (2) total light oils; (3) creosote oil; (4) anthracene oils; and (5) pitch. In obtaining these fractions, the character of the distillate is amply sufficient to indicate the point at which the receiver should be changed. No thermometer is necessary, nor any condensing arrangement to be attached to the retort. The lamp being lighted (a powerful Bunsen), the ammoniacal liquor and naphtha are collected together in a graduated cylinder, which is changed when a drop of the distillate—collected in a test-tube of water—begins to sink. After standing to allow perfect separation of the *ammoniacal liquor* and *light oils,* the volume of each is observed, and, if desired, the strength of the former can be ascertained in the usual way by distillation with lime and titration of the distillate. The quantity of light oils is too small to allow of any further fractionation for benzols, etc.

"The next fraction of the distillate consists of *creosote oil.* At first it will contain much naphthalene, and will probably solidify in white crystals on cooling, but afterwards a more fluid distillate is obtained. At a still later stage, a drop of the distillate collected on a cold steel spatula will be found to deposit amorphous solid matter of a yellow or greenish-yellow color, when the receiver is again changed, the fraction measured, and if desired, assayed for carbolic acid and naphthalene.

"The next fraction of the distillate is rich in anthracene, and not unfrequently condenses in the neck of the retort as a yellow, waxy substance, which may be melted out by the local application of a small Bunsen flame.

"The collection of *anthracene oil* is complete when no more distillate can be obtained, and the pitch intumesces and gives off heavy yellow fumes. The distilled fraction is then measured and cooled thoroughly, and the resultant pasty mass pressed between folds of blotting-paper, weighed, and assayed for real anthracene by the anthraquinone test. The result is calculated into *crude anthracene* at thirty per cent., a standard which is generally adopted by the manufacturers.

"When the distillation for anthracene oil is complete, the retort may be allowed to cool, and when almost cold its body should be plunged into cold water. This produces a rapid surface-cooling and shrinking of the pitch from the glass, which may then be broken away and removed by gentle tapping, leaving the cake of pitch clean and ready for weighing."

2. Special Tests for Tar Constituents.—(*a*) *Benzol.*—The following method, from Allen,[*] is the most convenient for testing benzol, and is reasonably accurate. One hundred cubic centimetres of the benzol to be tested is measured in an accurately graduated cylinder, and poured thence into a tubulated retort, of such a size as to be capable of retaining two hundred cubic centimetres, or eight fluidounces, when placed in the ordinary position for distillation. A delicate thermometer is fitted in the tubulure of the retort by a cork, so that it may be vertical and the lower end of the bulb be three-eighths of an inch distance from the

inner tube of a Liebig's condenser, and pushed down as far as it wil go. The condenser should be from fifteen to eighteen inches in length and well supplied with cold water. The neck of the retort should no project too far into the condenser; if necessary it should be cut short No cork or other connection is necessary between the retort-neck an condenser-tube. Before use, the tube of the condenser should be rinse with a little of the sample, and allowed to drain, or some of the benzo may be sprayed through it. The graduated cylinder employed fo measuring out the sample is next placed under the farther end of th condenser-tube in such a manner as to catch all the distillate, whil allowing it to drop freely. The retort is then heated by the naked flam of a Bunsen burner (which can be conveniently placed in a tin basi containing sand or sawdust, in order to absorb the benzol in the even of the retort cracking). The flame should be small, about the size an shape of a filbert, and when the distillation of the benzol commence must be so regulated that the condensed liquid shall fall rapidly i distinct drops, not in a trickle or a continuous stream.

When the distillation commences the flame is regulated, if necessar and the rise of the thermometer carefully watched. The moment registers a temperature of 85° C. the flame is extinguished. Four c five minutes are allowed for the liquid in the condenser to drain int the measuring cylinder, and then the volume of the distillate is carefull read off and recorded. The lamp is then relighted and the distillatio continued till the thermometer rises to 100° C., when the gas is turne off as before, and the volume of the distillate read off, after allowin time for drainage. The residual liquid in the retort is allowed to coo and is then poured, to the last drop, into the measuring cylinder. deficiency from the one hundred cubic centimetres originally taken w generally be observed. The difference between the collective volun after distillation and that of the original sample is to be added to t measure of the distillate collected at each temperature, and the cc rected volumes reported as the "strength" of the benzol examined. a matter of fact, the loss of volume by distillation is due far more expulsion of acetylene and other gases than to actual loss of benz Lunge, in "Coal-Tar and Ammonia" (2d edition, 1887), gives mu practical information bearing upon this subject, which, in matters lating to the production and sale of benzols, etc., in Europe, has receiv considerable attention.

(*b*) *Phenols.*—The detection of phenol is in many cases of conside erable importance, and several reactions have been proposed; the follo ing are taken from Allen, who has personally verified them. Upon ad ing a drop of a dilute aqueous solution of phenol to a small quantity a solution made up of one gramme of molybdic acid in ten cubic cen metres of sulphuric acid, a yellow-brown coloration is produced, whi changes to a permanent purple tint. Many substances interfere w this reaction owing to the fact that it depends upon the reduction the molybdic acid similar reactions. Sodium chloride, nitre, or boric acid is unobjectionable, but most mineral and organic acids, acetates, borax, sodium phosphate, glycerine, alcohol, and ether hinder the reaction. If an aqueous solution of phenol is warmed with ammonic hydroxide and a solution of sodium hypochlorite, a permanent deep-blue color is obtained, which is turned red upon addition of acids. One part of phenol in five thousand of water will react if twenty cubic centimetres are used, weaker solutions also, after a time. A modification of the above is to add to fifty cubic centimetres of the phenol solution five cubic centimetres of dilute ammonia, and then, slowly, fresh and dilute bromine-water, when a fine blue tint is produced which is permanent. Bromine vapors will answer instead of bromine-water.

If to a solution of phenol a drop of aniline be added, and then a solution of sodium hypochlorite, yellow striæ are produced which change to blue. This test is very delicate.

Upon the gradual addition of bromine to a solution of phenol a white turbidity (mono-brom-phenol, C_6H_4BrOH) is formed. If the solution is dilute no precipitate occurs, but upon the addition of more bromine, di-brom-phenol ($C_6H_3Br_2OH$) is formed; upon further addition of bromine a very bulky precipitate is produced, which is separated as the insoluble and characteristic tri-brom-phenol ($C_6H_2Br_3OH$). This determination of phenol was first suggested by Landolt, though brought to perfection and used as a volumetric method by Koppeschaar (Z. a. Chemie, xvi, 233).

For the assay of carbolic acid the specific gravity is always noted, which ranges between 1.04 and 1.065; the lower figure indicates a suspicious sample, and represents light tar oils. Water is estimated by agitating the sample with half its volume of a saturated solution of salt, the loss of volume indicates the amount of water originally present. To ascertain the quality of crude carbolic acid and probable yield of crystallized phenol, the following method of Lowe (Allen, Com. Org. Anal., 3d ed., vol. ii, Part ii, p. 252) is used. One hundred cubic centimetres are distilled and the distillate collected in graduated tubes. Water first distils, and is followed by an oily fluid; this is allowed to stand, when the volume of water is read off. If the oily liquid floats on the water, it contains light oil of tar. It should be heavier than water, in which case it may be regarded as hydrated acid containing about fifty per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid, and when it measures 62.5 per cent. the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 62.5 per cent. of anhydrous acid contains variable proportions of carbolic and cresylic acid. These may be approximately determined by ascertaining the solidifying point, which should be between 15.5° and 24° C., and by making, with known proportions of carbolic and cresylic acids, a standard sample that will have the same solidifying point.

(*c*) *Naphthalene.*—The assay of this substance generally consists in filter or bibulous paper, to pressure in a copying-press until the exudation of any oil ceases, when the cake is again weighed, and if desirable, distilled from a small retort. Good samples should not distil below 210°, and should yield ninety per cent. of distillate before the temperature exceeds 225° C. Upon warming sublimed naphthalene with pure sulphuric acid in a test-tube, the solution should remain colorless. If one per cent. of impurity is present, a decided pinkish tint is observed, which is darker the greater the amount. The determination of the specific gravity, the melting point (79° C.), and the boiling point (216° to 218° C.) are made by the usual methods.

(*d*) *Creosote Oils.*—The characteristics of this fraction were previously indicated. The specific gravity is determined either by the bottle or hydrometer; in cases where the sample contains much naphthalene, the specific gravity bottle is filled and the contents allowed to become solid, when the stopper is worked in. A sample should become quite clear upon warming to about 38° C., and ought not become turbid till cooled to 32° C. The liquefying point is determined by transferring a sample of the oil to a test-tube, immersing a thermometer, and warming gently till it becomes liquid. The point of turbidity is similarly observed, by allowing the tube to cool spontaneously. For the determination of the naphthalene, one hundred grammes are chilled to 4.5° C. in a small beaker, then transferred to a cloth filter, placed in a funnel provided with means for cooling to 4.5° during filtration. The filter and contents are removed and quickly pressed between bibulous paper in a copying-press, when the cake is pressed and weighed.

(*e*) *Anthracene.*—Commercial anthracene contains a very variable percentage of real anthracene, the usual proportions being from thirty to forty per cent., though formerly fifteen per cent. was common, and special lots now assay over eighty per cent. The value of anthracene does not entirely depend upon the amount of real anthracene alone, but also upon the freedom from objectionable impurities. In testing for *paraffin,* ten grammes of the sample are taken and treated with two hundred grammes of concentrated sulphuric acid, heated on a water-bath for about ten minutes, or until the anthracene is dissolved, when any *paraffin* will rise to the surface in oily globules. The solution is now poured cautiously into a tall beaker containing five hundred cubic centimetres of water, stirred, and cooled, when the paraffin rises and solidifies on the surface; it is washed with water, dried between filter-paper and weighed.

By the conversion of anthracene into *anthraquinone* the most satisfactory method of assaying is obtained. (See Allen, Com. Org. Anal., 3d ed., vol. ii, Part ii, p. 230.) One gramme of the carefully sampled specimen is placed in a flask holding five hundred cubic centimetres, forty-five cubic centimetres of the very strongest glacial acetic acid is added, and an inverted condenser, or long glass tube adapted to the flask. The liquid is then brought to the boiling point, and, while boiling the chromic acid solution is added to it gradually, drop by drop, by the flask, or inserted in the top of the vertical condenser. The chromic acid solution is prepared by dissolving fifteen grammes of crystallized chromic anhydride in ten cubic centimetres of water and ten of glacial acetic acid. The addition of the oxidizing agent should occupy two hours, and the contents of the flask should be kept in constant ebullition for two hours longer. The flask is then left for twelve hours, when the contents should be diluted with four hundred cubic centimetres of cold water, and allowed to rest for three hours longer. The precipitated anthraquinone is filtered off, and well washed on the filter with cold water, and with a boiling one per cent. solution of caustic soda and again with water. The anthraquinone is rinsed from the filter into a small dish, the water evaporated off, the residue dried at 100° C., and weighed. The following after-treatment is now universally employed: to the weighed residue ten times its weight of fuming sulphuric acid is added, and the whole heated to 100° C. on a water-bath for ten minutes, after which it is left in a damp place for twelve hours to absorb water, when two hundred cubic centimetres of water are added; the precipitated anthraquinone filtered off, washed with water, and then with one hundred cubic centimetres of a one per cent. boiling solution of caustic soda, and finally with boiling water, transferred to a dish, any water being evaporated off, and the whole dried at 100° C. and weighed. The weight of the anthraquinone multiplied by the factor, .856, gives the real anthracene in the weight of the sample.

Anthracene in Tar and Pitch.—Nicol (Z. a. Chemie, xiv, p. 318) treats twenty grammes in a small retort, receiving the vapors in a U tube kept at 200° C. The more volatile products do not condense, but the anthracene and other hydrocarbons do. When coking has taken place, the process is stopped, and the neck cut off, pounded, and the powder added to the distillate. The whole is then dissolved in glacial acetic acid and subjected to oxidation with chromic acid as above described. Watson Smith does not recommend the use of such a small quantity (twenty grammes); he employs a similar method but operates upon, at least, a litre, rejecting the portion distilling just before the coking. The anthracene oil is well mixed and an aliquot part employed.

(*f*) *Pitch.*—The uses to which this residue is put are such that an elaborate method of valuation is unnecessary, although the method for asphalt is applicable. To distinguish between the two, one gramme of the sample is treated with five cubic centimetres of petroleum-spirit, and rapidly shaken. The mixture is filtered, and five to six drops of the filtrate diluted to five cubic centimetres with petroleum-spirit, when a greenish fluorescence will be noticed in the case of tar. Five cubic centimetres of rectified spirit should then be added, the mixture shaken and allowed to stand. The upper layer will consist of strongly-colored petroleum-spirit, while the lower layer of alcohol will have a golden-yellow color if coal-tar is present. In the case of mineral asphalt, the alcohol is faintly straw-yellow and often colorless.

3. VALUATION OF AMMONIA-LIQUOR.—Ordinarily the Twaddle hydro

ammonia in the liquor so tested that one gallon will require two ounces of concentrated oil of vitriol to saturate it; by this means a liquor of 5° Tw. would be known as "Ten-ounce," 4° Tw. would be "Eight-ounce," etc. These results are fallacious, owing to the presence of substances which cause a false strength to be indicated.

The most accurate and practical method consists in decomposing ten cubic centimetres of the gas-liquor to be assayed in a flask by means of a solution of caustic soda, applying heat, and collecting the vapors of ammonia evolved in a known quantity of normal sulphuric acid contained in another flask suitably connected; the ammonia vapors neutralize part of this acid, and that which remains uncombined is exactly neutralized in the presence of litmus solution with normal ammonia, when the percentage of ammonia is at once determined.

4. ANALYSIS OF ILLUMINATING GAS.—The analysis of illuminating gas can be most conveniently carried out for technical purposes with the absorption apparatus devised by Hempel, although there are several other forms in use which give results equally, and in some cases more, accurate. Hempel employs, for measuring the gas under examination, a cylindrical tube, similar to an ordinary burette, graduated to one hundred cubic centimetres in one-fifths, and mounted in an iron base. This burette is open at the top, and at the bottom by means of a side-tube. Another tube similar to the first, but without graduations, is used as a "level-tube," and is connected to the burette by a caoutchouc tube of sufficient length that the level-tube can be raised to the height of the former without inconvenience. There are also used pipettes, the ordinary form of which consists of two glass bulbs, connected by means of capillary tubes, and fastened to a board provided with openings to accommodate the bulbs, and mounted upon a foot. From one of the bulbs a siphon-shaped tube extends, which projects a short distance beyond the stand, and to which is attached a caoutchouc tube connecting it with the top of the burette. The pipettes contain the several liquids and solid reagents necessary to absorb the constituents of the gas. Besides the simple form above mentioned, there is a "tubulated absorption pipette," so made as to allow the introduction of solids, and which can be readily altered to a pipette for the generation and retention of gases, as hydrogen and carbon dioxide, by means of zinc or calcite respectively, the acid required for the liberation of the gas being contained in the second bulb.

Another form is the "compound absorption pipette," which is employed for containing the reagents readily decomposed upon exposure to the atmosphere, or which give off noxious vapors.

The method of operating is as follows: The level-tube, previously filled with water, is raised until the gas-burette is completely filled, when it is connected by means of a caoutchouc tube to the "aspirating-tube," or source of the gas, when the level-tube is lowered, and the water flows out, causing the gas to take its place in the burette; one hundred cubic centimetres are obtained, which is noticed by causing the water-level in place on connecting the top of the burette to the end of the siphon-shaped tube before mentioned, when the level-tube is raised, and the gas is forced from the burette into the bulb of the pipette, the absorbent in which has been forced into the second bulb. When all the gas has passed over, compressors are applied and the pipette detached, and very gently agitated from two to five minutes, in which time the absorption will be complete; the pipette is again attached, the level-tube lowered, when the remainder of the gas is drawn back to the burette, which is closed, the water-level in each brought to coincide, and the reading taken. The difference between this reading and the original volume of gas taken is the volume absorbed. One constituent after another is in this way withdrawn by using pipettes containing solutions having affinity for the several gas components, as indicated below:

Carbon dioxide (CO_2).	Solution of potassium hydroxide.
Ethylene. (C_2H_4). Propylene (C_3H_6). Butylene (C_4H_8).	Fuming sulphuric acid or bromine-water. After agitation, the vapors remaining in the gas are removed by contact with potassium hydroxide solution.
Benzene vapor (C_6H_6).	Fuming nitric acid may be employed, and the nitrous vapor remaining removed by agitation in the potassium hydroxide pipette, or absolute alcohol is used.
Oxygen (O).	An alkaline solution of pyrogallol, or phosphorus chips in the presence of water, can be used.
Carbon monoxide (CO).	A solution of cuprous chloride in hydrochloric acid or ammonia.
Hydrogen (H). Methane (CH_4). Nitrogen (N).	Residue, uabsorbed. Constituents determined by combustion, mixing the residual gas with air, and passing the mixture over palladium sponge.

V. Bibliography and Statistics.

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STATISTICS.

1. Wood Distillation in the United States.—

	Hard woods.	Soft woods.	Total.
1907. Cords of wood distilled	1,219,771	62,349	1,282,120
1908. Cords of wood distilled	878,632	99,212	977,844
1909. Cords of wood distilled	1,149,847	115,310	1,265,157
1910. Cords of wood distilled	1,257,997	192,442	1,450,439

Of the 147 plants in operation in 1910, 117 were engaged in th distillation of hard woods, and 30 in the distillation of soft woods.

2. Production of Coke in the United States (in Tons of 200 Pounds).—

	1909.	1910.
Total production	35,076,902	36,228,773
Valued at	$81,638,058	$82,714,095
Of which Pennsylvania produced	23,098,483	22,875,000
Valued at	$46,196,966	$45,978,750

3. Production of Coke, etc., in By-product Ovens (in Tons of 200 Pounds).—

	1909.	1910.
Number of by-product ovens	3,914	4,078
Coke produced in tons	6,254,644	7,138,734
Value of coke produced	$21,703,462	$24,793,016
Value of by-products	8,073.948	8,479,517

These by-products in 1910 consisted of :—

27,692,858	cubic feet of surplus gas, valued at	$3,017,908
66,303,214	gallons of tar, valued at	1,599,453
70,247,543	pounds of sulphate of ammonia, valued at	1,841,062
20,229,421	pounds of anhydrous ammonia, valued at	1,725,266
4,654,282	gallons of ammoniacal liquor, valued at	295,868
	Total	$8,479,557

England produces the largest quantity of coal tar of any country i the world, the production in 1901 having been 908,000 tons.* The tota world's production has been estimated at 3,000,000 tons.

G. Lunge,* from information gathered by himself, puts the production of coal-tar for 1886 in Holland at 20,000 to 22,000 tons, in Belgium at about 30,000 tons, and in the United States at 120,000 tons, of which some 60,000 tons are distilled, 37,000 tons are employed for manufacturing roofing-paper, roof-coating, etc., and some 23,000 tons are used up in the raw state.

4. OF COAL-TAR DISTILLATION PRODUCTS.—The estimate of Mr. Wilton of the coal-tar production of the United Kingdom for 1885, which was 643,000 tons, includes the following additional details:

Ammoniacal liquor from tar alone..	3,600,000	gallons = 1200 tons of sulphate.
Carbolic acid (crude)	600,000	"
Creosote oil	21,600,000	"
Of this, there was liquid creosote.	10,800,000	"
Of this, there were creosote salts (crude naphthalene, etc.).....	56,620	tons.
Corresponding to pure naphthalene	25,620	"
Green oil	20,400,000	gallons.
Benzol and toluol	1,500,000	"
Solvent naphtha	620,000	"
Anthracene (pure)	3,420	tons.
Pitch	396,000	"

5. PRODUCTION OF SULPHATE OF AMMONIA.—a. *World's Sulphate of Ammonia Production.* (In metric tons of 2204.6 pounds.)

	1905.	1906.	1907.	1908.	1909.	1910.
England	273,550	294,170	318,400	330,450	354,747	374,925
Germany	190,000	235,000	287,000	313,000	330,000	373,000
United States	59,250	68,000	90,120	79,500	96,600	105,143
France	47,300	49,100	52,700	52,600	53,600	56,000
Belgium and Holland..	24,200	30,000	55,000	35,000	40,000	43,000
Spain	10,000	10,000	12,000	.....	12,000	9,000
Italy	4,500	5,000	11,000	80,000	12,000	12,000
Other countries	40,500	40,000	65,000	.....	73,000	79,000
	694,300	731,270	891,200	890,550	971,947	1,052,068

b. *Ammonium Sulphate and Sulphate Equivalent Produced in the United Kingdom.* (In tons of 2240 pounds.)

	1905.	1906.	1907.	1908.	1909.	1910.
Gas works	155,957	107,160	165,474	165,218	164,276	167,820
Iron works	20,376	21,284	21,024	18,131	20,228	20,139
Shale works	46,344	48,534	51,338	53,628	57,048	59,113
Coke ovens	30,732	43,677	53,572	64,227	82,886	92,655
Producer gas and carbonizingworks	15,705	18,736	21,873	24,024	24,705	27,850

c. *United States Ammonia Production, Expressed in Sulphate Equivalent.* (In tons of 2000 pounds.)

1905	65,296	1908.................	83,400
1906	75,000	1909.................	106,500
[illegible]	[illegible]	1910	116,000

CHAPTER XII.

THE ARTIFICIAL COLORING MATTERS.

I. Raw Materials.

1. Hydrocarbons.—*Benzene Series.*—In the manufacture of the a ficial coloring matters, the hydrocarbons which find application as r materials are limited mainly to benzene, naphthalene, and anthrace their homologues and derivatives; of which, probably, benzene is most important.

The benezene series is as follows:

		Boiling-point.	Specific gravity.
Benzene, C_6H_6		80.4° C.	.884 at 15°
Toluene, $C_6H_5.CH_3$		110° C.	.869 at 15°
Xylene, $C_6H_4.(CH_3)_2$	*o*-Xylene	142° C.	.893 at 0°
	m-Xylene	139° C.	.881 at 0°
	p-Xylene	138° C.	.880 at 0°
Pseudocumene, $C_6H_3.(CH_3)_3$		169.5° C.	.895 at 0°
Mesitylene, $C_6H_3.(CH_3)_3$		165° C.	.865 at 14°
Durene, $C_6H_2.(CH_3)_4$. (Fuses at 79°–80° C.)		192° C.	... ...
Pentamethylbenzene, $C_6H.(CH_3)_5$. (Fuses at 5.5° C.)		231° C.	... ...
Hexamethylbenzene, $C_6(CH_3)_6$. (Fuses at 166° C.)		265° C.	... ...

Of which only the first three are employed to any extent.

Benzene has been described in a previous chapter (see Tar Distill tion), but for the manufacture of colors an explanation is necessar the name *benzene,* chemically speaking, does not refer to the light fra tions obtained from petroleum, but applies solely to the substance d tilled from coal-tar; boiling at 80.4° to 81° C., having a specific gravi of .899° at 0°, with the definite composition C_6H_6. The term *benzol,* the other hand, is not given to a definite compound, but to a mixture *benzene* with variable quantities of *toluene* and *xylene,* with the oth homologous of the same series. The quantity of these homologous bodi contained has an influence upon the use to which the aniline oil obtain (by subsequent treatment of the benzol) can be put.

The pure benzene, free from the high-boiling homologues, is succe sively converted through several processes to dimethylaniline, which the base of the valuable methyl-violets. For the fuchsine process, be zol, seventy-five per cent. of which distils between 80° and 100° C. (co taining toluene), is employed, producing aniline, seventy-five per cen of which distils between 180° and 190° C. High-boiling benzol, 115° 120° C., yields aniline, which is the starting-point for the production the beautiful series of xylidine scarlets; the introduction, however, pure xylene has served to displace the above. Allen states (Commerci product of which ninety per cent. by volume distils before the thermometer rises above 100° C. A good sample should not begin to distil under 80° C., and should not yield more than twenty to thirty per cent. at 85°, or much more than ninety per cent. at 100° C. It should wholly distil below 120° C. An excessive distillate—*e.g.*, thirty-five to forty per cent. at 85° C.—indicates a larger proportion of carbon disulphide or light hydrocarbons than is desirable.

"The actual percentage composition of a ninety per cent. benzol of good quality is about seventy of benzene, twenty-four of toluene, including a little xylene, and four to six of carbon disulphide and light hydrocarbons. The proportion of real benzene may fall as low as sixty or rise as high as seventy-five per cent. Ninety per cent. benzol should be colorless and free from opalescence."

"*Fifty per cent. benzol,* often called 50/90 benzol, is a product of which fifty per cent. by volume distils over at a temperature not exceeding 100° C., and forty per cent. more below 120°. It should wholly distil below 130°."

"*Thirty per cent. benzol* is a product of which thirty per cent. distils below 100°, about sixty per cent. more passing over between 100° and 120°. It consists chiefly of toluene and xylene, with small proportions of benzene, cumene, etc."

The following table from Schultz (Steinkohlentheers) indicates the general properties of the three commercial benzols above described when subjected to distillation:

	Thirty per cent.	Fifty per cent.	Ninety per cent.
To 85°	0	0	25
" 90°	2	4	70
" 95°	12	26	83
" 100°	30	50	90
" 105°	42	62	94
" 110°	70	71	97
" 115°	82	82	98
" 120°	90	90	99

The theoretical quantities of commercially applicable products from benzol are:

For 100 parts, 157.6 parts nitrobenzol.
" " " 119.2 " aniline.
" " " 215.3 " dinitrobenzol.
" " " 155.1 " dimethylaniline.
" " " 191.0 " diethylaniline.

Toluene, or *Methylbenzene,* $C_6H_5.CH_3$, is obtained by careful distillation of coal-tar benzols, and can be obtained from the balsam of tolu and other sources. It is quite similar in its properties to benzene;

nitrotoluene, toluidine, benzylchloride, benzalchloride, and benzaldehyde,—the base of a valuable series of green colors. The theoretical yield of commercial products from toluene is as follows:

For 100 parts, 148.9 parts nitrotoluene.
" " " 116.3 " toluidine
" " " 115.3 " benzaldehyde.

Xylene, or *Dimethylbenzene,* $C_6H_4.(CH_3)_2$, exists under similar conditions to toluene, and is found in coal-tar. There are three xylenes, the ortho-, meta-, and para-, the second being most abundantly obtained. Owing to the slight difference between their respective boiling-points, a commercial separation by distillation is practically impossible.

The annexed table gives the nature and behavior of the three isomeric hydrocarbons mentioned.

		Ortho-xylene.	Meta-xylene.	Para-xylene.
Melting point		Fluid.	Fluid.	15° C.
Boiling-point		141° to 142° C.	139° C.	137.5° to 138° C.
Specific gravity		. . . .	.8668 at 19° C.	.8621 at 19.5° C.
Oxidized with	Dilute nitric acid	*o*-Toluic acid, melting point 102° C.	*m*-Toluic acid, melting point 160° C.	*p*-Toluic acid, melting point 178° C.
	Permanganate	Phthalic acid.	Isophthalic acid.	Terephthalic acid
	Chromic acid	Decomposed.		
Sulphuric acid (66° Bé.)		Sulphonic acid.	Two sulphonic acids.	No change.
Sulphuric acid (fuming)		Sulphonic acid.	Two sulphonic acids.	Sulphonic acid.
Melting point of the sulphochloride		52° C.	(*a*) 34° C., (*b*) liquid.	26° C.
Melting point of the sulphamide		144° C.	(*a*) 137° C., (*b*) 96° C.	148° C.

From Schultz, "Steinkohlentheers."

Naphthalene Series.—Naphthalene, $C_{10}H_8$, as a raw material, enters largely into the production of the extensive series of azo-coloring matters, and for such use it is converted into intermediary products, of which the alpha- and beta-naphthols are the most familiar. The occurrence, properties, and production of naphthalene are referred to on page 419.

Methyl-naphthalene, $C_{10}H_7CH_3$.—Two isomers exist in coal-tar, and can be separated from that fraction of the distillate boiling at from 220° to 270° C. The first of these is a liquid boiling at 243° C.; specific gravity 1.0287 at 11.5°. The second is a solid, looking like naphthalene, melting at 32.5° C. and boiling at 242° C.

Ethyl-naphthalene, $C_{12}H_{12}$.—Two isomers, α- and β-, are known. α-Ethyl-naphthalene, produced from α-brom-naphthalene and ethyl-bromide, and distilled in vacuum, boils at from 257° to 259.5° C. β-Ethyl-naphthalene, from β-brom-naphthalene, ethyl bromide, and sodium, boils at from 250° to 251° C.

Diphenyl, C H has been found in

n water, soluble in hot alcohol and in ether. It forms large colorless cales, melting at 71° C. and boiling at 254° C. Oxidized by chromic cid, it yields benzoic acid.

Stilbene, $C_{14}H_{12}$.—This compound, which is diphenylethylene $(C_6H_5.CH = CH.C_6H_5)$, is formed when toluene or dibenzyl is led over eated lead oxide. It crystallizes in colorless scales, melting at 125° C. orms the basis of numerous important dyes.

Anthracene Series.—Anthracene, $C_{14}H_{10}$, reference to which has been nade in the previous chapter, is employed for the production of ali-arine and allied bodies, the successful introduction of which caused a evolution in the processes of dyeing, and made useless for the time reat areas of land which were devoted to the culture of madder. An-hracene, as it occurs in commerce, is rarely pure, being made up of a ery large number of hydrocarbons, several of which have not been nvestigated. The following may be mentioned:

Methyl-anthracene, $C_{15}H_{12}$, closely resembles anthracene. It differs rom that body in having a methyl group substituted for an H atom f one of the benzene rings. It occurs in coal-tar in small quantity, and wing to the high boiling-point, over 360° C., it is found in the anthraene. Crystallizes in pale-yellow leaflets, melting at 199° to 200°.

Phenyl-anthracene, $C_{20}H_{14}$, is formed when phenyl-anthranol or œruleïn is heated with zinc-dust. Slightly soluble in hot alcohol, ether, enzene, carbon disulphide, and chloroform, and, upon cooling, crysallizes from the above solvents in yellow plates, melting at 152° to 153° . The solutions have a blue fluorescence.

Fluorene, or *Diphenylen-methane,* $C_{13}H_{10}$, is found in coal-tar, and an be obtained by passing diphenylmethane through a combustion-tube eated to redness; it can also be obtained by distilling diphenyleneketone ver heated zinc-dust, or by heating the same substance with hydriodic cid and phosphorus from 150° to 160°. Very soluble in hot alcohol, ess in cold; crystallizes in colorless plates having a violet fluorescence. Melts at 113° C., boils at 295° C.

Phenanthrene, $C_{14}H_{10}$.—This hydrocarbon is isomeric with anthraene, is found with it, and forms a large part of, the last fraction of oal-tar. Compared with anthracene, the melting point is considerably ower, while the boiling-points are somewhat closer. It is much more oluble in alcohol, by which means a separation is effected; the low meltng point materially assisting. Crystallizes in colorless, shining plates, nelting at 100° and boiling at 340°, insoluble in water, but soluble in ifty parts of alcohol in the cold, and in ten parts on boiling; easily oluble in ether and benzene. It imparts a blue fluorescence when disolved. When oxidized, phenanthrenquinone is formed. Technically, ut little use is made of it, being chiefly employed in the oil baths for lkali melts, heating autoclaves, subliming phthalic anhydride, etc.

Fluoranthene, $C_{15}H_{10}$, occurs in the highest boiling tar fractions; rystallizes in needles; melts at 109°.

Retene, $C_{18}H_{18}$, *Chrysene,* $C_{18}H_{12}$, and *Picene,* $C_{22}H_{14}$, are bodies which occur in the highest fractions with fluoranthene, and cannot be classed as raw materials,—no technical importance being attached to them.

2. HALOGEN DERIVATIVES.—*From Benzene.*—The following table of the halogen derivatives of benzene indicates those whose constitution is known. They are produced by the action of the halogens upon the hydrocarbons directly, or through the action of the halogen compounds of phosphorus upon phenols and aromatic alcohols. Two classes are produced, substitution and addition compounds. The former occur under ordinary conditions, while the latter are formed when the reaction takes place in direct sunlight. Of the two, the substitution products are the more stable, the addition products being easily decomposed.

The following table gives the formulas of the several halogen derivatives of benzene and the boiling-points of the more important of the several isomeric compounds:

Halogen substitution products of benzene.												
C_6H_6	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
C_6H_5	Cl	133°	. . .	. . .	Br	154°	. . .	. . .	I	185°	. . .
C_6H_4	Cl_2	179°	172°	173°	Br_2	224°	219°	219°	I_2	277°	285°
C_6H_3	Cl_3	213°	208°	218°	Br_3	276°	278°	. . .	I_3	. . .	. . .
C_6H_2	Cl_4	246°	246°	·254°	Br_4	329°	. . .	. . .	I_4	. . .	. . .
C_6H	Cl_5	276°	. . .	. . .	Br_5	. . .	. . .	. . .	I_5	. . .	. . .
C_6	Cl_6	332°	. . .	. . .	Br_6	. . .	. . .	. . .	I_6	. . .	. . .

From Toluene.—(1) *Benzyl-chloride* (*Chlorbenzyl*), $C_6H_5CH_2.Cl$, results from the action of hydrochloric acid upon benzyl alcohol ($C_6H_5.CH_2.OH$), or by acting on boiling toluene with chlorine, this method being the one most generally used; the product is washed with water containing a little alkali, when it is freed from impurities by distillation. It is a colorless fluid, specific gravity 1.113, boils at 179°, insoluble in water, but soluble in alcohol and ether, and possesses an exceedingly penetrating odor, acting upon the eyes and mucous membrane of the nose. Technically, it finds considerable application in the color industry.

(2) *Benzal-chloride,* $C_6H_5.CH.Cl_2$.—Formed when chlorine acts upon boiling benzyl-chloride, or when phosphorus penta-chloride acts upon benzaldehyde. It is a colorless liquid, having ordinarily but little odor, but upon the application of heat gives off a vapor producing effects similar to the preceding. Boils at 206° to 207°; specific gravity at 16° 1.295.

(3) *Benzo-trichloride,* $C_6H_5.C.Cl_3$, is obtained by acting with chlorine upon boiling toluene until no further increase in weight takes place, when it is washed in water containing alkali, dried, and distilled in a vacuum. Boils at 213° to 214°; specific gravity 1.38 at 14°. It has a penetrating odor, and is highly refractive.

nated compounds of the same, with or without the presence of iodine. They find no application industrially.

Halogen Derivatives of Naphthalene.—(1) *Naphthalene Dichloride,* $C_{10}H_8Cl_2$, is a liquid, easily decomposed; produced as an addition compound by the action of chlorine gas upon naphthalene.

(2) *Naphthalene Tetrachloride,* $C_{10}H_8Cl_4$.—This substance is manufactured in large quantities by passing chlorine gas through the melted hydrocarbon in a suitable apparatus, or by grinding the naphthalene to a paste with water and intimately kneading therein sodium or potassium chlorate, moulding into balls, and drying, after which they are immersed in concentrated hydrochloric acid. It crystallizes from chloroform in large rhombohedra, melting at 182°, and when boiled with nitric acid is converted into phthalic acid, which is the chief product obtained from it.

(3) *α-Brom-naphthalene,* $C_{10}H_7.Br$.—Formed by the direct bromination of the hydrocarbon, or by the substitution of bromine for the amido group in a brom-α-naphthylamine. It is a liquid, boiling at 277°; specific gravity 1.503 at 12°. Insoluble in water, soluble in acohol and ether.

(4) *β-Naphthyl-chloride,* $C_{10}H_7.CH_2Cl$, is formed when chlorine acts upon β-methyl-naphthalene at a temperature of 240° to 250°. Melts at 47°, boils at 168°.

(5) *β-Naphthyl-bromide,* $C_{10}H_7.CH_2Br$.—Formed when the vapor of bromine with CO_2 gas is brought in contact with β-methyl-naphthalene, heated to 240°. Crystallizes from alcohol in white plates, which melt at 56°.

Anthracene Derivatives.—(1) *Monochlor-anthracene,* $C_{14}H_9.Cl$.—When dichlor-anthracene is heated, hydrochloric acid is evolved, having the monochlor derivative. Soluble in alcohol, ether, carbon disulphide, and benzene. Crystallizes in yellow needles, melting at 103°.

(2) *Dichlor-anthracene,* $C_{14}H_8.Cl_2$, is produced when anthracene is allowed to remain in contact with chlorine, or when the monochlor derivative is similarly treated, being maintained at a temperature of 100°. Freely soluble in benzene, but not readily in alcohol or ether. Forms beautiful yellow lustrous needles, which melt at 209°. Treated with ulphuric acid at a low temperature, dichlor-anthracene-sulphonic acid ccurs in solution; this, when heated, yields sulphurous acid, hydrohloric acid, and the anthraquinone-disulphonic acid, which is the immediate base of the artificial alizarine.

(3) *Dibrom-anthracene,* $C_{14}H_8Br_2$.—Upon agitating bromine with a solution of anthracene in carbon disulphide, this derivative is formed. Difficultly soluble in alcohol, ether, and benzene; hot toluene or xylene answer best. Crystallizes in gold-yellow needles, melting at 221°, and ubliming without decomposition.

3. Nitro- Derivatives.—By the action of nitric acid upon the hydrocarbons nitro- derivatives are obtained, and one of the most important

(1) *Nitrobenzene,* $C_6H_5.NO_2$, was discovered by Mitscherlich, w obtained it by heating benzene or benzoic acid with fuming nitric ac It was first brought into trade, bearing the name "oil of mirban (artificial oil of bitter almonds), by Collas, and in 1847 a patent for manufacture from coal-tar was granted to Mansfield. It is obtained adding a cooled mixture of concentrated sulphuric acid and nitric a (150:100) to the hydrocarbon and agitating, taking care that the te perature does not go above 50° C. After the addition of the acid complete, heat is applied, and it is again agitated. The oily layer removed, washed with dilute alkali, dried, and distilled. Nitrobenze when pure, is a pale-yellow fluid, strongly refractive, having the od of bitter almonds, and a sweet, though burning, taste. Specific gravi 1.208 at 15°; boils at 206° to 207°, and when the temperature is r duced it crystallizes in large needles, which melt at + 3°. Nearly i soluble in water, though with alcohol, ether, and benzene it is readi soluble. It is exceedingly stable, and even at a boiling temperature is not acted upon by either bromine or chlorine. It is poisonous, an according to Roscoe and Schorlemmer (vol. iii, pt. iii), "especially wh the vapor is inhaled; it produces a burning sensation in the mout nausea and giddiness, also cyanosis of the lips and face, and in serio cases, which frequently end fatally, symptoms of a general depression.

(2) *Dinitrobenzene,* $C_6H_4(NO_2)_2$.—Three isomers of this derivati exist, being obtained when benzene is nitrated with the concentrate acids, as in the preceding case, but instead of being cooled is boiled f a short time, when the product is washed with water, pressed, dissolve in alcohol, from which the meta-nitro body crystallizes, followed upo standing by the paranitro compound. Upon distilling the alcohol r maining in the mother-liquors from the *para-* compound, a further yiel of the *meta-* body is obtained, finally the *ortho-dinitrobenzene,* whic occurs in small quantity, crystallizes, and is purified by treatment wit acetic acid, from which it is deposited in needles, having a melting poin of 117.9°. The *para-* compound occurs in monoclinic needles, meltin at 172°, and subliming. The *meta-* compound finds technical applicatio in the production of chrysoidine and Bismarck brown, and is manufac tured on a large scale by adding a mixture of one hundred kilos. nitri acid (specific gravity 1.38) and one hundred and fifty-six kilos. sul phuric acid (specific gravity 1.84) to one hundred kilos. of benzene When the reaction is over, a separation of the acids (which can be use again) from the product occurs; commercially, the product is washe with warm and cold water, further purification being unnecessary. I crystallizes in needles or rhombic tables, which melt at 98.8°, boiling a 297°. Difficultly soluble in warm water, easily in ether and alcohol.

Nitrotoluene.—(1) *Nitrotoluene,* $C_6H_4(NO_2)CH_3$, occurs in thre isomers. The *ortho-* derivative is a liquid boiling at 223°, and at 23.5 has a specific gravity of 1.162. Does not become solid at 20°. Th *meta-* derivative melts at 16°, boils at 230° to 231°. Specific gravity a 22° 1.168. *Para-* nitrotoluene, melting point 54°, distilling unchange less of a mixture of the three, is manufactured in large quantities and in the same manner as nitrobenzene. Ten parts of toluene are mixed, and continually agitated with eleven parts of nitric acid (specific gravity 1.22) and one part sulphuric acid (specific gravity 1.33). The product is treated with water, and afterwards with caustic alkali; distilled to remove uncombined toluene, and finally distilled with superheated steam. When fractionated, that part passing over at 230° yields, when purified, para-nitrotoluene, and is employed in the production of toluidine, tolidine, and fuchsine. The fraction between 220° and 223° is nearly all ortho-nitrotoluene.

(2) *Dinitrotoluenes,* $C_6H_3(NO_2)_2.CH_3$—α- or ordinary dinitrotoluene is produced when toluene is added to a mixture of fuming nitric and sulphuric acids and boiled; ortho-nitrotoluene is employed for the manufacture also. Crystallizes in needles, which melt at 70.5°; insoluble in water, little soluble in alcohol, ether, or carbon disulphide. β-dinitrotoluene, isomeric with the above, is produced under similar conditions; or it can be made by replacing the amido group of dinitroparatoluidine with hydrogen. Crystallizes in golden-yellow needles; melting point 61.5°.

Trinitrotoluene, $C_6H_2.(NO_2)_3CH_3$.—Produced by the action of nitric and sulphuric acids upon toluene, or dinotrotoluene, and heating for several days. α-Trinitrotoluene is soluble in alcohol, crystallizing from it in beautiful needles, which melt at 82°. β-Trinitrotoluene crysallizes from acetone in transparent prisms, which melt at 112°, while from alcohol it forms plates or flat white needles. γ-Trinitrotoluene is deposited from acetone in small hexagonal crystals, melting at 104°.

Mononitronaphthalene, $C_{10}H_7.NO_2$.—Two isomers exist; the α- compound is produced when ten parts naphthalene, eight parts nitric acid (specific gravity 1.4), and ten parts sulphuric acid (specific gravity 1.84) are combined in a nitrobenzene apparatus. The naphthalene is added in small portions and continually stirred. The product is washed with water, and freed from acid by treatment with alkali. Insoluble in water, easily in benzene, carbon disulphide, ether, and alcohol. Crysallizing in yellow needles, melting at 61°, boiling at 304°. The β- compound is produced when β-nitronaphthylamine is melted with nitrate f potassa. Soluble in alcohol, ether, or glacial acetic acid. Crystallizes in yellow needles; melts at 79°.

α-Dinitronaphthalene, $C_{10}H_6(NO_2)_2$, obtained in a similar manner to the above. Difficultly soluble in cold, easily in warm, benzol. From lacial acetic acid it crystallizes in needles, melting at 217°. β-Dinitroaphthalene, isomeric with the above, crystallizes in rhombic plates, melting at 170°.

4. Amine Derivatives.—The amine derivatives of benzene, toluene, nd xylene can be regarded as forming one of the most important groups f raw materials from which are obtained the *basic* coloring matters, ll of which contain nitrogen. The structure of the amines can readily e seen if we employ [illegible]

radical, a *primary amine* is produced; if two or all three are replaced, a *secondary* or *tertiary amine* respectively is formed.

Aniline, or *Amido-benzene,* $C_6H_5.NH_2$.—This substance was discovered by Unverdorben in 1826, who noticed its property of combining with acids to form salts. Runge, subsequently, experimenting upon coal-tar, found a volatile substance which, when treated with a solution of bleaching-powder, produced a blue coloration, giving rise to the name kyanol. It was he who noticed that when a drop of the "nitrate of kyanol" was brought in contact with dried cupric chloride, a black spot was formed. Fritsche, later, examined the distillation products of indigo, and found a body to which he gave the name *aniline.* Aniline was formerly obtained in large quantities by reducing the nitrobenzene with iron filings or scrapings and acetic acid, but now it is wholly produced with hydrochloric acid, the following reaction showing the change that occurs:

$$\underset{\text{(Nitrobenzene.)}}{C_6H_5.NO_2} + 3Fe + 6HCl =$$
$$\underset{\text{(Aniline.)}}{C_6H_5.NH_2} + 3FeCl_2 + 2H_2O.$$

The quantity of acid represented by the above equation is more than sufficient for the purpose, from the fact that ferrous chloride, ($FeCl_2$), a reducing agent itself, will act in the reduction of a further quantity of nitrobenzene:

$$C_6H_5.NO_2 + 6FeCl_2 + 6HCl =$$
$$C_6H_5.NH_2 + 3Fe_2Cl_6 + 2H_2O.$$

Aniline is a liquid, fluid at ordinary temperatures, but when frozen melts at —8°; boils at 182° when pure; specific gravity 1.036; colorless when freshly distilled, but becomes reddish-brown upon exposure to light and air; impurities hasten discoloration. Soluble in alcohol, ether, and benzene in all proportions; in water it is soluble to a slight extent, one hundred parts of water dissolving three parts aniline, while it, in turn, dissolves water to the extent of five per cent.

Aniline forms a series of well-crystallized salts, among which are the *hydrochloride,*—$C_6H_7.N.ClH$,—known as "aniline salt," largely employed in the production of black upon cotton; and the *sulphate,*—$(C_6H_7N)_2H_2SO_4$,—of considerable importance.

Methylaniline, $C_6H_5.NH(CH_3)$, is obtained by heating aniline hydrochloride or a mixture of aniline and hydrochloric acid with rather more than a molecule of methyl alcohol at 200° C. The product is then converted into sulphate and the easily soluble sulphate of methylaniline separated from the sparingly soluble aniline sulphate. The sulphate is decomposed by an alkali and the free base obtained by distillation. The commercial product contains from ninety to ninety-five per cent. of pure methylaniline. It is a colorless oil, boiling at 192° C., and has a specific gravity 0.976 at 15° C.

aniline (seventy-five parts), aniline hydrochloride (twenty-five parts), and methyl alcohol, free from acetone (seventy-five parts), in a cast-iron autoclave at from 230° to 270° C. The product is rectified. The yield is about one hundred and twenty parts from the above proportions. It is a colorless oil, boiling at 192° C., and specific gravity 0.96 at 15° C. Solidifies at + 5° C. to a crystalline solid. The commercial product is usually nearly pure.

Nitraniline, $C_6H_4(NO_2)NH_2$.—Both the *m*- and the *p*- nitraniline are used technically. The former is made by the partial reduction of dinitrobenzene; the latter from acetanilid, which is nitrated and then freed from the acetyl group by treatment with steam.

Toluidine, or *Amido-toluene,* $C_6H_4(CH_3)NH_2$, occurs in three isomers, according to the extent to which the nitration of the toluene was originally carried. *Ortho-toluidine* is produced by the reduction of ortho-nitro-toluene, by the same means as was applied in the case of aniline. It is a fluid, colorless at first, but becoming brown upon exposure. Specific gravity 1.000 at 16°, boiling point 197°; soluble to a slight extent in water (2:100) and in alcohol.

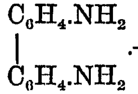
Meta-toluidine, occurring similarly to the preceding, is a liquid. Specific gravity .998, boiling at 197°, little soluble in water, but freely in alcohol and ether.

Para-toluidine is obtained in the form of large colorless leaflets, crystallizing from alcohol. Specific gravity .973, melting point 45°, and boiling at 198°; slightly soluble in water, readily in alcohol and ether. Commercial toluidine consists chiefly of a mixture of the ortho- and para-bodies, and containing very little aniline; it is of considerable importance in the color industry.

Xylidine, or *Amido-xylene,* $C_6H_3(CH_3)_2.NH_2$, homologous with aniline and toluidine, is produced from xylene, as aniline is from benzene,—nitration followed by reduction. Six isomers are obtainable, but the xylidine industrially employed consists of a mixture of five. At ordinary temperature it is a liquid, specific gravity .9184 at 25°, boiling point 212°. From this derivative the beautiful series of xylidine scarlets are produced.

Naphthylamine, $C_{10}H_7.NH_2$.—Two isomers exist. For α-Naphthylamine naphthalene is converted into the nitro- derivative as has been described, and equal parts of this body and water are heated to 80°, incorporated with an equal part of iron filings, and reduced with hydrochloric acid. The product is distilled with lime, and finally rectified by further distillation. Nearly insoluble in water, soluble in alcohol and ether; crystalizes in colorless needles or prisms, which melt at 50°, and boil at 300°. Upon contact with the air it acquires a red color, and oxidizing agents cause a blue precipitate to form in solutions of its salts. It finds extensive application in the preparation of several colors of importance. β-Naphthylamine is produced when gaseous ammonia combines with β-naphthol in the fused state; commercially it is obtained by the action ducts. It occurs in white or pearly leaflets, odorless, difficultly soluble in cold, freely in hot water, and in alcohol and ether. Melting point 112°, boiling at 294°. Unlike the α-naphthylamine, it is not acted upon by oxidizing agents.

Phenylendiamine, $C_6H_4(NH_2)_2$.—Both the *m*- and the *p*- compounds are used in practice. The former is obtained by the reduction of *m*-dinitrobenzene with iron and hydrochloric acid; the latter by the reduction of amidoazobenzene with zinc-dust in aqueous solution.

Benzidine (diamido-diphenyl),  $\begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{array}$.—This base is manufactured on a large scale as the basis of the substantive cotton dyes (see p. 464). For its preparation nitrobenzene is reduced by zinc-dust and caustic soda in the presence of alcohol. The hydrazobenzene so obtained is heated in the presence of hydrochloric acid to boiling and the benzidine precipitated from the solution by the addition of sulphuric acid. It forms a grayish-white crystalline solid, fusing at 122° C., and rather difficultly soluble in water.

Diphenylamine, $(C_6H_5)_2NH$, is made on a large scale by heating aniline with aniline chlorhydrate in autoclaves to between 220° and 230°. It forms a white or slightly yellowish solid, melting at 54°, and has a pleasant odor of flowers.

5. PHENOL DERIVATIVES.—*Phenol,* C_6H_5OH.—The occurrence of this body has been mentioned under tar products, page 418. It crystallizes in needles, which have the well-known odor of "carbolic acid." Specific gravity 1.08, and melting at 37.5°, boiling at 132° to 133°; soluble in water (1 : 15) and readily in alkalies, alcohol, and ether. It finds extensive application in the color and other industries, large quantities being consumed in the manufacture of picric acid.

Resorcin, or *m-Dioxybenzene,* $C_6H_4(OH)_2$, is obtained from benzene by fusing the sodium sulphonate of the latter with caustic soda. (See page 444.) Occurs in sweetish, colorless crystals, which, however, eventually become dark colored, melting at 110°, boiling-point, 271°; readily soluble in water, alcohol, and ether. Specific gravity 1.28.

Pyrogallol, or *Trioxy-benzene,* $C_6H_3(OH)_3$, is readily obtained from gallic or tannic acid when the same are heated to 210° to 220°. It can be obtained from benzene, but the above method is more generally adopted. Processes for its manufacture are detailed on page 452. Pyrogallol occurs in white leaflets, which melt at 115° and boil at 210°; soluble in water, alcohol, and ether.

Naphthols, $C_{10}H_7.OH$.—The two derivatives of naphthalene, α- and β-naphthol, find extensive application in the manufacture of artificial coloring matters. They are prepared from the two isomeric naphthalene sulphonic acids, α and β, which are discussed under Processes, page 452. α-Naphthol occurs as lustrous needles, which melt at 94°, boil at 278° to 280°; specific gravity 1.224; sparingly soluble in hot, insoluble from 285° to 290°; solubilities same as for the preceding. Allen (Commercial Organic Analysis, 2d ed., vol. ii, p. 511) gives the following table of the distinguishing characteristics of the two naphthols:

α-Naphthol.	β-Naphthol.
Crystallizes in small monoclinic needles.	Crystallizes in rhombic laminæ.
Melting point 94°; boils at 278° to 280°.	Melting point 122°; boils at 285° to 290°.
Faint odor, resembling phenol.	Almost odorless.
Volatilizes readily with vapor of water.	Scarcely volatile with vapor of water.
Aqueous solution becomes dark violet, changing to reddish-brown on adding solution of bleaching-powder.	Aqueous solution colored pale yellow by solution of bleaching-powder.
Aqueous solution becomes red, and then violet, on adding ferric chloride.	Aqueous solution becomes pale green on adding ferric chloride.

6. SULPHO- ACIDS.—This group constitutes an interesting and technically valuable series of bodies, which are obtained by the action of concentrated sulphuric acid upon the hydrocarbons, or upon coloring matters already formed.

(1) *Benzene-sulphonic Acid,* $C_6H_5.SO_3H$, is readily obtained by heating two parts benzene with three parts sulphuric acid to 100° C., diluting with water, saturating with carbonate of lead, and decomposing with sulphuric acid to liberate the sulphonic acid. The acid is soluble in water and alcohol, and crystallizes in small plates.

(2) *Benzene-disulphonic Acids,* $C_6H_4(SO_3H)_2$, are (mainly the meta variety) produced when benzene is heated with fuming sulphuric acid to 275°. Employed in the production of resorcin.

(3) *Toluene-sulphonic Acid,* $C_6H_4(CH_3)SO_3H$.—No importance.

(4) *Naphthalene-sulphonic Acids,* $C_{10}H_7.SO_3H$.—Two isomeric bodies are obtained when naphthalene is submitted to the action of sulphuric acid. At temperatures ranging from 80° to 100° the α-derivative is largely obtained, and at temperatures from 160° to 170° the β-derivative is produced. Their separation is based upon the different degrees of solubility of the lead salts upon concentrating their aqueous solutions, α-naphthalene-sulphonic acid being soluble in twenty-seven parts water, while the β-acid requires one hundred and fifteen parts.

(5) *Anthracene-sulphonic Acid,* $C_{14}H_9.SO_3H$, is produced similarly to the above, or by the reduction of sodium anthraquinone-sulphonate with zinc-dust and ammonia.

Phenol-sulphonic Acid, $C_6H_4(OH)SO_3H$.—Three isomers are known, two, the *ortho-* and *para-*, being produced by the direct action of sulphuric acid upon phenol, while the *meta-* compound must be produced by other means. The *ortho-* acid is largely obtained when one part of phenol is slowly mixed with one part of sulphuric acid, care being taken to keep the temperature from rising. The *para-* acid will be obtained if the mixture be heated to 100°. These bodies are much employed as anti-

Naphthol-sulphonic Acids.—The two naphthols are easily converted into mono-sulphonic acids upon being heated to 100° C. with concentrated sulphuric acid; disulphonic acids being produced if the temperature reaches 110° C. *β-naphthol-sulphonic acid,* $C_{10}H_6.SO_3H.OH$. One hundred parts of *β*-naphthol are added to two hundred parts of sulphuric acid (specific gravity 1.84) and carefully heated to 50° or 60°, when two acids result, ordinary *β-naphthol-sulphonic acid* (known also as "*Schäffer's acid,*" or "*acid S*") and *β-naphthol-α-sulphonic acid* ("*Bayer's acid,*" or "*acid B*"). When converted into their sodium salts they can be separated by treatment with alcohol, in which menstruum the latter acid is more soluble than the former. They are extensively used for the production of the croceïn scarlets; and upon nitration yield other colors of importance. If the mixed acid and naphthol is heated to about 20° C. Bayer's acid will be formed, while the employment of a temperature about 90° will cause the formation, as the chief product, of Schäffer's acid.

Disulphonic Acids of β-Naphthol, $C_{10}H_5(SO_3H)_2OH$, are obtained when the naphthol is subjected to a temperature of 100° to 110° with three times its weight of sulphuric acid (specific gravity 1.84). Upon dilution milk of lime is added, the precipitated calcium sulphate filtered off, carbonate of soda added, and the whole evaporated to dryness, and lixiviated with alcohol, when "salt G" (yellow shade) is dissolved from "salt R," red shade). Ordinarily, after the addition of the carbonate of soda, the solution is used without further treatment.

Anthraquinone-sulphonic Acid, $C_6H_4(CO)_2C_6H_3.SO_3H$, is formed when anthraquinone is treated with fuming sulphuric acid at 160° C. The unaltered anthraquinone is separated, the solution neutralized with soda, when the white soda salt settles out. The free acid occurs in yellow plates, soluble in water and in alcohol. When fused with either caustic soda or potash *alizarin* is obtained (when anthraquinone-disulphonic acid is used, either by itself or in the melt, *purpurin* is produced along with alizarin); anthraquinone-sulphonic acid being employed directly for the production of this most valuable coloring matter.

Sulphanilic (p-amidobenzene-sulphonic) Acid, $C_6H_4(HSO_3)NH_2$, is made by the action of sulphuric acid upon aniline at about 190° C. Is used very largely as basis of the manufacture of dye-colors.

Naphthylamine-sulphonic Acids are prepared from naphthylamine by treatment with sulphuric acid and the application of heat. Several derivatives are produced, which, however, find limited application, mainly in some patented specialties.

7. Pyridine and Quinoline Bases.—*Pyridine,* C_5H_5N, is regarded as a benzene nucleus (C_6H_6) with one of the CH groups replaced by an atom of nitrogen. It is obtained when bone oil or other nitrogen-containing organic bodies are distilled. It possesses a pungent odor, is liquid, boils at 116.7°, and is soluble in water; specific gravity .986. A large number of the pyridine derivatives bear a relationship to the alkaloids.

the CH groups. Quinoline is readily prepared by carefully heating in a flask one hundred and twenty grammes glycerine, thirty-eight grammes aniline, twenty-four grammes nitrobenzene (oxidizing agent), with one hundred grammes concentrated sulphuric acid; when the reaction is over, boil for two or three hours, dilute with water, and remove the unchanged nitrobenzene with steam, saturate with caustic alkali, distil, add sulphuric acid and sodium nitrite ($NaNO_2$) to destroy any aniline present, make alkaline, and again distil. Quinoline is a colorless fluid, having a penetrating odor, highly refractive, becoming brown upon exposure to the air; boils at 238°; specific gravity 1.094 at 20°.

Quinaldine (*a-Methyl-quinoline*), $C_9H_6(CH_3)N$.—Obtained by the action of hydrochloric acid upon paraldehyde and aniline, for several hours, with the aid of heat. It has a faint odor, is fluid, and boils at 238° to 239°. Technically employed, mainly for the production of "quinoline yellow," cyanine blue, quinoline red, etc.

Acridine, $C_{13}H_9N$.—Anthracene is the base from which this derivative is obtained by a substitution of a nitrogen atom for one of the CH groups. As in the previous instances many derivatives of the above bodies exist, which have considerable interest, but no technical importance is attached to them as raw materials.

8. DIAZO- COMPOUNDS.—These form the most extensive, and probably the most thoroughly investigated of the several groups of coal-tar colors. They are produced when nitrous acid (obtained from starch and nitric acid) is allowed to act upon the primary amines of the aromatic series, in which case the following change is noted, assuming aniline nitrate to be acted upon:

$$C_6H_5NH_2.HNO_3 + HO.NO = \underset{\text{(Diazo-benzene nitrate.)}}{C_6H_5N{=}N.NO_3} + 2H_2O.$$

Aniline hydrochloride, treated in the same manner, will yield diazo-benzene chloride:

$$C_6H_5.NH_2.HCl + HO.NO = C_6H_5N{=}N.Cl + 2H_2O.$$

The diazo-compounds differ from those of the *azo*-group in that one of the bonds of the diatomic nitrogen group —N=N— is satisfied with a *hydrocarbon* radicle, while in the latter it is saturated with an atom of oxygen, nitrogen, bromine, chlorine, etc., or with an acid or basic group. The annexed list of diazo- bodies illustrates the above:

$C_6H_5N{=}NCl$	Diazo-benzene chloride.
$(C_6H_5.N{=}N)_2SO_4$	" " sulphate.
$C_6H_5N{=}N.Br$	" " bromide.
$C_6H_5N{=}N.NH.C_6H_5$	Diazo-amido-benzene.

The *azo-* compounds have the two nitrogen atoms (—N=N—) united, each to a hydrocarbon group; *mixed azo-* compounds result if these hydrocarbon soda ($NaNO_2$) is added to a solution of aniline chloride in the presence of an excess of hydrochloric acid, the solution being kept cool by means of ice. The product finds application in the manufacture of aniline yellow and other colors.

Diazo-amido Compounds result from the action of salts of the diazo-derivatives upon the primary and secondary amines.

Diazo-amido-benzene, $C_6H_5.N_2.NH.C_6H_5$, occurs when nitrous acid is passed through a solution of aniline in alcohol; or by adding a solution of sodium nitrite to a mixture of aniline hydrochloride and aniline. Crystallizes in golden-yellow prisms or scales, insoluble in water, easily in ether, benzene, and alcohol; melting point 91°, exploding at a higher temperature.

(2) *Diazo-benzene-sulphonic Acid,* $C_6H_4.N_2.SO_3$ (the anhydride of the sulphonic acid of diazo-benzene).—Sulphanilic acid, $C_6H_4NH_2.SO_3H$ (see p. 445), is dissolved in water, and sodium nitrite added, when the whole is poured into dilute sulphuric acid, which causes a precipitation of the crystals.

9. Aromatic Acids and Aldehydes.—The *aromatic acids* form a class of bodies of considerable importance, derived from benzenes by substituting the carboxyl group CO.OH for hydrogen. The simplest of the series is *Benzoic Acid* (*Benzene-carboxylic Acid*), $C_6H_5.CO.OH$, which, besides finding extensive application in medicine, is also used in the color manufacture. It can be prepared by a number of methods, chiefly by the sublimation of gum benzoin; by treating the urine of herbivorous animals with hydrochloric acid, which causes the *hippuric acid* to break up, yielding the acid and glycocoll; and from benzotrichloride with water under pressure. It crystallizes in needles or scales, lustrous, and odorless when pure. Specific gravity 1.291, melting at 121°, and boiling at 249°; soluble in alcohol, ether, benzene, etc., sparingly in water.

Phthalic acid (*Benzene-dicarboxylic Acid*), $C_6H_4.(CO.OH)_2$.—Three isomers of the above are known, but only the *ortho-* acid will be considered. It is obtained from naphthalene tetrachloride by heating with nitric acid or more generally at present by treating naphthalene with strong sulphuric acid in the presence of mercury. It occurs in rhombic crystals, specific gravity 1.585, and melting at 213°; upon being heated, it is liable to split up into water and the anhydride; soluble in hot water, alcohol, and ether. When a phenol is heated with the phthalic anhydride phthaleïns result; of these, the *resorcin* and *pyrogallol-phthaleïns* are the most important, being the bases of the eosins and galleïns and cœruleïns.

Gallic Acid (*Trihydroxybenzoic Acid*), $C_6H_2(OH)_3.CO.OH$.—This acid occurs in several vegetable substances,—chiefly gallnuts, sumach, tea, etc. It is ordinarily prepared by heating gallo-tannic acid with dilute mineral acid, or by allowing crushed galls to remain exposed in a moistened state to the action of the atmosphere for some time, when a light brown in color. Specific gravity 1.70. When heated to 220° it decomposes, forming *pyrogallol* (Trihydroxybenzene, $C_6H_3(OH)_3$) and CO_2. Gallic acid is the chief source of pyrogallol, reference to the application of which has been made under phthalic acid.

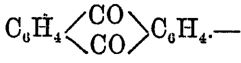
Benzaldehyde (*Benzoic Aldehyde*), $C_6H_5.CO.H$.—This body, also known as "Bitter Almond Oil," is a colorless liquid, possessing an agreeable odor, and high refracting power. Specific gravity 1.063, boiling at 180°, difficultly soluble in water (1:300), easily in alcohol and ether. Several methods are employed for the production of this substance; for industrial purposes, benzyl-chloride is boiled with nitrate of copper and water, half of the contents are distilled, when the oil layer is separated from the distillate and purified. Mercuric oxide has been used instead of the copper salt. It finds extensive application in the color industry, also for the production of cinnamic and benzoic acid, and several derivatives of value.

10. Ketones and Derivatives, Anthraquinone.—The ketones are closely related to the aldehydes, as will be seen from their structure,—$CH_3 - CO - H$, *Aldehyde,* $CH_3 - CO - CH_3$, *Dimethyl-ketone* (acetone).

The CO group—carbonyl—is possessed by both classes, but in the aldehydes is united, on the one hand to an alcohol radical, and on the other to an atom of hydrogen. The ketones, however, are distinguished by having two alcohol radicals (alkyls) linked by the CO group.

Benzophenone, $C_6H_5.CO.C_6H_5$, is a ketone of the benzene series, and can be obtained by distilling calcium benzoate, or by heating benzoyl chloride with aluminum chloride and benzene. It occurs in crystals having an aromatic odor, and which melt at 48° to 49°, subliming at 300°. Insoluble in water, soluble in alcohol and ether. It is of some importance, together with the amido- and oxy- derivatives, in the manufacture of certain colors.

Acetophenone (*Phenyl-methyl-ketone*), $C_6H_5.CO.CH_3$.—This is a mixed ketone, and contains two residues of different hydrocarbons united to the carbonyl group. Acetophenone can be obtained by distilling a mixture of the benzoate and acetate of calcium. It occurs in crystalline plates, melting at 14° to 15°, and boils at 198°.

Anthraquinone,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$.—This substance is of the utmost importance in the manufacture of alizarine. It can be obtained by several processes, the simplest of which is probably the distillation of calcium phthalate, or by oxidizing anthracene ($C_{10}H_8$) with bichromate of potash and sulphuric acid. Anthraquinone is very stable, oxidizing agents having but little effect upon it. When heated it sublimes, yielding yellowish rhombic crystals. Specific gravity 1.425, melting point 273°; insoluble in water, but somewhat in alcohol and ether. Upon fusion with caustic alkalies it yields benzoic acid. For use in the alizarine process, it must be converted into the sulphonic acid, and this fused with caustic

II. Processes of Manufacture.

1. OF NITROBENZENE AND ANILINE.—The commercial production of nitrobenzene is carried out essentially in the following manner, although the details may vary in the different works. Sulphuric acid, 66° Bé., and nitric acid, 42° Bé (= seventy per cent. HNO_3), are mixed together, in the proportion of fifteen parts by weight of the former to ten parts of the latter, in a lead-lined wood tank (preferably situated above the nitrating apparatus) and allowed to become cold. Three hundred pounds of this "nitrating acid" are run into the nitrating apparatus, either by gravity or by pressure, when the benzene is allowed to flow in in a slow, steady stream. During the admission of the benzene the temperature, which should be maintained between 80° C. and 90° C., is regulated by means of water kept at about 50° C. circulating around the vessel, or stopping the inflow, should the temperature give indication of rising, thereby producing the dinitro- derivative. About one hundred pounds of benzene are used, although this quantity is subject to change, according to quality. After the nitration is finished, the contents of the vessel are emptied slowly into large tanks, the acid layer being drawn off first, and the nitric acid recovered therefrom, and the nitrobenzene, insoluble in the acid, coming last, is immediately poured into a tank containing water, and washed, followed by a wash with caustic alkali, and finally agitated with water.

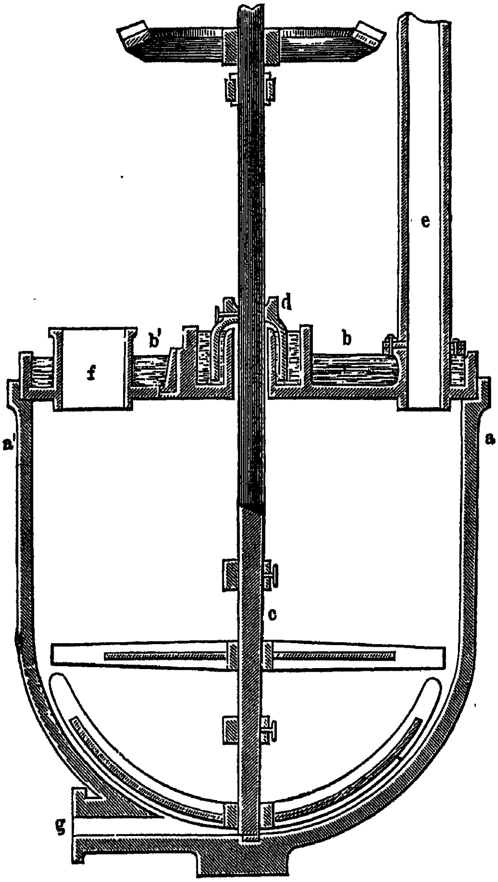
The quantities by weight of the two acids to effectually nitrate either benzene, toluene, or xylene, are shown below:

100 kilos. benzene....	120 kilos. nitric acid.	180 kilos. sulphuric acid.
100 " toluene....	150 " " "	175 " " "
100 " xylene.....	90 " " "	150 " " "

Or, of a standard mixture of one hundred kilos. nitric acid and one hundred and fifty kilos. sulphuric acid, there will be required for the effectual nitration of one hundred kilos. of the above tabulated hydrocarbons three hundred, two hundred and sixty, and two hundred and twenty-five kilos. respectively. The form of nitrating apparatus in use is usually cylindrical, with a flat or round bottom. Fig. 109 illustrates the latter form. The cover is provided with several openings: *f* is for general charging; *e* is for the gas exit, while provision is made for the introduction of the thermometer, and for carrying the agitator shaft. The opening for withdrawing the charge is at *g*. The best plan in arranging the plant is to provide for the acid mixing and nitrating on one floor, on the floor below the washing, and, if desirable, a steam still employed to separate the benzene which has not been acted on by the acids, and which is always found dissolved in the nitrobenzene. On the lowest floor, the alkali and final water-wash. If all the operations are performed on one level, a "monte-jus" should be used for the transportation of liquids.

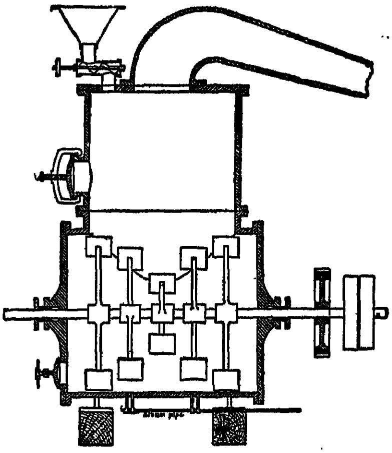
acid. The apparatus employed are generally of two kinds, vertical and horizontal, the method of working being in each case the same. In the former, the agitator is attached to an upright hollow shaft, so constructed as to provide for the admission of steam to the bottom of the vessel. The cover supports the gearing, and gooseneck for leading the vapors to the condenser, etc. The horizontal form is shown in Fig. 110; the construction provides for agitators attached to a horizontal revolving shaft passing through boxes in the heads. Steam enters through the pipes underneath. A steady supply of fine iron is maintained by means of the mechanical feed on the cover. The operation is conducted by adding some of the iron fillings with water, followed by the acid and nitrobenzene; steam is turned on, and, the agitators set in motion, at once the reaction begins, and a mixture of nitrobenzene, aniline, and water appears in the condenser, which is continually returned to th

FIG. 109.



tillate comes over regularly, the iron can be fed steadily, or at uniform intervals. If all the iron is added at once, serious loss is occasioned by a reduction of aniline to benzene and ammonia. For a charge of six hundred kilos. of nitrobenzene, about seven hundred kilos. of iron filings will be required and sixty kilos. of 21° Bé. hydrochloric acid. The solubility of the distillate in hydrochloric acid is noted, until a point is reached at which no nitrobenzene separates in an unaltered condition. Formerly it was the general practice to add lime to the tank, and distil off the aniline by means of steam; now the contents are emptied into large tanks containing water and allowed to subside for a day or more, when the lower layer, consisting of aniline, is drawn off and pumped into a large iron still mounted over an open fire and rectified. One hundred parts of nitrobenzene will yield about seventy-five parts of aniline if the process is carefully attended. Ordinarily, the yield will be from seventy-one to seventy-four parts.

Fig. 110.



2. Of Phenols, Naphthols, etc.—*Phenol.*—See Chapter XI., "Coal-tar Distillation," p. 418.

Resorcin is manufactured commercially from the soda salt of meta-benzene-disulphonic acid, by fusing with caustic soda and subsequent extraction with ether. One hundred kilos. of fuming sulphuric acid are contained in a large cast-iron vessel provided with means for agitating the contents, and into it is gradually allowed to flow twenty-eight kilos. of benzene; the whole is maintained at a moderate temperature for several hours, and finally raised to about 270° C. to 275° C., after which the contents are transferred to a large volume of water and boiled. Lime is added, the precipitated sulphate removed, and the soluble lime salt decomposed by the addition of the requisite quantity of carbonate of soda; carbonate of lime is precipitated, filtered, and the precipitate freed from the excess of solution in the filter-press. This solution is evaporated to dryness in iron pans. For the resorcin melt, sixty kilos. of the above salt and one hundred and fifty kilos. of 76° caustic soda are fused together for about eight hours at a temperature near 270°; when fusion is finished the melt is cooled, leached out with boiling water, and boiled with hydrochloric acid for some time, when the heat is withdrawn, and the solution allowed to become cold, and subjected to the action of ether or benzene in an extraction apparatus, which removes the resorcin. The benzene is distilled off and recovered, while the crude resorcin remaining is dried at about 210°. Pure resorcin is obtained from the above by distillation.

this substance, all being based upon the use of an aqueous extract of gallnuts or of gallic acid. One process is carried out by heating a glycerine solution of gallic acid to about 200° C., diluting with an equal volume of water, and extracting therefrom the pyrogallol with ether, which is evaporated off and recovered. Another process is to heat one part of gallic acid and two parts water in a closed vessel to 200° to 210° C. for half an hour, when it is cooled, and heated with bone-black, the solution filtered, and evaporated to the crystallizing-point. The crystals are further purified by being distilled in a vacuum.

Alpha- and Beta- Naphthols.—α-Naphthol is manufactured on a large scale in the same general manner as resorcin. α-Naphthalene-sulphonic acid is first prepared by heating naphthalene with fuming sulphuric acid to 90° C., diluting with water, and completely neutralizing with milk of lime, filtering from the magma of sulphate which is passed through a filter-press, the solution of the soluble lime salt decomposed with carbonate of soda, filtered and pressed again and the solutions finally evaporated to crystallization, when, on cooling, the β-naphthalene-sulphonate separates out and is removed. The α- salt is fused with caustic soda, when the corresponding naphthol is obtained.

β-Naphthol, of much more commercial importance than the preceding, is manufactured similarly. The naphthalene-sulphonic acid is made as above, but at a temperature of 200° C., in order to obtain a large yield of the β-derivative. This is converted into the soda salt, dried, and one part by weight fused with two parts of caustic soda dissolved in the smallest quantity of water, at a temperature of 270° to 300° C.; when the reaction is over, the melt is treated with water, the β-naphthol separated by the addition of hydrochloric acid, filtered, dried, melted, and poured into cylindrical moulds.

3. OF AROMATIC ACIDS AND PHTHALEÏNS.—*Benzoic Acid* can be manufactured by several processes and from different sources. For technical purposes the manufacture from benzoin resin and from hippuric acid need not be considered, as it is made almost exclusively on a large scale from the chlorine derivatives of toluene, such as benzal chloride, $C_6H_5.CHCl_2$, and benzo-trichloride, $C_6H_5CCl_3$. The former, when heated with water or milk of lime under pressure, is changed into benzaldehyde, C_6H_5CHO, which, however, always has some benzoic acid formed with it as a side-product. The benzo-trichloride, similarly with water or milk of lime, yields benzoic acid according to the reaction $C_6H_5.CCl_3 + 2H_2O = C_6H_5.COOH + 3HCl$. The benzoic acid so obtained is almost always contaminated by some chlorbenzoic acid.

Phthalic Acid and Phthalic Anhydride.—The process for their manufacture at present preferred is to heat one hundred parts of naphthalene with fifteen hundred parts of concentrated sulphuric acid and fifty parts of mercuric sulphate. The naphthalene at first goes into solution as a sulpho acid, which, on heating gradually to 300° C., is decomposed with liberation of sulphur dioxide, carbon dioxide, and water, phthalic acid is obtained by acting upon phthalic acid, heated to about 200° C., with carbon dioxide and subliming.

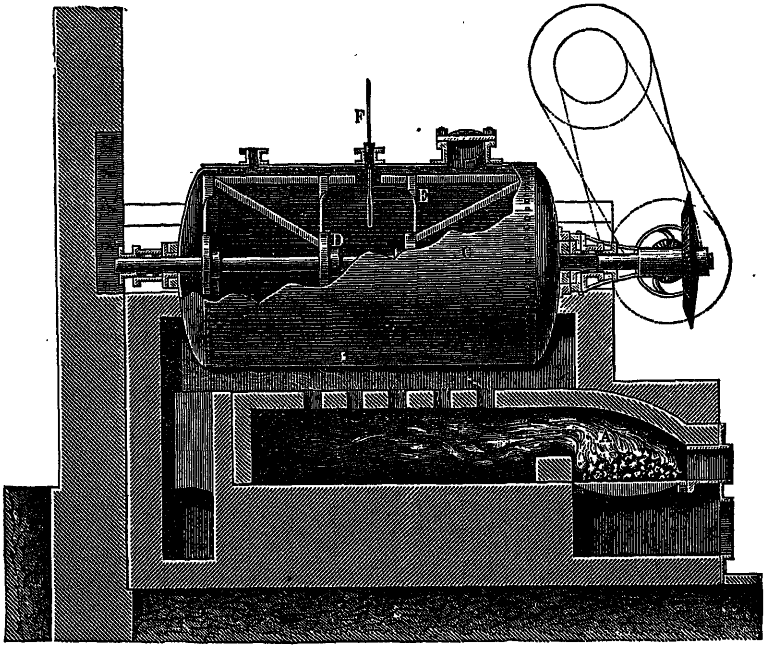
Phthaleïns.—When phthalic acid or its anhydride acts upon phenols a class of bodies termed "phthaleïns" are formed with elimination of water. *Phenolphthaleïn* is manufactured by heating the anhydride, phenol, and sulphuric acid for ten to twelve hours at 120° C.; the sulphuric acid acts only as a dehydrating agent. The melt is boiled with water, the residue dissolved in caustic soda, and the phthaleïn is precipitated upon the addition of an acid. *Resorcin-phthaleïn,* or *Fluoresceïn,* is obtained by heating three parts of phthalic anhydride with about four parts of resorcin until the fusion yields no more vapors, and becomes solid at a temperature not exceeding 210° C. The melt is dissolved in dilute caustic soda, with an addition of phosphate of soda and chloride of calcium to remove impurities. The fluoresceïn is precipitated from the solution by the addition of dilute hydrochloric acid.

4. OF ANTHRAQUINONES, ETC.—Anthracene in a finely-divided state is suspended in water by agitation, and oxidized by means of potassium bichromate and sulphuric acid at a boiling temperature; allowed to cool, and the anthraquinone is collected on filter-frames, washed with water and dried, and for further purification is treated with concentrated sulphuric acid, and heated to 110° to 120° C., when the dark mass obtained is treated with steam, which causes a dilution, followed by a gradual separation of the anthraquinone in crystals. These are washed with hot water, and afterwards with hot dilute soda to remove organic acids. The yield is about fifty to fifty-five per cent. of the weight of the anthracene used.

Anthraquinone-monosulphonic Acid. (See p. 445.)—This is manufactured by heating one hundred kilos. anthraquinone with one hundred kilos. fuming sulphuric acid (containing forty-five to fifty per cent. anhydride) to 160° C. in an enamelled cast-iron vessel mounted in an oil-bath. By varying either the quantity of sulphuric acid or the temperature the alpha- or beta-disulphonic acid will result. The separation of the two latter from the monosulphonic acid is effected by converting the sulphonic acids into lead salts, decomposing these with carbonate of soda, and acting upon the resulting soda salts with dilute sulphuric acid, which has but a slight solvent action upon the monosulphonic acid.

Alizarin.—The alizarin process is carried on in large vessels or autoclaves, mounted as shown in Fig. 111. To the central shaft *D* agitators are attached, so that the charge may be constantly mixed. *F* is a thermometer, and the openings in the top to the right are for introducing the charge, and the small one on the left for admitting steam and water. The process is commenced by melting two hundred and fifty to three hundred parts of caustic soda in a small quantity of water, and then adding twelve to fifteen parts of chlorate of potash and one hundred parts of the sodium anthraquinone-sulphonate, when the vessel is closed and the agitator put in motion, the whole being kept at a temperature chloric acid. The alizarin is washed to free it from soda salts, passed through filter-presses, and is ready to be either dried and ground, or ground in glycerine to a paste. Neutralizing the soda solution with sulphurous acid instead of with hydrochloric acid enables a recovery of the caustic soda. The yield from one hundred kilos. anthraquinone is one hundred and five to one hundred and ten kilos. alizarine (Schultz). Several processes are employed, varying mainly in the duration of the melt and in the proportion of materials used. Instead of soda, lime is employed, in which case a "lake" is formed.

FIG. 111.



5. OF QUINOLINE (CHINOLINE) AND ACRIDINE.—Quinoline is produced from nitrobenzene and aniline. Twenty-four grammes of the former and thirty-eight grommes of the latter, with one hundred and twenty grammes of glycerine, are placed in a flask (provided with a return condenser) containing one hundred grammes of concentrated sulphuric acid; when the reaction is over, the contents are boiled for some time, diluted, and the unconsumed nitrobenzene is distilled off; an excess of alkali is added to the solution, and the quinoline distilled off with a current of steam. It can also be obtained from crude quinoline from coal-tar with phthalic anhydride and zinc chloride. *Acridine* is found along with crude anthracene, from which it is separated by treatment with dilute sulphuric acid, precipitating with chromate of potash, recrystallizing, precipitating by ammonia, dissolving in hot water. from which

compound to be changed in fuming sulphuric acid, whereby one or more H atoms are replaced by HSO_3 groups, producing mono-, di-, or trisulphonic acids. Examples of this process are given under Resorcin (see p. 451), the Naphthols (see p. 452), and will frequently be referred to in classifying the artificial dye-colors.

7. Diazotizing.—By the action of nitrous acid upon primary aromatic amines a diazo- compound is formed, as in the following reaction:

$$\begin{array}{r|c|l} C_6H_5.N & H_2H & NO_3 = C_6H_5.N{=}N.NO_3 + 2H_2O. \\ +N & O_2H & \end{array}$$

These diazo- compounds are susceptible of a great variety of reactions whereby other groups or atoms of elements may be substituted. Thus, by the aid of the diazotizing reaction it is possible to replace a NO_2 or a NH_2 group by OH, H, Cl, Br, I, CN, etc. It is therefore of the greatest importance in synthetic organic chemistry.

The process is carried out in one of two general ways: (*a*) by conducting a current of nitrous acid gas through a solution of the substance to be diazotized, the nitrous acid in this case being most conveniently obtained by acting upon starch with concentrated nitric acid in a suitable generator, or (*b*) by diazotizing in a bath together with the nitrous acid-yielding substance (nitrite of soda generally). In this case the gas is evolved by adding an acid, usually sulphuric, to the solution. Diazotizing is always conducted at a low temperature.

The development of productive values from coal by distillation and working up of the intermediate products to those classed as final products is thus shown by Ost (Lehrbuch der Chem. Technol., 6th ed., p. 555):

1000 kilos. of coal valued at 10 marks yield—

700 kilos. of coke, valued at 10.5 marks; 30 kilos. of coal-tar valued at 0.7 mark; 6 kilos. of impregnating oils valued at 0.25 mark; 15 kilos. of pitch valued at 0.6 mark; 1.1 kilos. of ammonium sulphate valued at 2.75 marks; and 1 kilo. of potassium cyanide valued at 1.3 marks.

30 kilos. of coal-tar valued at 0.7 mark yield—

5 kilos. of benzol valued at 1.1 marks; 2 kilos. of naphthalene valued at 0.16 mark; 0.25 kilo. of anthracene valued at 0.07 mark; and 0.15 kilo. of carbolic acid.

From these intermediate products are obtained:

2.5 kilos. of fuchsine valued at 16 marks; 0.75 kilo. of indigo valued at 6 marks; 0.2 kilo. of alizarine valued at 1.4 marks; and 0.2 kilo. of picric acid valued at 0.35 mark.

III. Products.

It would be impossible in the space of this chapter to do more than give a classification of the artificial dye-colors and enumerate a few of the are exclusively known frequently bear so little relation to the chemical names that it would be idle for us to attempt to cover the ground in any other way than by a simple outlining at present. But before taking up this classification it will be well to examine what general principles, if any, underlie the production of a dye-color. O. N. Witt * has proposed a theory which explains in a very simple way this color formation in the aromatic series. He names a series of radicals or groups which by their entrance alone or with others change a colorless hydrocarbon into a colored compound. These radicals, which he calls "chromophor" groups, are only capable of producing the "chromogens," or parent substances of dye-colors, which chromogens, however, are at once changed into dye-colors of distinct basic or acid character when a salt-forming group enters. Thus, from two molecules of benzene by the entrance of the chromophor group —N=N— is formed *azo-benzene*, an orange-colored chromogen, but not capable of dyeing silk or wool. When the NH_2 group enters there results, however, *amido-azo-benzene*, a real dyestuff. Or from benzene by the entrance of the chromophor group NO_2 is formed the chromogen trinitro-benzene, which by the entrance of the salt-forming group OH becomes trinitro-phenol (or picric acid), a yellow dye-color.

Witt indicates some eleven of these chromophor groups, to which we shall refer under the appropriate heads in our classification. Of salt-forming groups which change the chromogens to dyestuffs, two are specially to be noted, the amido group NH_2, which imparts a basic character to the dye-color, and the hydroxyl group OH, which gives the dye-color an acid character. Almost all dye-colors are changed to colorless compounds by the action of reducing agents. The nitro- compounds are changed into the corresponding amido- derivatives, the azo- compounds into hydrazo- or even amido- compounds, while more complex dye-colors are changed by careful reduction into bodies richer in hydrogen, which are known as "leuco" compounds. From these "leuco" compounds the corresponding dye-colors are then formed more or less easily by oxidation. In some cases atmospheric oxidation alone suffices, as with indigo, in others more energetic oxidizing agents, such as lead peroxide, are needed.

Again, the study of dye-colors soon shows that they possess different characters with reference to the ease with which they may be fastened upon the fibre to be dyed or the kind of mordant needed to effect such fastening upon the fibre. We therefore distinguish between basic, acid, and indifferent or neutral dyestuffs. Basic dyes like magneta fasten upon the animal fibre at once, and upon the vegetable fibres after treatment with tannic acid and similar acid mordants. They are used in the form of their salts. The acid dyes are frequently sparingly soluble, and are either brought into soluble condition by forming alkaline salts and sulphonic derivatives, which are then used for dyeing, or they are used with fibres previously mordanted with metallic hydroxides or salts, as in

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the case of alizarin. In the latter case, however, the color acid forms a variety of different colored compounds (lakes) with the different bases. To the third class (indifferent or neutral bodies) belong indigo-blue and some other substances.

The classification which is now generally accepted is that based in the main upon Witt's chromophor groups, and we will simply note a few illustrative compounds under each group.

1. ANILINE OR AMINE DYE-COLORS.

(*a*) TRIPHENYL-METHANE DYES $\left(\text{Chromophor group, } \begin{array}{l} -\text{C}= \\ \llcorner\!\!-\!\!-\text{N}= \end{array}\right)$.—*Benzaldehyde Green* (or Malachite Green), known also under a variety of other names, is made by the action of benzaldehyde upon dimethyl-aniline. The commercial dye is the oxalate or zinc chloride double salt.

Brilliant Green (or Solid Green) is the corresponding derivative from diethyl-aniline. The sulphate or zinc chloride salt is used as dye.

Magenta (Aniline Red, or Fuchsine) is a mixture of the chlorhydrates of para rosaniline and rosaniline, and is obtained by oxidizing aniline oil with arsenic acid or nitrobenzene. A large number of side-products are obtained in the manufacture of magenta, and have been used under the names of cerise, cardinal, amaranth, chrysaniline, phosphine, maroon, mauvaniline, etc.

Acid Magenta (Fuchsine S) is the sodium or ammonium salt of para-rosaniline and rosaniline trisulphonic acids, and is prepared by sulphonating the ordinary magenta.

Aniline Blue (spirit soluble Blue) is a salt of triphenylated para-rosaniline, and is made by the action of a large excess of aniline upon rosaniline. If magenta is used instead of rosaniline a reddish-blue is obtained.

Diphenylamine Blue (spirit soluble) is probably the chlorhydrate of triphenylated para-rosaniline, and is made, as the name indicates, from diphenylamine, which is heated with oxalic acid to 120° to 130° C.

Alkali Blue (Nicholson's Blue, Soluble Blue) is the sodium salt of the mono-sulphonic acid of a spirit soluble blue, and is made by sulphonating the latter.

Patent Blue is the disulpho salt of m-oxymalachite green. It colors wool a very fast greenish-blue and resists alkalies. Is much used as a substitute for indigo carmine.

Hofmann's Violets consist of salts of the ethyl and methyl derivatives of rosaniline and pararosaniline, and are made by the action of methyl or ethyl chloride or iodide upon magenta in the presence of caustic soda. It is of historic interest, but has been replaced almost completely by methyl violet.

Methyl Violet is a salt of pentamethyl pararosaniline, and is produced by the direct oxidation of the purest dimethylaniline with copper chloride.

Crystal Violet is the chlorhydrate of hexa methyl pararosaniline.

(*b*) DIPHENYL-METHANE DYES.—*Auramine*, an important yellow dye, is prepared by heating tetramethyl diamido diphenylmethane with sulphur, ammonium chloride and common salt in a current of ammonia gas.

Pyronine is a red dye obtained by condensing formaldehyde with dimethyl-*m*-amidophenol and oxidizing the product.

(*c*) AZINES (EURHODINES AND SAFRANINES).—Chromophor group $=N-N=$. *Neutral Red* (Toluylen Red) is a basic dye-color prepared by the action of nitroso-dimethyl-aniline upon *m*-toluylen-diamine. It is used with cotton after mordanting with tannic acid and tartar emetic.

Safranine (Aniline Rose) is prepared by the oxidation of amidoazotoluene and toluidine, or of *p*-toluylen-diamine, ortho-toluidine, and aniline. The commercial salt is the chlorhydrate of the safranine base.

Naphthalene Red (Magdala Red) is the compound in the naphthalene series corresponding to the preceding. It is obtained by fusing the chlorhydrate of α-naphthylen-diamine, α-naphthylamine, and amidoazonaphthalene. It forms a dark-brown powder, soluble in alcohol with strong red fluorescence. It is used largely in silk-dyeing and for velvet because of its fine color and fluorescence.

Mauveïn (Perkin's Violet) is of historic interest mainly as the first aniline color. It was obtained by W. H. Perkin in 1856 by the oxidation with sulphuric acid and bichromate of potash of a mixture of aniline and toluidine.

Methylene Violet is a reddish-violet dye obtained by the action of hydrochloride of nitroso-dimethyl-aniline upon a mixture of the hydrochlorides of *m*- and *p*-xylidine.

Indoines are basic coloring matters dyeing cotton deep shades from dark violet to indigo-blue, fairly fast to light and washing. They are made by combining diazotized safranines with α- and β-naphthol and conversion into hydrochlorides.

(*d*) INDULINES AND NIGROSINE.—*Induline, spirit soluble* (Coupier's Blue, Guernsey Blue, etc.) is prepared by heating amidoazobenzene with aniline to 160° C.

Induline, water soluble (Indigo substitute), is the sodium salt of the disulphonate of the preceding, and is extensively used for silk and wool.

Paraphenylene Blue is a dark blue dye of the induline class obtained by the action of *p*-phenylene-diamine upon hydrochloride of amidoazobenzene.

Naphthyl Blue is the sodium sulphonate of anilido-phenyl-naphthinduline. Dyes silk blue with a red fluorescence, and is faster to light than the ordinary indulines.

Nigrosine is prepared by heating nitrophenol with aniline and aniline chlorhydrate. The alcohol soluble compound is the simple salt of the base, while the sodium sulphonate forms the water soluble compound.

(*e*) ANILINE BLACK.—For the preparation of aniline black, aniline which develops it gradually. It is a very fast black. Quite a variety of oxidizing agents may be used. Potassium chlorate and copper sulphate are frequently used in admixture, and vanadate of ammonia is also of special serviceableness in connection with the chlorate. Electrolysis of a concentrated solution of an aniline salt will also produce aniline black.

2. PHENOL DYE-COLORS.

(*a*) NITRO-DERIVATIVES.—*Picric Acid* (Trinitrophenol) is made by nitrating carbolic acid direct with strong nitric acid, or, better, by acting upon phenol-sulphonic acid with strong nitric acid. Forms light yellow leaflets or scales, and has been used as a dye for silk and wool.

Naphthol Yellow (Martius Yellow, Manchester Yellow, etc.) is the sodium, potassium, or calcium salt of dinitro-α-naphthol, and is prepared by the nitration of α-naphthol either directly, or after conversion into the mono-sulphonic acid.

Naphthol Yellow S is a sulphonate of the preceding, and is made by nitrating the α-naphthol-trisulphonic acid. The color is faster than picric acid or the simple naphthol yellow and is more extensively used.

Aurantia is the ammonium salt of hexa-nitro-diphenylamine, and is made by the nitration of diphenylamine. It was formerly used for wool and silk, but is now used only for leather coloring.

(*b*) ROSOLIC ACIDS.—*Rosolic Acid* and *Aurin* (Pararosolic Acid) may be prepared from rosaniline and pararosaniline respectively by treatment with sodium nitrite followed by boiling in the presence of sulphuric acid. These two coloring matters are no longer of commercial importance.

Yellow Corallin is prepared by heating pure phenol with concentrated sulphuric acid and oxalic acid for some hours until the evolution of gas nearly ceases. The crude product of the reaction obtained by pouring the melted mass into water is changed into the commercial dye by dissolving it in caustic soda solution and evaporation to dryness.

Red Corallin (Paëonin) is obtained by the action of ammonia under pressure upon the yellow corallin, and represents an intermediate product between aurin and para-rosaniline.

(*c*) PHTHALEINS.—*Phenol-phthalëin* is not used as a dyestuff, but as an indicator in alkalimetry.

Fluorescëin (Resorcin Phthalëin) is made by heating molecular proportions of resorcin and phthalic anhydride to 195° to 200°. Fluorescëin is not used as such for dyeing, but is converted into the eosins. The sodium salt of the fluorescëin comes into commerce under the name of uranine.

Eosins.—The several halogen substitution derivatives of fluorescëin form the class of dyes known as *eosins.* Thus, the potassium or sodium salt of tetrabrom-fluorescëin is the *eosin yellow shade,* while the corresponding salts of tetraiodo-fluorescëin constitute *eosin blue shade. Methyl* and *Ethyl Eosin* (Primrose) are the methyl and ethyl ethers of is the potassium salt of di-iodo-fluorescëin. *Rose Bengale* is the sodium salt of tetraiododichlor-fluorescëin. *Phloxin* is the potassium salt of tetrabromdichlor-fluorescëin, and *Cyanosine* is the potassium salt of the methyl ether of phloxin. *Rhodamine* is the phthalëin of diethyl-meta-amidophenol. *Cyclamine* is obtained by the action of iodine upon thionated dichlorfluorescëin. *Violamine* is obtained by the action of *o*-toluidine upon fluorescëin chloride and sulphonation of the product. Wool and silk especially are dyed with the eosins, and cotton after mordanting with various metallic salts.

Gallëin is the phthalëin of pyrogallol, and is prepared by an analogous method to that described under fluorescëin. It is very little used in dyeing, but serves for the preparation of

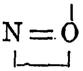
Cœrulëin.—This dye is obtained by heating gallëin with twenty times its weight of strong sulphuric acid. Forms a dark amorphous mass, which dissolves in alkalies with a beautiful green color. Cœrulëin forms a colorless compound with sodium bisulphite, which is known as *Cœrulëin S,* and is much used in dyeing, as it is easily decomposed by steaming.

3. Nitroso and Oxyazine Colors.

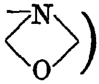
(*a*) Nitroso Colors (Chromophor group $= N - OH$).—*Gambine* is obtained by the action of nitrous acid upon *α*-naphthol. It dyes iron-mordanted fabrics green.

Dinitrosoresorcin is obtained by the action of nitrous acid upon resorcin. Dyes like the previous color.

Dioxine is obtained by the action of nitrous acid upon dioxynaphthalene. Dyes bright green or brown shades on metallic mordants.

(*b*) Indophenols and Indamine (Chromophor,  $N = \overset{|}{O}$).—*Indophenol* (*α*-Naphthol Blue) is prepared by oxidizing dimethyl-paraphenylene-diamine and *α*-naphthol with bichromate of potash and acetic acid Indophenol may be reduced by glucose and caustic soda to a leuco-compound known as *Indophenol white,* which is also sold commercially. When cotton goods are printed with leuco-indophenol, the blue color may be developed in dilute bichromate of potash solution.

Indamines are obtained by heating the indulines with *p*-phenylene-diamine and *p*-phenylene-diamine hydrochloride. Dyes deep indigo-blue shades on cotton mordanted with tannin and tartar emetic.

(*c*) Oxyazines (Chromophor ).—*Azurine* is obtained by the action of nitrosodimethyl-aniline hydrochloride upon *sym*-dioxy-benzoic acid. Dyes a violet blue on chrome-mordanted wool or cotton.

Gallocyanine is obtained by the action of nitrosodimethyl-aniline upon gallic acid. It is a gray paste, insoluble in water, but soluble in alcohol with bluish-violet color.

Prune Pure is the methyl-ether of gallocyanine.

hydrochloride upon β-naphthol. Dyes cotton mordanted with tannin and tartar emetic indigo-blue.

Nile Blue, Capri Blue, and *Gallamine Blue* are all oxyazine colors obtained by analogous reactions of nitrosodimethyl-aniline or the corresponding amidophenol.

Resorcin Blue.—By the action of nitrous acid upon resorcin is produced diazoresorcin, which by the action of concentrated sulphuric acid is changed into diazoresorufin. This yields a hexabrom-derivative, the ammonium salt of which is the commercial dye. It is used for dyeing silk and wool a blue color, which has a red fluorescence, especially by artificial light. By combining with yellow dyes it yields a fluorescent olive color.

(*d*) THIAZINES (*Chromophor*  $\left\langle {}^{N}_{S} \right\rangle$).—*Methylene Blue* is prepared by oxidizing dimethyl-*p*-phenylenediamine and dimethyl-aniline in the presence of sodium thiosulphate and zinc chloride. The commercial salt is a zinc double chloride of the sulphur base, called tetra-methyl-thionin.

4. AZO DYE-COLORS.—Chromophor group, $— N = N —$.

A. MONOAZO DYES.—(*a*) *Amidoazo Dyes.*

Chrysoidine (Diamidoazobenzene Hydrochloride) is obtained by admixing solutions of diazobenzene hydrochloride and *m*-phenylene-diamine. Forms reddish-brown crystals. Its solution absorbs actinic rays.

Phenylene Brown (Vesuvine) is triamido-azobenzene hydrochloride. Forms a brown powder soluble in water.

Butter Yellow is dimethylamidoazobenzene. This yellow dye is soluble in oils and is much employed for coloring butter, oils, etc.

Acid Yellow (Fast Yellow) is the sodium salt of the disulphonic acid of aniline yellow (amidoazobenzene). It is used largely in dyeing compound shades.

Dimethyl-aniline Orange (Helianthin) is the ammonia salt of dimethyl-aniline-azobenzene-sulphonic acid. Dyes silk and wool a fiery orange. It is also used as an indicator in alkalimetry, as the light yellow color of the solution is immediately turned red by the addition of a drop of hydrochloric acid.

Diphenylamine Orange (Tropæolin OO, Orange IV) is formed by the action of diazobenzene-sulphonic acid upon diphenylamine. Dyes silk or wool a very fine golden yellow.

Metanil Yellow is the sodium salt of phenylamidoazobenzene-*m*-sulphonic acid. Forms a yellow soluble powder.

Archil substitute (naphthion red) is made by combining *p*-nitraniline with naphthionic acid or β-naphthylamine-sulphonic acid.

(*b*) *Oxyazo Dyes.*—Sudan G (Aniline-azorescorcin) is a brown powder hardly soluble in water, soluble in alcohol. It is used for coloring spirit varnishes, oils, etc.

Sudan Brown (Pigment Brown) is made by the action of hydrothalene and β-naphthol. Forms a red-brown powder, soluble in sulphuric acid with fuchsine-red color.

Alizarin Yellow is a yellowish-brown dye made by combining *p*-nitraniline with salicylic acid.

Fast Brown N (Naphthylamine Brown) is made by combining naphthionic acid with α-naphthol. Dyes wool brown from an acid bath.

Crocëin Orange (Ponceau 4GB) is prepared from hydrochloride of diazobenzene and β-naphthol monosulphonic acid. It is a fiery red powder, dyeing a reddish orange on wool.

Orange G is the sodium salt of diazobenzene-β-naphthol-disulphonic acid. It dyes an orange-yellow shade.

Cochineal Scarlet 2*R* results from the action of diazotoluene upon α-naphthol-monosulphonic acid. It forms a cinnabar-red dye-color.

Azococcin 2*R* results from the action of hydrochloride of diazoxylene upon α-naphthol-sulphonic acid. It forms a red-brown powder, difficultly soluble in water. It is used in silk dyeing.

Wool Scarlet R results from the action of hydrochloride of diazoxylene upon α-naphthol-disulphonic acid. It forms a brown-red powder, soluble in water with yellowish-red color.

Ponceau 2*R* (Xylidine Red) results from the action of hydrochloride of diazo-*m*-xylene upon β-naphthol-disulphonic acid. It forms a red powder, easily soluble. It has been used in large quantities as a substitute for cochineal.

Ponceau 3*R* (Cumidine Red) results from the action of hydrochloride of diazo-*m*-cumene upon β-naphthol-disulphonic acid. It is used as the preceding, but gives redder shades.

Anisol Red and *Phenetol Red* are formed by the action of anisidine and amido-phenetol respectively upon β-naphthol-disulphonic acid.

Fast Red B (Bordeaux B) is formed by the action of hydrochloride of diazonaphthalene upon β-naphthol-disulphonic acid.

α-Naphthol Orange (Tropæolin OOO, No. 1) is the sodium salt of *p*-sulphanilic-acid-azo-α-naphthol. Forms orange-yellow scales, tolerably soluble in water. It dyes silk and wool a reddish orange.

β-Naphthol Orange (Tropæolin OOO, No. 2, Mandarin) results from the action of *p*-diazobenzene-sulphonic acid upon β-naphthol in alkaline solution. It forms an orange-red soluble powder, and is used largely for wool-dyeing.

Fast Red A (Rocelline, Cerasine, etc.) is prepared by uniting α-diazonaphthalene-sulphonic acid with β-naphthol. It forms a brown-red powder, more soluble in hot than in cold water. It is used largely as a substitute for barwood and orseille.

Azorubin S (Fast Red C, Carmoisin) is the sodium salt of the disulphonic acid of naphthalene-azo-α-naphthol. It forms a reddish-brown soluble powder.

Brilliant Ponceau 4*R* (Cochineal Red A) and *Fast Red D* (Amaranth) are both sodium salts of trisulphonic acids of naphthalene-azo-β-naphthol, isomeric with each other. The former is

Roxamine is the sodium salt of dioxyazo-naphthalene-sulphonic aci It dyes wool red from an acid bath and is used as an orchil substitute.

B. Disazo Dyes.—(*a*) *Disazo Dyes from Azo Dye-colors* (*Primar Disazo Dyes*).—*Resorcin Brown* is the sodium salt of a sulphonic aci of resorcin-disazo xylene-benzene. Forms a brown soluble powder.

Fast Brown results from the action of two molecules of α-diaz naphthalene-sulphonic acid upon one molecule of resorcin.

Acid Brown G is formed by the action of hydrochloride of diaz benzene upon chrysöidin-sulphonic acid. Dyes wool brown in aci solution.

Bismarck Brown is the hydrochloride of benzene-disazo-phenylen diamine. It is much used in coloring leather.

(*b*) *Disazo Dyes from Amido-azo Dyes* (*Secondary Disazo Dyes*).– *Cloth Red G* (Azococcin 7B) results from the action of diazoazo-benzen upon α-naphthol-sulphonic acid. Forms a brown powder not readil soluble in water. Used in wool-dyeing, either alone or in connectio with logwood, fustic, etc.

Brilliant Crocëin (Cotton Scarlet) results from the action of hydrochloride of diazoazo-benzene upon β-naphthol-disulphonic acid. Form a reddish soluble powder.

Biebrich Scarlet (Ponceau B).—It is the sodium salt of amido-azo benzene-disulphonic-acid-azo-β-naphthol. Forms a brown-red fairl soluble powder. Dyes wool and silk in acid bath a red color like cochineal.

Crocëin Scarlet 3B (Ponceau 4RB) results from the action of diazo azo-benzene-monosulphonic acid upon β-naphthol-monosulphonic acid Forms a red-brown powder dissolving with scarlet-red color. Used i wool- and silk-dyeing.

Bordeaux G is obtained by the action of amido-azo-toluene-monosulphonic acid upon β-naphthol-monosulphonic acid S. Dyes wool re from an acid bath.

Naphthol Black is the sodium salt of the tetrasulphonic acid of naphthalene-disazo-naphthalene-β-naphthol. Forms a violet-black powder Used exclusively in wool-dyeing.

Wool Black is the sodium salt of the disulphonic acid of a benzene-disazo-benzene-*p*-tolyl-β-naphthylamine. It forms a bluish-black solubl powder. Dyes a deep blue-black color and is quite stable.

Naphthylamine Black and *Anthracite Black* are obtained by the action of disulpho-naphthylene-azo-α-naphthylamine upon α-naphthylamine and diphenyl-*m*-phenylene-diamine respectively.

Fast Violet is the sodium salt of the disulphonic acid of a naphthalene-disazo-benzene-β-naphthol. Forms a dark brown soluble powder Used in wool-dyeing.

Chromatropes 2R, 2B, 6D, etc., are combinations of diazo compound with dioxy-naphthalene-disulphonic acid. They give colors varying fro scarlet to magenta, which on subsequent treatment with a boiling solu zidine Dyes).—These dyes are distinguished from all other coal-tar dyes by the readiness with which vegetable fibres may be dyed with them without previous mordanting, so that they are equally applicable to vegetable or animal fibres, and can be used with goods of mixed fibre. They are often called *substantive cotton dyes.* Their affinity for the fibres indeed goes so far that they can be used like mordants to facilitate the fastening of other coal-tar dyes upon the vegetable fibres.

The commercial products consist generally of the potassium, sodium, or ammonium sulphonates of the dye-color.

Naphthalene Red is the sodium salt of naphthalene-disazo-binaphthionic acid. Dyes unmordanted cotton red from a boiling alkaline bath.

Diamine Gold is the sodium salt of disulpho-naphthalene-disazo-biphenetol. It dyes unmordanted cotton yellow.

Chyrsophenine is the sodium salt of disulpho-stilbene-disazo-biphenetol. Dyes like the previous color.

By the diazotizing of this same diamido-stilbene-disulphonic acid are also derived *Hessian Yellow, Hessian Purple N* and *B,* and *Hessian Violet.*

The diazo compound from the molecule of benzidine is similarly combined with a series of compounds to produce the well-known benzidine dyes, *Congo G* and *P, Congo Yellow, Sulphanil Yellow, Brilliant Congo G, Cloth Brown, Diamine Black, Diamine Blue, Diamine Scarlet, Diamine Brown, Diamine Green,* and *Congo Corinth G.*

Congo Red is the sodium salt of diphenyl-*p*-disazo-naphthionic acid. Forms a reddish-brown powder, soluble in water with fine red color. This solution is so sensitive to acids that a single drop of very dilute sulphuric acid suffices to convert the whole of the liquid to a beautiful blue. It is therefore a valuable indicator in volumetric analysis.

Benzopurpurin is formed by the action of tetrazo-ditolyl chloride upon naphthylamine sulphonate of soda. It is a dark red powder, dissolving easily in water. The scarlet obtained from this dye is not changed by dilute acid as is that from Congo red.

Azo Blue is formed by the action of tetrazo-ditolyl chloride upon β-naphthol-sulphonate of potash. It is a dark blue powder, dissolving easily in water. It is fast to acids but not to light.

Diazotized tolidine yields, besides the two dyes last mentioned, *Delta-purpurin 5B, Chrysamine, Azo Blue,* and *Azo Mauve.* Dianisidine and diphenetidine also yield, when diazotized, well-known dyes of this class, such as *Benzoaurine, Heliotrope,* and *Benzo-indigo-blue.*

Carbazol Yellow and *Naphthol Blue-black* are also colors of this class.

Supplementary to the Azo Dyes.—*Tartrazin* is formed by the action of two molecules of phenyl-hydrazin-*p*-sulphonic acid upon one molecule of dioxytartaric acid. Orange-yellow powder, easily soluble in water. It is a valuable woollen dye, very fast to light and fulling.

Primuline and Ingrain Colors.—Primuline is mentioned here because of its ready convertibility into azo colors (ingrain colors). It is the sodium salt of the sulpho-is a yellow powder, very soluble in hot water, and dyes unmordante cotton direct from a neutral or alkaline bath. Its great importanc however, lies in the fact that as the sulpho- acid of a primary amine i can be diazotized (see p. 446), and then is capable of combining wit the whole range of phenols and amines to form azo colors. These operations can readily be carried out upon the fibre, whence the colors s obtained have been called ingrain colors. This diazotizing and developing with the phenol or amine may be effected upon silk, wool, or cotto fibre previously dyed with the primuline base. In this way yellows oranges, purples, reds, scarlets, maroons, and browns are produced.

When paranitraniline is diazotized we obtain azo-*p*-nitraniline. I sulphuric acid is added to the compound so formed and the diazo compound admixed with a large excess of salt, the sodium sulphate s produced protects the diazo compound from light, even in the dr state, until ready for use in the dye-bath for dyeing goods padded wit naphthols, naphthylamines, etc.

5. Quinoline and Acridin Dyes.—*Quinoline Yellow* is the sodiu salt of quinoline-phthalon-sulphonic acid. It forms a yellow powder soluble in water or alcohol with yellow color. Used for wool- and silk-dyeing.

Flavaniline is obtained by heating acetanilid with anhydrous zin chloride for several hours to 250° C. The commercial salt is the hydrochloride of the base so obtained. Was formerly used for wool- and silk-dyeing and for cotton after mordanting with tannin and tartar emetic.

Cyanine (Quinoline Blue) is prepared by treating a mixture of quinoline and lepidine with amyl iodide. It forms a fine blue color, but unstable to light. It is not of importance in textile coloring, but is used in the manufacture of orthochromatic photographic dry plates.

Quinoline Red is obtained by the action of benzo-trichloride upon a mixture of quinaldine and isoquinoline. Is also employed in the manufacture of orthochromatic photographic plates.

Acridine Yellow is the hydrochloride of diamido-dimethyl-acridine. Dyes silk greenish-yellow with green fluorescence, and cotton mordanted with tannin yellow.

Phosphine (Chrysaniline) is, as was before noted (see p. 457), a by-product in the manufacture of magenta, but is probably diamido-phenyl-acridine. The phosphine of commerce is the nitrate or chlorhydrate of the base chrysaniline. Used at present chiefly in silk-dyeing.

6. Artificial Indigo.—Artificial indigo is now an extensive article of commerce, and in purity and uniformity distinctly excels the natural product. The first important synthesis was that utilizing what is known as "propiolic paste," which is a moist paste containing a definite percentage (usually twenty-five per cent.) of *o*-nitrophenyl-propiolic acid prepared from synthetic cinnamic acid. Professor Baeyer found that this *o*-nitrophenyl-propiolic acid when in alkaline solution is readily changed by reducing agents, like grape-sugar, milk-sugar, sulphides, sul-

tions. This "propiolic paste" was used for a time in calico-printing, being printed on the goods along with the reducing agent, but the decomposition of the xanthogenate of soda develops mercaptan, the unpleasant odor of which adheres very persistently to the goods, and the blue color is slightly gray in shade. It has therefore been given up for the present.

Kalle's artificial indigo (due to Baeyer in conjunction with Drewsen) is prepared by converting *o*-nitrobenzaldehyde into *o*-nitrophenyllactoketone by the action of acetone. The product of the reaction is then changed to a soluble compound by treatment with sodium bisulphite, and is sold under the name of "indigo salt." This salt, if dissolved in water or thickened with any suitable substance and afterwards applied to woollen fabrics and these passed through a solution of caustic soda of 20° B., causes the full color of indigo to develop.

The *o*-nitrobenzaldehyde can be made from *o*-nitrotoluene by direct oxidation with manganese dioxide and sulphuric acid. Considerable indigo is made this way at present, but the amount of toluene available is not sufficient to allow of its replacing the whole of the natural indigo.

Following these syntheses comes that of Heumann from phenyl-glycocoll, which, when fused with caustic alkali, yields pseudo-indoxyl, and this is easily changed into indigo by atmospheric oxidation.

Similarly, phenyl-glycocoll-*o*-carboxylic acid (from chloracetic and anthranilic acids), heated with caustic alkalies, yields the same results.

The method of Heumann was, however, not commercial until a cheap production of phenylglycine-*o*-carboxylic acid was devised by the Badische Aniline and Soda Fabrik. The starting point in this is naphthalene, a cheap and abundant product of coal-tar. Naphthalene on treatment with strong sulphuric acid and mercury is converted into phthalic anhydride. From phthalic anhydride phthalamide is produced by the action of ammonia and from this anthranilic acid is formed by the action of chlorine and caustic soda. Anthranilic acid and chloracetic acid then react to form phenylglycine-*o*-carboxylic acid, which by heating with caustic soda is converted into indigo, or rather into indoxyl-carboxylic acid, the alkaline solution of which is changed by atmospheric oxidation finally into indigo. This artificial indigo of the Badische Co. is known as *indigo pure,* and usually occurs as a paste containing twenty per cent. of indigo suspended in water.

7. OXYKETONE COLORS $\left(\text{Chromophor} \quad \overset{\overset{\text{O}}{\|}}{-\text{C}-}\right)$.

(*a*) ANTHRAQUINONE DERIVATIVES.—*Alizarin.*—This term may be applied commercially to the pure dioxyanthraquinone found in the madder-root and made artificially from anthraquinone-monosulphonic acid, or to the two trioxyanthraquinones obtained from anthraquinone-disulphonic acid, and known more accurately as anthrapurpurin and flavopurpurin. The first or true alizarin is the blue shade alizarin. This is a yellow powder coming into commerce as a ten per cent. or twenty per cent. paste. When dried and sublimed it uble only in cold alcohol. Sulphuric acid dissolves it, and on diluting the alizarin is precipitated again unchanged. It acts as a weak acid, and forms alizarates with the alkalies and metallic hydroxides.

Quinizarin, which is made by the condensation of phthalic anhydride with hydroquinone, is an isomer of alizarin and is a dioxyanthraquinone. Both alizarin and quinizarin yield purpurin or trioxyanthraquinone on oxidation. Quinizarin is of no importance as a dyestuff by itself, but is converted into valuable acid dyestuffs on condensation with primary aromatic amines and subsequent sulphonation. Such dyestuffs are *alizarin cyanine green* and *alizarin pure blue.*

Anthrarufin is also an isomer of alizarin. It is the parent substance of the important blue acid wool dye *alizarin saphirol,* which is probably diamidoanthrarufin-disulphonic acid.

Anthrapurpurin (Isopurpurin), as before stated, is a trioxyanthraquinone, but is generally produced along with the preceding compound in the manufacture of commercial alizarin, as both the mono-sulphonic and the disulphonic acids are obtained in sulphonating anthraquinone. Anthrapurpurin is obtained in the purest state by melting pure β-anthraquinone-disulphonic acid with caustic soda and chlorate of potash. It melts at 360° C.

Flavopurpurin is obtained also in the manufacture of commercial alizarin, and can be prepared as sole product by melting α-anthraquinone-disulphonic acid with caustic soda and chlorate of potash. Forms orange-colored needles, melting at over 300° C. A mixture of anthrapurpurin and flavopurpurin with little alizarin constitutes the commercial yellow shade alizarin.

Purpurin is also a trioxyanthraquinone, but differs in its molecular formula from both anthrapurpurin and flavopurpurin, and is therefore one of three isomers. It is not a constituent of commercial artificial alizarin, but is found accompanying true alizarin in the madder-root. It forms red needles, beginning to sublime at 150° C. and melting at 253° C. It is soluble in boiling water with dark-red color.

Alizarin Bordeaux B is a tetraoxyanthraquinone, and is made by oxidizing alizarin with fuming sulphuric acid and saponification of the ether so formed.

Alizarin Cyanine R is penta-oxyanthraquinone obtained by oxidizing the *alizarin bordeaux* in sulphuric acid with manganese dioxide and heating the intermediate sulphuric ether with dilute acid. Dyes wool mordanted with alumina violet, with chromium blue.

Alizarin Orange (Nitroalizarin) is formed from alizarin by the action of nitrous acid, or by the action of nitric acid of 42° B. upon alizarin suspended in glacial acetic acid. It forms a yellow paste of twenty per cent. dry material. Aluminum salts form an orange color, chromium salts a brown-red shade. Used with silk. wool, and cotton.

Alizarin Red is the sodium salt of alizarin-monosulphonic acid, and *Alizarin Maroon* is amidoalizarin.

Alizarin Blue is a

Dark blue powder, almost insoluble in water. Hence is used either by reduction with zinc-dust, grape-sugar, or similar reducing agent and subsequent atmospheric oxidation, as in indigo-dyeing, or by forming a soluble compound with alkaline bisulphites, designated as *Alizarin Blue S*. This latter is much faster to light than the original color.

Alizarin Indigo-blue S and *Alizarin Green S* are similar sodium bisulphite compounds,—the first of penta-oxyanthraquinone-quinoline and the second of tri- and tetra-oxyanthraquinone-quinoline and their sulphonic acids.

Anthracene Brown (Anthragallol) is a trioxyanthraquinone. It is formed by heating benzoic and gallic acids with concentrated sulphuric acid, or by heating pyrogallol with phthalic anhydride and zinc chloride. It comes into commerce as a dark brown paste, and yields very fast shades.

Ruffigallol is a hexaoxyanthraquinone, and is made by the action of sulphuric acid upon gallic acid.

Indanthrene X is obtained by fusing β-amidoanthraquinone with caustic potash. It dyes cotton from a reduced vat (like indigo) bright blue shades which are extremely fast to light.

(*b*) OXYKETONE COLORS OTHER THAN ANTHRAQUINONE DERIVATIVES.—*Alizarin Yellow A* is made by the condensation of benzoic acid with pyrogallol, and is a trioxybenzophenone, while *Alizarin Yellow C* is made by the condensation of acetic acid with pyrogallol in the presence of zinc chloride. It is a gallacetophenone.

Anthracene Yellow is obtained by the treatment of dioxy-β-methylcoumarin with bromine.

Alizarin Black S is the sodium bisulphite compound of naphthazarine (dioxynaphthoquinone).

Galloflavin is formed by the atmospheric oxidation of gallic acid in alkaline solution. Forms a dirty-yellow paste, insoluble in water or hydrochloric acid. Wool mordanted with chromium salts takes a color resembling that obtained from fustic.

8. THE SULPHUR OR SULPHIDE COLORS.

Cachou de Laval was obtained already in 1873 by the fusion of organic substances such as sawdust, bran, etc., with sodium sulphide. It dyes cotton brown.

The fact that diphenylamine and its derivatives fused with sulphur and sodium sulphide yielded a series of colors has been utilized in the preparation of the *Immedial colors*. *Immedial black* produces a fast black upon cotton which can be oxidized on the fibre to *Immedial blue.*

IV. Analytical Tests and Methods.

In this section it is not the intention to exhaust the subject of the chemical examination of coal-tar colors, but to briefly indicate the more important and characteristic tests. The complete chemical analysis of the artificial organic dyes is very seldom resorted to, the analyst usually determining the *identity* of the coloring matter by means of the tabular schemes which have been published from time to time as new products have appeared on the market, and estimating the *moisture* of the sample and such foreign substances as the sulphates of soda, and of magnesia, salt, sugar, starch, and dextrine, sand, etc. Of considerable value in connection with the above is a dyed sample of cloth or yarn, which, although not strictly a chemical test, is one of equal importance, especially for the information of the immediate user of the dye. The recognition of dyes, either by themselves or on the fibre, is often desirable, but this requires considerable care and judgment, from the fact that a very large number are simply mixtures, some with as many as five separate dyes; in such cases the task is almost hopeless. These mixtures are sometimes made at the color manufactory, and again by the local agent; in the latter case, usually to supply some particular shade called for, and generally without any regard to the chemical nature of the constituents; this indiscriminate mixing accounts in a measure for the streakiness and uneven effects noticed in dyeing piece goods and yarn with such colors, which cannot always be detected by dyeing the small test samples in the laboratory.

Fastness to Light is determined by exposing one-half of a dyed skein or piece of dyed cloth to the action of direct sunlight for a definite time, say thirty days or longer.

Fastness to Soap.—A piece of dyed cloth or yarn is worked in a *neutral* soap lather, washed, dried, and compared with the original.

Comparative Dye-trials.—For this purpose vessels of glass, porcelain, or tinned copper are most convenient,—the latter is the best suited,—and if means can be had to provide heating by steam, it leaves nothing to be desired. When several comparative dyeings are to be made at one time of the same class of samples, one equal temperature is necessary.

For Wool and Silk.—In either case it is best to use a vessel containing about one litre. From twenty to twenty-five grammes of wool (yarn or fabric) and about five to ten grammes of silk answer well for the tests. The quantity of dye used varies, although two standards, representing one per cent. and five per cent. of the weight of the wool or silk, answer, as they give two shades which are convenient for estimating the dyeing value of the sample. To make the test, the color is weighed out carefully, washed into the dye-bath containing water, and brought to the boil, into which the material, previously wetted out, is immersed and kept moving about for a definite time, say twenty to thirty minutes, or until the bath is exhausted of color, when it is withdrawn, washed, dried, and the shade compared with a swatch of the same weight, treated under exactly the same conditions as to temperature, time, etc.

To determine the relative dyeing values of color samples, two solutions of equal value are made of equal (known) weights of the dyes, and two dyeings are made as above, only adding the dye solution to the bath as fast as it is taken up by the fabric; a point will be reached when no more color will be taken up, when the addition must stop, the differ-the relative amounts absorbed by the fabric can be calculated. The above applies equally to silk. No general rule can be given which will embrace the application of the colors to fibres in testing, reference must be had to the various classes of dyes and methods in Chapter XIV.

For Cotton.—Few colors are directly applicable to this fibre without previously mordanting it with suitable substances which will cause the color to remain. In the laboratory, a quantity of cotton is taken (yarn or piece), boiled well in water and immersed in a five per cent. solution of tannin for about twelve hours, when it is removed and boiled in a bath containing two and a half per cent. of tartar emetic for thirty to forty-five minutes, washed, dried, and kept for use. (Other mordants—*e.g.*, tin, iron, alumina, etc.—are used according to the kind of work done in the establishment.) In the matter of printed goods, swatches of cotton cloth, mordanted on one piece with several bases, are made by the printer, and these are then passed through one solution of color, and the effect can be conveniently noticed.

For Woollen Yarn Printing.—Pastes are made up of the color in varying strengths with starch or flour, and with such assistants as may be required, such as oxalic or tartaric acids, stannous chloride, etc., in the following manner: Five grammes of color are taken and mixed with a little water containing dextrine or glycerine, and this is made up to five hundred cubic centimetres with a paste of flour (one pound per gallon). Twenty or thirty strands of yarn about a metre long are taken, held at one end, and the color-paste rubbed well in for a space of about six inches with a glass rod or spatula; one-tenth of the color-paste is emptied out, and the remaining is diluted again to five hundred cubic centimetres, and this is then applied to the yarn, leaving a space of an inch or so from the first. The diluting operation is continued so that the printings on the yarn will represent color in the proportion of 1, .9, .8, .7, etc., giving a range of shades of one color. The yarn so printed is then steamed for about twenty to thirty minutes under pressure, or longer without pressure, washed, and dried. This method is of much value in matching and valuing shades in tapestry carpets.

By Colorimetry.—This method involves the use of two graduated glass tubes, closed at one end, each of the same diameter, thickness, and length. The standard sample of dye being weighed and dissolved in water, is poured into one tube, while an equal weight of the sample to be tested is poured into the other, and by holding the tubes to the light the depth of color is seen. If one is darker in shade than the other, it is diluted until the shades are equal, when, by knowing the number of cubic centimetres of water added to equalize the tint, the relative strength of the dyes can be ascertained.

Mixtures of Dyes can be detected by sprinkling some of the powder on the surface of distilled water, and noticing the color of the streaks formed as the particles subside, or by dissolving the dye in a little alcohol and water contained in a small exaporating dish or beaker, and immersing therein the end of paper, owing to the fact that the constituents of the mixture do no always possess the same degree of capillarity. These bands can be cu off and separately tested by proper reagents according to the scheme fo identification of dyes following. Fractional dyeing has also furnishe information of value; usually wool or silk being employed.

Identification of Coal-tar Dyes.—Weingärtner's comprehensive tables which follow, afford means of determining the group to which a sampl of dye under examination belongs. The dyes are divided convenientl into two divisions, *basic* and *acid coloring matters*, and the latter int *soluble* and *insoluble in water.*

I. *The Dye is Soluble in Water.*—Add a few drops of a solution o tannin * to a solution of the dye, and note the formation of a precipitate, after heating.

A. Precipitation takes Place.—The color is basic.—A small quantit of the original color is dissolved in water, and reduced with hydrochloric acid and zinc-dust, rapidly filtered, and neutralized with sodiu acetate; small strips of filter-paper are immersed in the solution, and exposed to oxidize.

The Original Color Reappears on the Paper.					The original color does not reappear.
Reds.	Oranges and yellows.	Greens.	Blues.	·Violets.	
Fuchsine, Magenta, Roseine. With *sulphuric acid*, brown. Neutral Red. With *sulphuric* acid, *green*. With *caustic soda solution*, yellow-brown precipitate. Safranine. With *sulphuric acid*, green. *Caustic soda*, brownish-red precipitate. Pyronine. Acridine Red. Toluylene Red.	Phosphine, Chrysaniline. With *sulphuric acid*, reddish-yellow precipitate. Green fluorescence. *Caustic soda*, light-yellow precipitate. Soluble in ether with green fluorescence. Flavaniline. With *sulphuric acid*, dirty yellow precipitate. Soluble in ether with blue fluorescence. Acridine Yellow. Acridine Orange.	Malachite Green, Victoria Green. With *sulphuric acid*, yellow, on diluting with water, green. *Ammonia* causes gray or red precipitate. Brilliant Green. With *sulphuric acid*, same as above, color reappears slowly. *Ammonia*, little or no precipitate. Methyl Green, Paris Green. With *sulphuric acid*, same as above, color not reappearing on dilution. *Ammonia*, solution decomposed, no precipitate. Azine Green.	Methylene Blue. With *sulphuric acid*, green. *Caustic soda* causes violet-black precipitate. New Blue. With *caustic soda*, blue-black precipitate. Muscarine. *Caustic soda* causes brownish-red precipitate. With *tannin*, indigo-blue precipitate. Capri Blue. Meldola's Blue. Metaphenylene Blue. Indamines.	Methyl Violet. *Sulphuric acid* causes a yellowish-brown coloration; on dilution changes to green and violet-blue. Neutral Violet. *Sulphuric acid* causes bright violet color; on dilution changes to blue. Mauveine. *Sulphuric acid* causes gray color; on dilution changes to light blue and violet-red. Amethyst. *Sulphuric acid* gives green color; blue on dilution. Prune. Paraphenylene Violet.	Chrysöidine. Color, orange. In *sulphuric acid*, dissolves to a brownish-yellow solution. Vesuvine. Color, brown, upon silk, orange. In *sulphuric acid*, soluble to a pale liquid. Auramine. Color, yellow. With *alkalies*, white precipitate. On warming with *sulphuric acid*, solution decolorized Victoria Blue. Color, blue. In *sulphuric acid*, brownish-red, changes to bluish-green.

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* Twenty-five parts of tannin, twenty-five parts of acetate of soda, and tw hundred and fifty parts of water.

B. No Precipitation takes Place.—The color is acid.

<table>
<tr><th colspan="5">Reduce with Hydrochloric Acid and Zinc-dust.</th><th rowspan="4">The solution becomes brownish-red. The color of the ammoniacal solution reappears on the paper.</th></tr>
<tr><th colspan="2">The color reappears on the filter-paper.</th><th colspan="3">The color does not reappear on the filter-paper.</th></tr>
<tr><th colspan="2">e aqueous solution is acidulated with hydrochloric acid, and agitated with ether.</th><th colspan="3">The original coloring matter, when heated on platinum foil,</th></tr>
<tr><th>he ether takes up the color.</th><th>The ether remains uncolored.</th><th>Deflagrates <i>without</i> colored vapors.</th><th colspan="2">Burns without deflagrating, but <i>with</i> colored vapors. A piece of unmordanted cotton cloth is heated in a solution of the original dye.</th></tr>
<tr><td rowspan="2">Phthaleïns.
n. With <i>sulphuric acid</i>, solu- n yellow. By <i>heating</i>, hydro- mic-acid vapors are evolved. <i>drochloric acid</i> precipitates or- ge-colored flakes.
osine. <i>Sulphuric acid</i> causes d-yellow solution. Hydro- mic acid evolved on <i>heating</i>. th <i>hydrochloric acid</i>, brown kes precipitated.
xin. Same as above. Flesh- ored precipitate with hydro- oric acid.
Bengale. No fluorescence in ter. With <i>sulphuric acid</i>, or- ge color. On <i>heating</i>, iodine ors are evolved.
soline. Brown-yellow solu- n; on adding <i>hydrochloric acid</i>, olorized with formation of wn precipitate.
llin, Aurin. Brick-red solu- n. With <i>hydrochloric acid</i>, low precipitate. No vapors <i>heating</i>.</td>
<td rowspan="2">Sulphonated Rosaniline Derivatives.
Acid Fuchsine, Acid Magenta. Aqueous solution, bluish-red. In <i>sulphuric acid</i>, yellow, changing to red on dilution.
Acid Green. Pale green in aqueous solution. <i>Alkalies</i> decolorize.
Alkali Blues. <i>Alkalies</i> decolorize; restored by <i>acids</i>.
China Blue. Aqueous solution, blue. <i>Alkalies</i> have no action.
Acid Violet. Aqueous solution, violet. <i>Ammonia</i> decolorizes. In sulphuric acid, orange solution. On dilution, gray-violet.
Indulines, Nigrosines. Aqueous solution, grayish-violet. Blue precipitate with <i>hydrochloric acid</i>. With <i>ammonia</i>, violet-red precipitate.</td>
<td rowspan="2">Nitro-Coloring Matters.
Picric Acid. Aqueous solution, greenish-yellow. No precipitate with <i>hydrochloric acid</i>. Detonates when mixed with <i>carbonate of soda</i> and <i>heated</i>.
Martius Yellow. With <i>hydrochloric acid</i>, yellowish-white precipitate. Soluble in ether.
Naphthol Yellow. No precipitate with <i>hydrochloric acid</i>. Insoluble in ether.
Aurantia. Concentrated aqueous solution, red; when diluted, yellow. <i>Alkalies</i> throw down deep-red precipitate.</td>
<th>The dyed cloth is treated with a warm solution of soap. The color remains.</th><th>The color is removed by the soap solution.</th>
<td rowspan="2">Anthracene Derivatives.
Alizarin S. Aqueous solution, brownish-yellow. <i>Ammoniacal solution</i>, fuchsine-red.
Cœruleïn S. Aqueous solution, olive brown. <i>Ammoniacal solution</i>, green.
Alizarin Blue S. Aqueous solution, reddish-brown. <i>Ammoniacal solution</i>, greenish-blue.</td></tr>
<tr><td>Benzidine Derivatives.
Congo Red. Aqueous solution, red. In <i>hydrochloric acid</i>, blue.
Benzopurpurin. Aqueous solution, orange. In concentrated <i>hydrochloric</i> and <i>sulphuric acids</i>, brown precipitates.
Azoblue. Aqueous solution, violet-blue. <i>Alkalies</i> change to blood-red.
Erythrosin. Aqueous solution, blood-red. Iodine vapors given off on heating dry.</td>
<td>Azo- Derivatives.
The following color reactions are all with <i>sulphuric acid</i>:
Fast Yellow,—Yellow.
Tropæolin OO,—Violet.
Azoflavin,—Red.
Methyl and Ethyl } Bronze,—Yellow.
Yellow N,—Blue-green.
Luteolin,—Greenish-yellow.
Tropæolin O,—Orange-brown.
Mandarin,—Carmine-red.
Biebrich Scarlet,—Green.
Croceïn Scarlet,—Indigo-blue.
Xylidine Scarlet,—Violet.
Croceïn Scarlet 7B,—Blue.
Ponceau Scarlet R, 4R and G,—Eosine-red.
Coccin,—Fuchsine-red.
Roccellin,—Violet.
Bordeaux, R and G,—Blue.</td></tr>
</table>

II. *The Dye is Insoluble in Water.*—Treat with a five per cent. solution of caustic soda.

THE DYE DISSOLVES.		THE DYE DOES NOT DISSOLVE.				Insoluble in seventy per cent. alcohol.
essary, the soda solution is filtered, and the discharged with zinc-dust, small slips of filter-r are immersed in the solution, and exposed to ir.		Soluble in seventy per cent. alcohol.				
		The solution is not fluorescent.		The solution is fluorescent.		
iginal color of solution reap-s.	The original color does not reappear.	With thirty-three per cent. soda solution, change to reddish-brown.	With thirty-three per cent. soda solution, no change.	With thirty-three per cent. soda solution, fluorescence disappears.	With thirty-three per cent. soda solution, fluorescence remains.	INDIGO. Ground fine, and reduced with *zinc-dust* and *ammonia*, yellowish solution, producing blue stains on filter-paper. ANILINE BLACK.
CYANIN. *Soda ion*, violet; *sulic acid*, blue. IN. In *sulic acid*, blue. ÉIN. *Soda so-*, green; *sulic acid*, green. FLAVIN. *Soda ion*, yellow; *sulic acid*, yellow. RIN BLUE. RIN BLACK. GALLOL.	CANARIN. *Soda solution*, yellow. Insoluble in *sulphuric acid*. ALIZARIN. *Soda solution*, blue-violet; changed to red on heating with zinc-dust. ANTHRAPURPURIN. Fuchsine red in *alkalies*. FLAVAPURPURIN. Same. CHRYSAMIN. In *soda solution*, orange. In sulphuric acid, fuchsine-red. NITROALIZARIN. *Soda solution*, red. Reduced with *zinc-dust*, stains paper indigo-blue. ALIZARIN BLUE. Difficultly soluble in *soda* to green solution; stains filter-paper violet. ALIZARIN BROWN. *Soda solution*, olive-brown. In *sulphuric acid*, red-brown.	INDULINES and NIGROSINES. In *alcohol*, solution greenish-blue. Agitated with *benzol*, shows marked brown-red fluorescence. ROSANILINE, or DIPHENYLAMINE BLUE. *Alcohol* solution deep blue. On adding *hydrochloric acid*, becomes green. No fluorescence with benzol.	INDOPHENOL. *Alcoholic solution*, blue. On adding *hydrochloric acid*, becomes brownish-red. SUDAN II. AND III.	MAGDALA RED. *Alcoholic solution*, blue, with a cinnabar-red fluorescence.	PRIMROSE. *Alcoholic solution* has blue-red color, with yellow fluorescence. CYANOSIN. *Alcoholic solution*, bluish-red, with dark-red fluorescence.	PRIMULINE BASE.

Dextrine.—This substance is estimated by weighing one or two grammes of the dye in a small tared beaker, provided with a glass rod. The dye is dissolved in a little water, and absolute alcohol added, when the dextrine will be thrown down, and adheres closely to the glass. The contents are emptied, and the glass rinsed two or three times with alcohol, dried, and weighed.

Starch.—The presence of this substance must not be taken as an adulterant in every case it is found; owing to its peculiar properties it acts as a drier or absorber of moistness, and hence prevents the caking of the dye. By dissolving a quantity of the dye in water, and allowing the solution to stand in a conical glass for a while, any starch present will subside, the clear liquid is poured off, and the residue repeatedly washed with distilled water and alcohol until no color remains, it can then be examined with the microscope; a drop is placed on a slide with a drop of water, the cover-glass put on, and a drop or two of iodine solution placed on the edge, and allowed to displace the water by the aid of a piece of filter-paper opposite the iodine, will, if starch is present, develop the characteristic reaction,—blue.

Sugar.—Estimated as for dextrine; the alcohol used should be saturated with sugar. Sugar can be estimated in dyes by precipitating the coloring matter with basic acetate of lead, and proceeding as for raw sugar with the polariscope (see page 173), or by inverting and estimating with Fehling's solution (page 175).

Sand and Iron Filings are gross adulterations occasionally met with in dyes from unprincipled dealers. Their presence would have been noticed under the *insoluble matter* determination. Iron filings can be easily determined with a magnet.

A careful microscopic examination of ground and crystallized dyes will throw much light on their preparation; bronze-powder and sugar crystals have been thus found.

Paste-dyes, etc., are best estimated by evaporating a weighed quantity to absolute dryness in a small glass mortar, grind thoroughly, add water, and filter through a tared filter, wash with water, dry, and weigh. If this is not done, trouble will be met; paste-dyes not filtering well if simply diluted with water.

The Examination of Dyed Fibres can well be accomplished by the aid of the following table, which is adapted from those of Hummell,* of R. Lepetit,† and of Lehne and Rusterholz,‡ and embraces a majority of the more important coloring matters which have found application. The reagents employed are hydrochloric acid (HCl), concentrated, 21° Beaumé, and dilute, one part of acid 21° B. and three parts water; sulphuric acid (H_2SO_4), concentrated, 66° B., and dilute, one part of acid 66° B. and five parts of water; nitric acid (HNO_3), concentrated, specific gravity 1.40, dilute one part of the strong acid and two parts of water; caustic soda solution (NaOH), concentrated, 38° B., and dilute, one

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* Hummell, The Dyeing of Textile Fabrics, London, 1885.

part of the strong solution and ten parts of water; ammonia, specific gravity .960; alcohol, ninety-six per cent.; stannous chloride, tin salt ($SnCl_2 + 2H_2O$), and concentrated hydrochloric acid equal parts; acetate of ammonia solution, by neutralizing ammonia with pure acetic acid and bringing exactly to 5° B.

The initials or names in parentheses following the names of the dye-colors are those of the manufacturers who furnish the particular dye-stuff, and will be readily understood by those accustomed to handle these wares.

A separate column has not been made for nitric acid, but where its action is distinctive it is noted under the head of remarks.

Method of Procedure.—For the testing with concentrated acids and caustic alkalies small watch-crystals are most advantageously used. These are then placed upon white paper in order to be able to observe carefully the changes of color. The concentrated acids are most conveniently dropped from small dropping tubes or pipettes, so that they can be added drop by drop until the fibre is completely covered. After addition of the acids four to five minutes are allowed, and the action is then noted. The watch-crystals are then heated carefully by using a very small flame or placing them upon a steam-coil, but the liquids upon the watch-crystals should not be allowed to boil. After waiting a few minutes and allowing them to cool, water is added to the contents of the watch-crystals.

All the other reactions of the tables are carried out in test-tubes The fibre is placed in the test-tube, covered with the reagent, and allowed to stand for several minutes, then heated without quite bringing the liquids to the boiling-point, when the action is carefully noted Finally the liquids are boiled for a short time. The solution is then poured off and caustic alkali or acid, as the case may be, is added, and any change carefully noted. After the tests with concentrated hydrochloric or sulphuric acids the fibres are well washed with water in order to observe whether the original color is thereby restored.

DETECTION OF COLORING MATTERS ON THE FIBRE.

test, small portions of the dyed fabric, or fibres, are placed in the several reagents, contained in porcelain evaporating dishes, and the reaction noted.

Red Dyes.

F COLORING ATTER.	HCl.	H_2SO_4.	NaOH.	NH_4OH.	$SnCl_2+HCl$.	Alcohol.	Remarks.
AGENTA. S. F.—R. H. .)	Bluish-red liquid extracted; color of fibre unchanged.	Same as with HCl.	Decolorized in the cold.	Same as with NaOH: color restored on exposure.	Color extracted on boiling.	But little extracted.	
N.	Dilute, no action; concentrated, fibre bright yellow, liquid amber-yellow.	Dilute, no action: concentrated, *red color* extracted. Concentrated H_2SO_4 at ordinary temperature entirely dissolves cotton dyed with alizarin-red, and the alizarin separates out as a flocculent precipitate, which can be collected, dried, and sublimed.	Fibre and solution violet.	No action.	Fibre orange-yellow, liquid bright yellow.	No action.	Gives no fluorescent solution on boiling with $Al_2(SO_4)_3$. (Distinction from madder and purpurin.) Bleaching-powder and chromic acid bleach it. Boiled with $Ba(OH)_2$ solution, fibre becomes violet. HNO_3 gives yellow spot. An alkaline solution of K_3FeCy_6 has no action, nor has $K_2Mn_2O_8$. HNO_2 vapor converts it into yellow nitro-alizarin. On heating, alizarin-red loses brilliancy and becomes brownish, but regains most of the brilliancy on exposure to air. The ammoniacal, aqueous, or alcoholic solutions give characteristic absorption spectra.
.	Fibre yellow.	Same as with HCl.	Solution bright red.	Same as with NaOH.	In the cold, solution yellow.	Color extracted.	
PURPURIN Bayer.)	Dilute HCl, fibre reddish-brown, solution colorless. Concentrated HCl, fibre dark brown.	Fibre black-blue, solution blue-black; on dilution changes to violet.	No reaction.	No reaction.	Fibre brownish-red, pink, and finally decolorized.	Extracts traces of color.	Nitrous acid, fibre brownish-black. Picric acid, fibre reddish-brown. All these dyes which resist NaOH are attached by a hot soap solution.
PURPURIN (Bayer.)	Dilute HCl, fibre blue-black, solution colorless. Concentrated HCl, same.	Fibre black-blue, solution dark blue; on dilution blue.	No reaction.	No reaction.	Fibre blue-black, light gray, finally colorless.	No reaction.	Nitrous acid, fibre blue-black and violet. Picric acid, fibre dark brown.

ICH SCARLET.	Fibre violet, liquid colorless; liquid becomes greenish-blue on standing.	Fibre and solution green.	Fibre dark bluish-red, liquid colorless.	No reaction.	Fibre decolorized.	Little or no action.	HNO_3 gives a dark-blue spot, which changes to brown with a dark-blue border.
IANT CONGO. 'er.)	Dilute HCl, fibre brown-red, solution colorless. Concentrated HCl, fibre blackish-violet with a reddish tint.	Fibre blue-black, solution blue; on dilution purple-violet.	No action.	No reaction.	Fibre brownish-red, becomes decolorized.	Extracts some color.	Nitrous acid, fibre black; turns black-violet with ammonia. Picric acid, fibre brown.
›ISINE. 'er.)	Dilute HCl, no reaction. Concentrated HCl, fibre dark violet; original color restored on washing.	Fibre and solution blackish-violet.	Fibre turns slightly brown, solution light pink.	Fibre unaltered, solution pink.	Little action in the cold; on heating, fibre is decolorized.	No action.	HNO_3, brown-violet spot, disappearing on washing.
CORINTH. 'er.)	Dilute and concentrated HCl, fibre black.	Fibre black, solution dark blue.	Fibre reddish-blue, solution colorless; color appears on washing.	Fibre reddish, solution pale pink.	Fibre black, blue, gray, and finally colorless.	Solution scarcely colored.	Nitrous acid, fibre dark blue; washed with ammonia turns magenta-red.
RED, (Berlin. Ges.)	Fibre at once bluish-black, solution colorless.	Fibre bluish-black, solution dark-blue; turns blue-black on dilution.	Little change, solution colorless.	No reaction.	Fibre blue-black, blue, gray, and finally colorless.	No reaction.	Nitric acid, blackish-blue spot, original color restored by ammonia. Nitrous acid, fibre reddish-brown; ammonia does not restore original color, but turns the fibre brownish-purple and the solution bluish-red. Picric acid fibre bluish-black.
IN SCARLET (Bayer.)	Fibre at first violet, liquid colorless; on standing, fibre becomes blue, liquid greenish-blue.	Concentrated acid, fibre and solution blue.	Fibre blue.		Fibre decolorized.	Little or no action.	Nitric acid gives at first a dark-blue spot, which changes to bright yellow with a greenish-blue border.
I-PURPURIN (Bayer.)	Dilute, fibre reddish-brown; concentrated, fibre olive-black.	Fibre dark brown, solution dirty green; reddish-brown on dilution.	No reaction.	No reaction.	Fibre first brown, gradually colorless.	Extracts some dye.	
I-PURPURIN (Bayer.)	Dilute, fibre brown-red, solution colorless; concentrated, fibre greenish-black.	Fibre blue-black, solution dark blue; on dilution at first gray, then brown-red.	No reaction.	No reaction.	Fibre dark brown, then lighter, then pink, and finally colorless.	No reaction.	Nitrous acid, fibre violet-black; turns violet-red on the addition of ammonia. Picric acid, fibre brownish-red.
T RED gy.)	Dilute, fibre black-violet; concentrated, fibre blue, solution colorless.	Fibre blackish-blue, solution black-violet; on dilution grayish-blue.	Fibre darker, and assumes a blue tint, solution pale brown-red.	Fibre brilliant red, solution scarcely reddish.	Decolorized.	No reaction.	Nitrous acid, fibre reddish-brown; unchanged by ammonia. Picric acid, brown spot.

F COLORING ATTER.	HCl.	H_2SO_4.	NaOH.	NH_4OH.	$SnCl_2 + HCl$.	Alcohol.	Remarks.
.	Fibre pale yellow.	Fibre bright yellow at once.	Fibre yellow, solution pink, fluorescent.	Fibre yellow, solution yellow, fluorescent.	Fibre orange-yellow, solution pale yellow.	*Soluble* eosins not extracted if well dyed. *Spirit* eosins readily extracted by absolute alcohol.	Hot water containing a little NH_4OH extracts a pink liquid from soluble eosins.
PURPLE N. .)	Dilute fibre black, solution colorless.	Fibre black, solution blue; after dilution grayish-blue.	No reaction.	No reaction.	Fibre black, then colorless.	Scarcely colored.	Nitrous acid, fibre violet-black; brown-red with ammonia. Picric acid, fibre brown.
A RED.	No reaction.	No reaction.	No reaction.	No reaction.	Little action; fibre slightly blue.	Little extracted; solution pink fluorescent.	To detect in presence of eosin, extract in boiling alcohol,—this removes eosin, which is then tested; wash the fibre or fabric, and test for Magdala red.
A. SINE.)	Fibre and solution yellow: original color restored on washing.	Same as with HCl.	Fibre paler, afterwards colorless.	Decolorized.	Almost decolorized; color partly restored on boiling.	A bluish-red color extracted.	Sodium sulphide decolorizes. To distinguish from orchil and aurin: *Amyl alcohol* extracts a blue-red color from material dyed with magenta, but extracts a yellow color from aurin, while from orchil a pink or violet color is obtained. An *alcoholic extract* of magenta is decolorized with NH_4OH, while one of aurin is turned bluish-red. Orchil remains unchanged.
N 2B. .)	Fibre first black-violet, finally black, solution pale indigo-blue.	Fibre blackish-blue, solution indigo-blue; reddish-violet on dilution.	Fibre violet, solution reddish-violet.	Same as preceding.	Slowly decolorized in the cold, rapidly on heating.	No reaction.	Nitric acid, violet spot; disappears on washing.
N J.	Fibre yellow.	Fibre yellow.	Fibre and solution pink.	Same as preceding.	Yellowish on boiling.		
INE. CHROMINE.) LA.)	Fibre and solution red-brown.	Fibre black-violet, solution same; becomes red on dilution.	Fibre dirty dark brownish-red.	No reaction.	Fibre turns gradually reddish-brown.	No reaction.	Fast to soap, light, and acids of ordinary dyeing strength.
IN.	Boiled, fibre orange-yellow, solution yellow.	Same as preceding.	Heated, fibre and solution cherry-red.	Boiled, solution pale pink, fibre not changed.	Brownish-red, solution amber-yellow.	Solution red.	Nitric acid gives a bright yellow spot. Bleaching-powder bleaches it. Boiled with a solution of $Al_2(SO_4)_3$ and cooling, gives an orange fluorescent solution.

IIN. S. F.)	Fibre brick-red, solution colorless; color restored after washing.	Same as preceding.	Fibre little darker, with bluish tint, solution uncolored.	Fibre little darker, solution slightly pink and fluorescent.	No action in cold; on heating, solution becomes brown-red; solution slightly pink.	Extracts some dye; fluorescent solution.	Nitric acid, orange spot, disappearing on cooling. Nitrous acid, no reaction.
IN.	Concentrated, fibre blue.	Fibre black, changes to green.	Solution pink.	Same as preceding.	Decolorized on heating.	Color extracted; red fluorescence.	
r 2R. and B.)	Nearly decolorized on boiling; much color extracted.	Dilute, no action: concentrated, color extracted.	Nearly decolorized.	Fibre paler.	Decolorized.	Little or no action.	Nitric acid gives violet spot, which changes to bright yellow.
r 3R. and B.)	Fibre not changed on boiling, solution bluish-red.	No action.	Nearly decolorized.	Little effect.	Fibre decolorized.	Little or no action.	With nitric acid, same as for Scarlet 2R.

Yellow and Orange Dyes.

IN.	Fibre nearly decolorized, solution colorless; on dilution original color restored.	Fibre decolorized, solution colorless.	Fibre decolorized, solution colorless; after washing, color partly restored.	Fibre pale yellow, solution colorless.	Gradually decolorized in cold, quickly on heating.	No reaction.	Nitric acid, white spot; gradually turns orange in the centre.
ANT YELLOW.	Concentrated, fibre dark yellow.	Fibre black-violet, solution violet.	Fibre cherry-red, solution slightly pink.	Same as preceding.	Fibre dirty yellow; gradually decolorized.	No reaction.	
AMIN er.)	Dilute, fibre pale yellow, concentrated, fibre reddish-brown, solution pink, yellow on dilution.	Fibre magenta-red, solution red-violet.	Fibre dark orange.	Fibre light orange, solution colorless.	Slowly decolorized.	No reaction.	Nitric acid, brown spot; gradually turns reddish-gray.
OIDINE.	Fibre red.	Yellow color extracted.	Paler and yellower.	Fibre yellower.	Almost decolorized.	Yellow color extracted.	
OPHENIN. er.)	Concentrated, fibre blackish-violet, solution scarcely colored.	Fibre brown, then dark red-violet, blue on dilution.	Solution pale yellow; no change to fibre.	No reaction.	Fibre brownish-yellow, then decolorized.	No reaction.	Nitric acid, violet spot.
ELLOW. . S. F.)	Red.	Fibre brownish-red, solution red.	Solution brownish-yellow.	Little or no action.	Fibre bright red, finally decolorized.	Some color extracted.	Nitric acid, bright red spot.
N YELLOW. er.) nhardt.)	Dilute, fibre lighter, concentrated, fibre blackish-blue, solution violet.	Fibre dark violet, solution red-violet.	Fibre dark red, solution light pink.	Fibre dark orange, solution slightly colored.	Pale yellow, gradually decolorized.	No reaction.	

Yellow and Orange Dyes.—Continued.

AME OF COLORING MATTER.	HCl.	H_2SO_4.	NaOH.	NH_4OH.	$SnCl_2 + HCl$.	Alcohol.	Remarks.
APHTHOL YELLOW.	Decolorized almost completely.	Same as preceding.	Fibre orange, solution yellow.	Fibre paler, color extracted on boiling.	Fibre and solution decolorized.	Some color extracted.	Water extracts the color, H_2SO_4 decolorizes the yellow solution. Boiling cyanide of potassium extracts a red color. Loses color when heated on the fibre.
RANGE No. 2.	Bluish-red.	Same as preceding,—bluer.	Fibre deep red.	No reaction.	Decolorized.	No reaction.	
RANGE No. 3.	Fibre red, solution pink.	Bright bluish-red.	Fibre dull yellowish-red.	Solution slightly yellow, fibre unchanged.	Decolorized.	But little color extracted.	
RANGE No. 4.	Fibre reddish-violet, solution violet.	Same as preceding.	No reaction.	Solution slightly yellow, fibre unchanged.	At first fibre becomes deep violet on heating, gradually lighter, and finally decolorized.	Yellow color extracted.	
HOSPHINE.	Fibre nearly decolorized, solution yellow.	Solution greenish-yellow.	Fibre paler and yellower.	Fibre paler and bright yellow.	Nearly decolorized.	Little color extracted.	
ICRIC ACID.	Color extracted on boiling, solution greenish-yellow.	Decolorized.	Fibre becomes orange, solution yellow.	Fibre paler, color extracted on boiling.	Decolorized.	Color extracted.	Picric acid has a bitter taste. Heated with cyanide of potassium becomes red. In compound colors, should be extracted with alcohol and tested with cyanide as above.
RIMULINE ORANGE.	Fibre reddish-brown, solution same.	Fibre orange-brown, solution dark red.	Fibre dark red-brown, solution scarcely colored.	No reaction.	Fibre orange-brown, then decolorized.	Some color extracted.	Nitric acid, red-brown spot.
RIMULINE YELLOW.	No reaction.	Fibre dark yellow, then pale yellow.	Fibre orange-yellow, colorless solution.	No reaction.	Little action.	No reaction.	Nitrous acid, fibre dark orange, and on addition of ammonia orange-brown. β-Naphthol turns dyed fibre red.
UINOLINE YELLOW. (B. A. S. F.)	Fibre more yellow, solution colorless; on dilution, original color of fibre is restored.	Same as preceding.	Fibre at first dark yellow, and gradually decolorized; color restored on washing.	Little action.	On heating, solution becomes yellow, fibre pale yellow.	No reaction.	
ARTRAZINE. (B. A. S. F.)	Fibre orange, solution yellow.	Same as preceding.	Fibre orange, solution orange-yellow.	Same as preceding.	Decolorized on heating.	No reaction.	

ENE ORANGE Oehler &	Dilute, fibre pink, concentrated, fibre paler, solution yellow; on dilution fibre turns pink.	Fibre and solution yellow.	Fibre orange, solution colorless.	No reaction.	Fibre at first pink, then decolorized on heating.	No reaction.	Nitric acid, red-violet spot turns gray. Nitrous acid, fibre grayish, on adding ammonia reddish-gray.
ENE ORANGE Oehler &	Dilute, no reaction; concentrated, fibre violet, solution reddish; on dilution fibre and solution assume original color.	Fibre magenta-red, solution slightly colored.	Fibre light orange, solution scarcely colored.	No reaction.	Fibre pink, decolorized on heating, solution colorless.	No reaction.	Nitrous acid, fibre turns gray, on adding ammonia becomes dirty yellow.

Green Dyes.

IN. (B. A.	Fibre duller, solution claret-red.	Same as preceding, solution dirty yellow.	No reaction.	No reaction.	Fibre brownish-red, solution brown; color gradually restored on washing.	No reaction.	Nitric acid, brown spot.
N GREEN.	Fibre yellowish-gray, solution orange-red.	Fibre and solution light brown.	Fibre dark green, solution pale green.	No reaction.	Slight decolorization, solution brown.	No reaction.	Nitric acid, yellow-brown spots.
A GREEN. CHITE N.)	Fibre and solution bright orange; color restored on washing with water.	Fibre nearly decolorized, solution bright orange.	Decolorized.	Decolorized.	Fibre almost decolorized, liquid yellow.	Color extracted.	

Blue Dyes.

N BLUE.	Fibre violet, solution yellowish-red.	Dilute, fibre violet, solution slightly red, concentrated, violet solution.	Fibre bluish-green.	No reaction.	Fibre at first violet, brownish-red on heating, solution brown.	No reaction.	Nitric acid, yellow spot, afterwards brown. Soap and bleaching-powder, no action.
BLUE.	Fibre greenish-blue, solution almost colorless.	Fibre and solution reddish-brown on standing.	Fibre reddish-brown, afterwards decolorized.	Decolorized.	Fibre not changed, colorless solution.	Color extracted by *absolute* alcohol.	Nitric acid gives a light-green spot with black border.
E. (Bayer.)	Concentrated fibre, blackish-blue, colorless solution.	Fibre bluish-black, blue solution.	Fibre cherry-red, solution pale pink.	Fibre violet-red, pink solution.	Fibre, blue-black, slowly decolorized.	No reaction.	Picric acid, fibre blackish-brown.
BLUE.	Fibre dark-gray, solution yellow, blue on dilution.	Fibre blue-black, green, finally yellow, solution yellow, blue on dilution.	Fibre darker.	No reaction.	No reaction.	Solution pale blue.	Nitric acid, black spot.

Blue Dyes.—Continued.

F COLORING ATTER.	HCl.	H_2SO_4.	NaOH.	NH_4OH.	$SnCl_2 + HCl$.	Alcohol.	Remarks.
ZOMINE G. r.)	Fibre blue-black, colorless solution.	Fibre black-blue, solution greenish-blue, reddish-blue on dilution.	Fibre dark red, solution pink.	Fibre dark-violet, solution cherry-red.	Decolorized.	No reaction.	Boiled with soap, solution turns blue.
ENOL BLUE.	Fibre grayish-brown.	Same as preceding.	No reaction.	No reaction.	Decolorized.	Blue color extracted.	Heated with olive oil, purple color extracted.
IE.	Fibre violet, solution deep blue.	Solution dark blue.	Red-violet color extracted, zink-dust added decolorizes solution; violet color restored by exposing the filtered solution to the air.	Same as preceding.	Extracts a violet or green color.	Bluish-violet color extracted.	Induline NN is not changed by bleaching-powder. Nitric acid gives a dark bluish-green spot.
LENE BLUE.	Fibre nearly decolorized, solution bluish-green.	Fibre and solution green.	Fibre bluish-violet.	No action.	Decolorized.	Greenish-blue color extracted.	Nitric acid, green spot. Bleaching-powder changes it to green, and finally decolorizes it. On cotton it is faster than most anilines, resisting action of soaps, light, and weak bleaching-powder.
IYLENE G. (Bayer.)	Fibre brownish-violet, solution brown-orange.	Fibre brown-black, solution dark brown, blue on dilution.	Fibre brown, solution brown-orange.	Fibre brownish-violet, solution pink.	Fibre decolorized.	Solution pale violet.	HCl vapors change color of fibre to a chocolate-brown.

Violet Dyes.

IN.	Fibre and solution dull yellow.	Same as preceding.	Fibre bluer.	No reaction.	Same as with HCl.	No reaction.	Destroy color by boiling with HCl, wash, and add NaOH; the alizarin on the fibre is dissolved with purple color.
OLET.	Dilute, fibre bluer, concentrated, fibre blackish-blue, solution colorless.	Fibre black-blue, solution blue-green.	Fibre red, solution colorless.	Fibre dark violet, solution pale magenta-red.	Fibre slowly decolorized.	No reaction.	Picric acid, fibre black. Dilute acetic acid, fibre blue.

IOLET.	Fibre blue-black.	Fibre black, solution gray-blue, greenish-blue, finally red on dilution.	Fibre black-blue, solution pale violet.	Fibre unchanged, solution pale violet.	Fibre decolorized.	Little action.	Nitric acid, blue-black spot.
YANINE.	Unchanged.	Fibre dark blue, solution intensely blue, magenta-red on dilution.	Fibre black-violet, solution dirty purple.	Same as preceding.	Fibre gray, solution colorless.	No reaction.	Nitrous acid, fibre dirty gray-violet, solution blue-green, green, finally yellow.
ROPE.	Dilute, fibre dark violet, concentrated, fibre black-blue, solution light blue, violet on dilution.	Fibre black-blue, solution blue.	Fibre dark red, solution colorless.	No reaction.	Fibre dark gray, slowly decolorized.	No reaction.	Nitrous acid, fibre greenish-gray, washed and treated with ammonia turns bluish-orange, solution pale brown. Picric acid, fibre dark brown.
L VIOLET.	Fibre yellowish-brown, liquid amber-yellow; on diluting with water violet color restored.	Same as preceding.	Fibre at first pale reddish-violet, afterwards decolorized.	Fibre pale lilac, nearly decolorized.	Fibre green, nearly decolorized on standing, solution yellowish-green.	Color extracted.	
RINE.	Fibre blue-black, solution dirty-blue.	Fibre greenish-black, solution greenish, dirty violet on dilution.	Fibre brownish-black.	Fibre violet-blue, solution pale violet.	Fibre blackish; on heating, blue, green, finally yellowish-gray.	No reaction.	Nitric acid, black spot.

Brown Dyes.

IN.	Fibre brownish-orange; color restored by ammonia.	Same as preceding.	Action slight, fibre bluer, solution tinted bluer.	Unchanged.	Same as with HCl.	No action.	
BROWN. er.)	Dilute, fibre reddish-brown, concentrated, fibre darker, solution purple-red.	Fibre brown-black, solution dark brown.	No reaction.	No reaction.	Fibre lighter and yellowish, solution brownish-yellow.	Little color extracted.	
CK-BROWN.	Fibre reddish-brown, solution red.	Same as preceding, darker.	Fibre brownish-yellow.	Fibre unchanged, solution brown.	Almost decolorized.	Red or pink color extracted.	Boiling water extracts color, glacial acetic acid more so, with yellowish-green fluorescence.
BROWN RG. in. Act. Ges.)	Fibre dark red-violet, solution violet; on dilution fibre becomes brown again.	Same as preceding.	Fibre brilliant dark red, solution cherry-red.	Same as preceding.	Fibre darker, and quickly decolorized on boiling.	No reaction.	Nitric acid, black spot, quickly turning to light red-brown.
HYLAMINE N.	Fibre brownish-yellow, solution orange.			Fibre yellow.	Fibre purple, solution pale pink.	Solution bluish-pink.	

Black Dyes.

ME OF COLORING MATTER.	HCl.	H_2SO_4.	NaOH.	NH_4OH.	$SnCl_2 + HCl$.	Alcohol.	Remarks.
IZARIN BLACK. B. A S. F.)	Fibre unchanged, solution pale greenish-blue.	Same as preceding.	Fibre unchanged, solution pale blue.	No reaction.	No reaction in cold; fibre brown on boiling; solution yellow.	No reaction.	Nitric acid. after a while dark olive-green spot.
ILINE BLACK.	No action, or color becomes greenish-black; restored by alkalies; acid solution brownish.	Same as preceding.	No action.	No reaction.	Fibre greenish-gray; color restored by ammonia.	Brownish-red color extracted.	Bleaching-powder changes color to brownish-red; weak oxidizing agents have no action.
PHTHOL BLACK. M. L. and B.)	Fibre unchanged, solution reddish.	Fibre unchanged, solution olive-green.	Fibre unchanged, solution pale red.	No reaction.	Boiling, fibre light green, blue after washing.	No reaction.	Nitric acid, brown spot after a time. This dye is a mixture.
SORCIN BLACK.	Fibre drab, solution orange-brown.	Fibre and solution brown.	Fibre unchanged, solution green.	No reaction.	Fibre and solution light brown.	No reaction.	Nitric acid, brown-yellow spot.
OL BLACK. Berlin. Act. Ges.)	Fibre unchanged, solution light blue, pink on dilution.	Same as preceding.	No action in cold; dark violet on boiling; solution violet.	No reaction.	Fibre decolorized.	No reaction.	Nitric acid, light red-brown spot.

V. Bibliography and Statistics.

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Coal-Tar Colors in Aniline Lakes, G. Zerr, translated by Mayer, London and Philadelphia.

STATISTICS.

1. Crude Materials of the Color Industry.—Schultz (Chemie des Steinkohlentheers, 1900, 3d ed., p. 9) states that the present production of coal-tar throughout the world is as follows: England, 660,000 tons; Germany, 160,000 tons; France, 80,000 tons; Belgium, 50,000 tons; Holland, 30,000 tons; America, 120,000 tons; total, 1,100,000 tons.

The yearly production of benzol and toluol from coal-tar and coke-oven gases was estimated by Dr. H. Brunck in 1901 to be from 25,000 to 30,000 tons, of which benzol made up four-fifths. Of this production Germany furnished at that time one-third, but the proportion has probably increased since.

The same authority estimated the yearly production of naphthalene to be from 40,000 to 50,000 tons.

The German production of phenol and cresol in 1902 was estimated by Witt (Die Chem. Industrie des Deutschen Reiches, 1902, p. 199) to be from 4400 to 4800 tons per annum, of naphthalene to be about 17,000 tons, and of anthracene to be from 4400 to 4800 tons.

2. German Coal-tar Color Statistics.—The German trade in aniline oil, aniline salts and other crude coal-tar products was:

	1900.	1902.	1904.	1905.	1907.
Imports in tons	1,241	1,233	2,099	1,624	137
Value in marks	1,120,000	1,130,000	1,890,000	1,460,000	130,000
Exports in tons	12,613	15,969	16,756	19,421	8,704
Value in marks	11,350,000	14,690,000	20,110,000	23,890,000	8,050,000

(Gustav Müller, Die Chemische Industrie, Berlin, 1909, p. 378.)

The German trade for the same years in aniline and other unspecified coal-tar colors was:

	1900.	1902.	1904.	1905.	1907.
Imports in tons	1,174	1,179	1,461	1,743	2,054
Value in marks	3,820,000	3,650,000	4,240,000	4,790,000	5,240,000
Exports in tons	23,781	28,805	30,831	36,570	43,716
Value in marks	77,290,000	89,300,000	88,590,000	100,650,000	112,500,000

(Ibid., p. 379.)

The German trade in alizarin and alizarin colors in recent years has been:

	1900.	1905.	1907.
Imports in tons	39	79	53
Value in marks	40,000	110,000	100,000
Exports in tons	8,591	9,339	10,442
Value in marks	11,170,000	15,530,000	23,430,000

(Ibid., p. 377.)

The German trade in indigo was as follows:

	1902.	1903.	1904.	1905.	1907.
Imports in tons	527	291	260	197	127
Value in marks	3,690,000	1,790,000	1,350,000	1,200,000	1,080,000
Exports in tons	5,284	7,233	8,730	11,165	16,350
Value in marks	18,460,000	20,690,000	21,660,000	25,720,000	42,580,000

(Ibid., p. 375.)

The value in marks of the coal-tar colors exported by Germany in recent years as summarized is as follows:

	1900.	1905.	1907.
Alizarin .... Alizarin dye colors. }	11,170,000	15,500,000	9,630,000 13,800,000
Indigo	9,360,000	25,700,000	42,580,000
Aniline and unspecified coal-tar colors	77,290,000	100,700,000	112,480,000
	97,820,000	141,900,000	178,490,000

(Ibid., p. 380.)

To these may be added the totals for the two following years, viz.:

For 1908, 208,654,000 marks, and for 1909, 235,354,000 marks.

(Fischer's Jahresbericht der chem. Tech., 1910, p. 583.)

3. United States Importations of Dye-colors.

	1908.	1909.	1910.
Alizarin and alizarin dyes in pounds......	3,964,126	3,749,869	3,023,348
Value	$753,371	$1,215,700	$647,944
Aniline salts (pounds).................	5,407,790	6,132,517	5,866,982
Value	$462,332	$543,538	$515,623
Coal-tar colors and dyes valued at.......	$4,883,675	$5,901,842	$6,011,054
Indigo (pounds)	6,078,073	8,249,972	7,538,689
Value	$1,058,354	$1,400,286	$1,195,942

(Commerce and Navigation U. S., 1910.)

CHAPTER XIII.

NATURAL DYE-COLORS.

I. Raw Materials.

THE raw materials to be described here are a series of vegetable dyes coming into commerce partly as compact heart woods and roots and partly as masses of separated coloring matters, together with a few dried animal remains yielding coloring matters. We shall take them up most conventiently in groups according to the colors yielded.

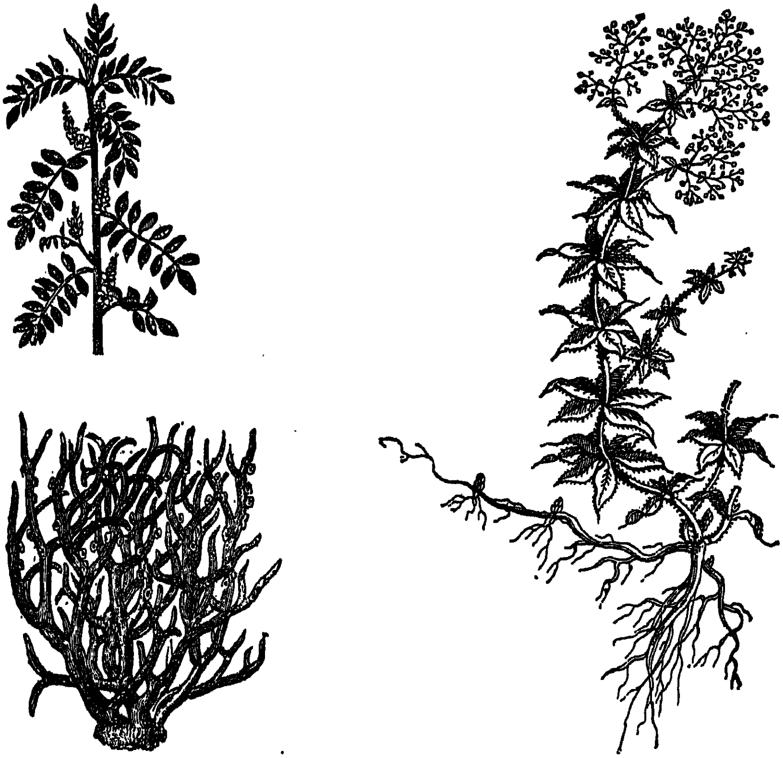
A. RED DYES.

1. *Brazil-wood and Allied Woods* (syn. *Rothholz, Bois de Brésil*).—The various species of *Cæsalpinia* yield woods which appear to contain a common chromogen, *brasilin*, $C_{16}H_{14}O_5$. This seems already in the wood to be changed in part into the corresponding coloring matter, *brasilëin*, $C_{16}H_{12}O_5$. And the change may be made complete by oxidizing the alkaline brasilin solution in the air by acting upon a hot solution of brasilin with an alcoholic iodine solution. Liebermann and Burg ascribe to the crystals of brasilin the formula $C_{16}H_{14}O_5 + H_2O$, and call attention to the fact that it bears the same relation to hæmatoxylin, $C_{16}H_{14}O_6$ (see p. 496), that alizarin bears to purpurin. The best-known varieties of the wood are known by the following special names: Pernambuco-wood, from *Cæsalpinia crista*, grown in Brazil and Jamaica, yellowish-red in the interior, becoming red and reddish-brown on the surface. Brazil-wood, from *Cæsalpinia Brasiliensis*, grown in Brazil, as well as the Antilles and Bahamas, is brick-red in the interior, becoming brown-red on the surface. It is inferior in coloring power to Pernambuco-wood. Sapan-wood, from *Cæsalpinia sappan*, grown in Siam, China, Japan, Ceylon, and the Indian Archipelago, is somewhat lighter in color than the other varieties. It is yellowish-red in the interior and bright red on the surface. Lima-wood, or Nicaragua-wood, from *Cæsalpinia bijuga*, is grown in Central America and the north coast of South America. The Santa-Martha-wood of Mexico and Peach-wood are by some writers considered as of the same species as Nicaragua-wood, and by others are derived from *Cæsalpinia echinata*. They have a dirty-red color in the interior, becoming paler on the surface. Bahia-wood, California-wood, and Terra-Firma-wood are other less known varieties of the same class.

2. *Sandal-wood, Caliatur-wood, Bar-wood,* and *Cam-wood* (syn. *Santelholz, Bois de Santal rouge*) form another group of woods which are alike in many particulars and contain probably the same coloring matter, *santalin*, C H O. They differ as a class from the

in contrast to the others as "open woods." The Sandal-wood (Red Sanders), from *Pterocarpus santalinus,* is grown in the East Indies, Ceylon, and Madagascar, and is a very hard and heavy wood, dark brown on the surface and blood-red in the interior. Caliatur-wood comes also from the East Indies, and though used as a substitute for the sandal-wood is considered as a distinct variety. Sandal-wood is said to contain some sixteen per cent. of santalin. Bar-wood, from *Baphia nitida,* comes from Sierra Leone, Africa, and is a dark-red wood, containing twenty-three per cent. of santalin. Cam-wood (or Gaban-wood) is supposed by many to be the same as bar-wood, but by others is ascribed to species of *Peterocarpus.* It comes, like bar-wood, from the west coast of Africa. Madagascar-wood is a minor variety resembling Caliatur-wood.

FIG. 112.



3. *Madder* (syn. *Krapp, Racine de Garance*) is the dried and broken root of the *Rubia tinctorium* and allied species. It grows wild in Asia Minor, Greece, and the Caucasus, and has been cultivated in France Alsace, Silesia, Hungary, Holland, etc. The appearance of the plant

In the Levant, the five- to six-year-old plants are plucked, in Europe those two to three years old. While the Turkish madder (known a Lizari or Alizari) was the earliest in use, the French variety grown i the neighborhood of Avignon, in part upon marshy soil (*palus*) and i part upon soil containing lime (*roseé*), has long been considered th best. Other varieties are the Dutch or Zealand madder, the Alsatia the Silesian, and the Russian madder. That which has not been free from the brown outer crust before grinding is inferior to that which h been so freed, and which is known as "crop-madder," while the in purest variety, obtained by grinding the rootlets, crusts, and wood parts of the roots, is called "mull-madder."

From the madder-roots are also prepared by fermentation and filtr tion of the separated dye-colors the commercial extracts known "madder flowers" and "guarancine." One hundred kilos. of madd will yield fifty-five to sixty kilos. of madder flowers.

The tinctorial value of the madder depends upon the existence of t two coloring matters, alizarin, $C_{14}H_8O_4$, and purpurin, $C_{14}H_8O_5$, both which have been mentioned under the artificial dye-colors derived fro anthracene. (See p. 466.) These are not found free in the growi plant, but combined as glucosides and other compounds easily deco posable by fermentation. As a nitrogenous and soluble ferme *erythrozym* is present; so soon as the solutions of madder extract a exposed to the air the *ruberythric acid* (or alizarin glucoside) is deco posed into alizarin and dextrose and the *pseudo-purpurin* (or natural occurring purpurin-carboxylic acid) is decomposed into purpurin a carbon dioxide. Two other anthracene derivatives also occur in madd both probably as decomposition products of pseudo-purpurin, *munjist* $C_{15}H_8O_6$, and *xanthopurpurin*, $C_{14}H_8O_4$ (the latter of which is isome with alizarin).

The importance of madder and madder preparations has almost tirely disappeared with the development of the artificial alizarin ma facture. The colors obtainable from alizarin, isopurpurin or anth purpurin, and flavopurpurin, which are the products of the syntheti methods, have almost entirely replaced those formerly obtained fr madder.

4. *Safflower* (syn. *Safflor, Fleurs de Carthame*) consists of the dr flowers of the *Carthamus tinctorius*, a plant first grown in Egypt a the East Indies, but now grown in Asia Minor, Spain, Alsace, Aust and Central Germany. The flowers are of a deep reddish-orange co and contain, besides a yellow coloring matter of no technical val *carthamin*, or *carthamic acid*, $C_{14}H_{16}O_7$, a red dye of considerable portance for silk- and cotton-dyeing. It forms from .3 to .6 per c of the weight of the flowers. "Safflower carmine" is a solution of carthamin in soda, and "plate carthamine" is a pure preparation the dye which has been dried in crusts upon glass or porcelain pla The most important commercial varieties of safflower are the Egypti which is the richest in dye-color, the East Indian, the Spanish, and German. Safflower comes from Spain and France, the production

ing amounted in recent years to 400,000 pounds. However, it is now almost entirely displaced from use as a dye by the artificial dyes.

5. *Orseille*, or *Archil* (syn. *Orséille, Persio, Cudbear*).—The various species of lichens, as *Rocella tinctoria* and *Rocella fuciformis* from Angola, Zanzibar, Ceylon, and Mozambique, as well as from the Azores and South American coast, contain a mixture of phenols, phenol-ethers, and phenol-acids, such as orcin (or orcinol), erythric, orcellinic and lecanoric (or diorcellinic) acids. These by the action of air and ammonia yield *orcëin*, contained in the orseille (archil) extract as a red dye, and on drying the extract the cud-bear or persio as a reddish-violet powder.

Archil extract occurs in commerce in two forms, paste and liquor. The solid matter consists mainly of the impure orcëin in combination with ammonia. Its preparation will be referred to later. Cudbear (or Persio) differs mainly from the orseille extract in being free from all excess of ammonia and moisture and in being reduced to a fine powder. An illustration of the orseille-yielding lichens is given in Fig. 112 (see page 489) in the lower left-hand figure.

6. *Cochineal* (syn. *Cochenille*) is the dried female insect *Coccus Cacti*, which lives and grows on the plants of the Cactus family, especially the "nopal," or *Cactus opuntia.* The nopal-plant is indigenous to Mexico, but is also cultivated largely in Central America, the Canary Islands, the Island of Teneriffe, Algeria, and the East Indies.

The commercial varieties of cochineal are known as the *silvery-gray* and the *black* cochineal. These varieties are apparently produced according to the method adopted for killing the insects when they are swept off the leaves of the nopal-plant. If killed by immersion in hot water or by steam they lose the whitish dust with which they are covered and constitute the black variety (*zaccatila*); if killed by dry heat in ovens this dust remains and they yield the silvery-gray variety (*blanco*). This latter is considered the better, and is sometimes simulated by dusting the black variety with powdered talc, gypsum, barytes, or stearic acid. The natural gray powder is a variety of wax known as *coccerin.*

The coloring matter of the cochineal is *carminic acid,* $C_{17}H_{18}O_{10}$, and may amount to fifteen per cent. of the weight of the dried cochineal, although Liebermann states that the average is from nine to ten per cent. Carminic acid is a purple substance soluble in water and alcohol, but only slightly so in ether. Chlorine readily destroys the carminic acid and nascent hydrogen reduces it to a leuco body, which again becomes red on exposure to the air. Chemically it is a glucoside, being capable of decomposition into *carmine-red,* $C_{11}H_{12}O_7$, and a sugar, $C_6H_{10}O_5$.

Carminic acid dissolves in caustic alkalies with a beautiful red color, forms purple precipitates with barium, lime, lead, and copper, and a fine red lake with alumina. A decoction of cochineal behaves with reagents somewhat differently from a solution of the pure carminic acid carmine." This as well as other preparations from cochineal will be referred to again under products. (See p. 507.)

7. *Kermes* (syn. *Kermés, Alkermes*) is a corresponding substance to cochineal, and consists of the dried female insects *Coccus Ilicis,* which burrow under the epidermis of the leaves or young shoots of the kermes oak (*Quercus coccifera*), growing in the south of France, Spain, and Algeria. The coloring matter of the kermes insect has not been sufficiently investigated; it is said to be identical with that of cochineal. It is not used any longer in dyeing.

8. *Lac dye* (syn. *Färberlack*) is the product of the *Coccus Lacca,* an East Indian insect which lives on the branches of the fig and other trees. The female insects exude a resinous substance which encloses them and attaches them to the twig. This constitutes the "stick-lac" (see p. 108), which contains about ten per cent. of coloring matter. This latter may be obtained by treating the stick-lac with carbonate of soda. The coloring matter of lac dye has been studied by Schmidt, who terms it *laccainic* acid, $C_{16}H_{12}O_8$, and found it to be very similar to carminic acid in most of its reactions. Many writers consider the two to be identical.

B. YELLOW DYES.

1. *Old Fustic* (syn. *Gelbholz, Bois jaune*) is the trunk wood of *Morus tinctoria,* indigenous to the West Indies and South America. It is also yielded by the *Maclura tinctoria* and *Broussonetia tinctoria.* The wood is hard and compact and has a pale citron-yellow color. It contains two coloring principles, *morin,* or *moric acid,* $C_{15}H_{10}O_7$, which occurs in the wood combined with lime, and *maclurin,* or *moritannic acid,* $C_{13}H_{10}O_6$, both of which are yellow dyes and are contained in the commercial extract.

2. *Young Fustic* (syn. *Fisetholz, Bois de fustet*) is the bark-free wood of the *Rhus cotinus,* a variety of sumach growing in the Levant, Spain, Hungary, Tyrol, and Italy. The coloring matter is stated by Schmidt to occur as a soluble compound of *fustin* and tannic acid. This *fustin* is a glucoside, and is decomposed by dilute sulphuric acid into *fisetin,* $C_{15}H_{10}O_6$, and isodulcite. A decoction of young fustic gives a fine orange color with alkalies and bright orange precipitates with lime and baryta-water, stannous chloride and lead acetate. It also gives a fine orange color with alumina mordants. Is largely used in the dyeing of glove-leathers.

3. *Quercitron* is the crushed or rasped bark of the *Quercus nigra* or *Quercus tinctoria,* indigenous to North America, and grown also in Germany and France. It forms a brownish-yellow powder, from which an extract is also made. The coloring principle is *quercitrin,* $C_{21}H_{22}O_{12}$, a glucoside, which is decomposed by dilute sulphuric acid into *quercetin,* $C_{15}H_{10}O_7$, and isodulcite. Besides quercitin, the bark contains *quercitannic acid,* $C_{17}H_{10}O_6$. Quercitin is difficultly soluble in water, but easily soluble in alkalies with golden-yellow color. "'Flavine" is the commercial name of a preparation of quercitron obtained by

acid; it is a varying mixture of quercitrin and isodulcite, having some sixteen times the coloring power of the bark.

Flavine and quercitron bark are used chiefly for dyeing cottons and woollens with tin mordants.

4. *Persian Berries,* or *Avignon Berries* (syn. *Gelbbeeren, Graines jaunes*), are the dried fruit of different buckthorn (*Rhamnus*) species. The different commercial varieties are the Persian (from *Rhamnus amygdalinus* and *Rhamnus-cleoïdus*), coming from Aleppo and Smyrna, regarded as the richest in dye color and the best in use, the French, or Avignon (from *Rhamnus infectoria* and *Rhamnus saxatilis*), the Levantine, or Turkish (from *Rhamnus infectoria* and *Rhamnus saxatilis*), and the Spanish (from *Rhamnus saxatilis*) and the Hungarian (from *Rhamnus amygdalinus,* etc.).

The coloring matter of the Persian berries is called by Liebermann *xanthorhamnin,* or *chrysorhamnin,* and is a glucoside, yielding under the influence of dilute acids *rhamnetin,* $C_{16}H_{12}O_7$ (or methyl-quercetin, $C_{15}H_9O_7CH_3$), and isodulcite. Persian berries are used for yellows on wool and cotton with alumina or tin mordants.

5. *Weld* (syn. *Wau, Gelbkraut, Gaude*) consists of the leaves and other parts of the *Reseda luteola,* a variety of mignonette. It is cultivated in almost all parts of Europe, notably in the south of France, Germany, and England. The coloring matter is known as *luteolin,* $C_{15}H_{10}O_6$, and forms yellow crystals of silky lustre, insoluble in water, soluble in alcohol. It dissolves in alkalies with deep yellow color. It is used especially in silk-dyeing.

6. *Annatto* (syn. *Orlean,* or *Roucou*) is prepared from the fleshy pulp of the seed-shells of the *Bixa orellana,* indigenous to the West Indies and South America, but cultivated also in the East Indies. The commercial annatto forms a soft reddish-yellow paste of buttery consistency, or sometimes it is dried in hard cakes. It contains two coloring matters, *bixin,* $C_{28}H_{34}O_5$, and *orellin,* the former of which—the more important—is a red dye and the latter a yellow. The bixin dissolves in alkalies with yellow color. It is but little used in silk-dyeing. Orellin is as yet only slightly studied, and is considered by some to be simply an oxidation product of bixin. By far the largest amount of annatto is used not in dyeing but in coloring butter and cheese. (See p. 295.)

7. *Turmeric* (syn. *Gelbwurz, Curcuma*) is the tuber of the *Curcuma tinctoria* and *Curcuma rotunda.* The roots are usually grayish-yellow on the exterior but deep yellow in the interior. The plant is indigenous to Central Asia. The varieties of it are the Chinese, Java, and Bengal, of which the latter is considered the best. The coloring principle is *curcumin,* $C_{21}H_{20}O_6$, which acts like a weak acid. The pure color is bright orange-red, but it dissolves in alkalies with a red-brown color. It is seldom used as a dye, and then only for shading blacks on silk.

C. BLUE DYES.

1. *Indigo* (syn. *Indig-blau, Indigo*).—This is by far the most important of all the vegetable dyes. It has been known from very early

teenth century, where its use was at first prohibited because of the general culture of the woad, and indeed it was only in 1737 that its employment was legally permitted in France. However, in time it displaced the woad almost entirely, so that the latter is used now only in a few special cases.

The indigo-plant is an *Indigofera*, the more important varieties of which are the *Indigofera tinctoria*, cultivated in India, particularly in Bengal, Coromandel, Madras, Java, and Manila; the *Indigofera Anil*, cultivated in Guatemala, Caracas, Brazil, and the Antilles; the *Indigofera Argentea*, cultivated in Egypt, Senegal, and the Isle of France. Of lesser importance are the *Indigofera disperma* and the *Indigofera pseudotinctoria*, both cultivated in the East Indies. The *Indigofera tinctoria* is shown in Fig. 112 (see p. 489) to the left of the illustration above. The indigo dye does not exist as such in the plant but as the result of fermentation, whereby the naturally occurring *indican*, a glucoside, is decomposed, most probably according to the reaction:

$$\underset{\text{Indican.}}{2C_{26}H_{31}NO_{17}} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Indigo-blue.}}{C_{16}H_{10}N_2O_2} + \underset{\text{Indiglucin.}}{6C_6H_{10}O_6}.$$

The plants are cut at two or three different periods in the year when they have just come into bloom. They are at once packed into bundles and put into the soaking-vats covered with water. A fermentation here ensues, which is completed in from ten to eighteen hours, according to the temperature of the air and the ripeness of the plants. When the supernatant liquid has taken a yellowish-green color and has a pleasant sweetish taste, the fermentation is stopped and the liquid is run off into vats placed at a lower level. Here it is beaten vigorously with sticks or paddles for from one and a half to three hours by men who enter the vats for the purpose. The liquid is changed by this treatment to a deep-blue color and becomes covered with froth of like color. When the men leave the vat to rest, the separated indigo rapidly settles, and in some two to three hours the supernatant liquid can be run off from stopcocks placed in the side of the vat at levels above the indigo precipitate. Milk of lime is often added to hasten the settling of the separated indigo, and more recently dilute ammonia has been used. The addition of this latter reagent is said to increase the yield of indigo and to improve its quality, as it contains less indigo-brown and resinous impurities. The thin paste of indigo and water is then drawn off, boiled to prevent subsequent fermentation, and strained through a sheet. It is then put into square press-boxes lined with cloth and provided with holes in the sides and bottom for thorough drainage of the indigo. Pressure is then applied, gentle at first but stronger as the indigo hardens and acquires a firmer consistency. The mass is then cut into cubical blocks, which are stamped with the name of the factory and put on shelves in the drying-house to slowly dry out, great care being taken to avoid drafts of air, which might cause the cakes to crack in drying. Three hundred kilos of and with this two other coloring matters, indigo-brown and indigo-red, besides indigo-gluten, moisture, and a variable amount of mineral matter.

The commercial varieties of indigo are, first, the Asiatic, of which the Bengal indigo is the best, followed by the Java, Madras, Coromandel, and Manila varieties; second, the American, of which the Guatemala is the best, followed by the Caracas and the Brazilian varieties; and, third, the African, including the Egyptian, Senegal, and Isle de France varieties.

Indigo-blue is insoluble in water, alcohol, ether, dilute acids, and alkalies, soluble in fuming sulphuric acid, aniline, nitrobenzene, chloroform, and glacial acetic acid. It may be sublimed by heat, although with partial decomposition when the sublimation is carried out at ordinary atmospheric pressure. By the action of alkaline reducing agent it is changed to indigo-white, $C_{16}H_{12}N_2O_2$, and dissolved. Upon thi reaction and the subsequent change of the indigo-white, when deposite upon the textile fibre, by atmospheric oxidation back again into indigo-blue, is based the use of indigo in vat-dyeing. (See p. 536.) Indig has been extensively used for cotton and wool dyeing, but is being largel replaced by the artificial indigo.

2. *Wood* (syn. *Waid, Pastel*).—The leaves of the *Isatis tinctori* and *Isatis lusitanica* moistened, slightly fermented, and then compacte and dried into balls constitute the woad of commerce and furnish a additional source of indigo. As before stated, the use of the woad fo dyeing antedated the use of the indigo-plant, and the cultivators of th woad, particularly in Central Germany, long fought against the introduction of the richer tropical indigo-yielding material, but in vain. Th woad-culture is still carried on in different parts of Europe, particular in France and Germany, but in small degree compared with its forme development. The woad contains only .3 per cent. of indigo reckone on the weight of the fresh leaves, or as it is often calculated, one hundred kilos. of woad have the same coloring power as two kilos. of indig The woad balls improve in quality by keeping for some years, the bes variety coming from the south of France under the name of Paste The woad is rarely used by itself in dyeing operations, but along wit indigo as a means of inciting the fermentation in the " woad-vat process of dyeing.

A few other plants, such as *Polygonum tinctorium*, indigenous t China, and *Eupatorium tinctorium*, indigenous to Brazil, have bee found to contain indigo, and have been used locally for blue-dyeing.

3. *Logwood* (syn. *Blauholz, Bois de Campêche*).—This is the hear wood, freed from bark and sap-wood, of the *Hæmatoxylon Camp chianum*, a tree indigenous to Campeachy Bay, Central America, bu grown now in various parts of Central and South America and th West Indies. The commercial varieties are the Campeachy, Yucata Laguna, Honduras, Jamaica, Haiti, St. Domingo, Monte Christo, Fo Liberté, and Guadeloupe logwoods. The principal sources now a

large yield of coloring matter obtainable from it and the readiness with which it "bronzes" when submitted to the "curing" process. The wood comes in logs or sticks of smaller size, and is then chipped or rasped by the makers of extracts, who sell it in the chipped or rasped condition as well as in the form of prepared extract. The wood has a dark-red color on the exterior but is yellowish-red in the interior, has a weak odor of violets and a peculiar sweetish but astringent taste. On moistening the wood or chips with ammonia it takes a dark-violet color. Logwood contains some nine to twelve per cent. of the chromogen, *hæmatoxylin,* $C_{16}H_{14}O_6$, which is present in the wood partly in the free state but mainly as glucoside. It forms colorless prismatic crystals difficultly soluble in water, easily soluble in alcohol and ether. From the hæmatoxylin by oxidation in the presence of alkalies, and particularly ammonia, is produced *hæmatëin,* $C_{16}H_{12}O_6$, the true dye-color. This forms small crystals or crystalline scales of dark-red color and greenish metallic lustre, which show plainly upon the wood, especially after the fermentation or curing. It is difficultly soluble in water, alcohol, and ether. Hæmatëin forms a crystalline compound with ammonia, $C_{16}H_{11}(NH_4)O_6 + H_2O$, which, however, is decomposed by acids or by heating to 130° C., leaving pure hæmatëin. Zinc and sulphuric acid readily reduce the hæmatëin to hæmatoxylin again. Logwood is used on an extended scale in dyeing wool, silk, cotton, and leather. It is used for deep blues, blacks, and jointly with other coloring matters for composite shades of color.

4. *Litmus* (syn. *Lakmus, Tournesol*).—This is a dyestuff very similar in character to orseille and persio (see p. 491), and also derived from the class of lichens. For its preparation the same lichens may be used, although at present the different species of *Lecanora* serve as the chief material, such as *Lecanora orcina, L. dealbata, L. parella,* which occur in the French Pyrenees, and the *Lecanora tartarea,* occurring in Iceland and Scandinavia. The lichens are allowed to ferment after the addition of stale urine or ammonia and carbonate of potash. When the mass has assumed a deep-blue color, chalk or gypsum is added, and it is shaped into small cubes and dried. The coloring matter is *azolitmin,* $C_7H_7NO_4$, which differs by one atom of oxygen only from the orcëin of orseille extract, $C_7H_7NO_3$. It acts like a weak acid, the salts of which are blue in color (the potassium compound existing in the commercial litmus), and which when set free by acids is reddish in color.

D. GREEN DYES.

We have practically nothing here that has assumed practical value as yet. The only ones needing mention at all are:

1. *Chlorophyll.*—This is the green coloring matter of fresh vegetation, and is abundantly present in nature, but it has not been found possible hitherto to isolate it in a pure state adapted for use. Schütz has, however, separated it from the yellow coloring matter accompanying it, *xanthophyll.* It is stated that chlorophyll forms a beautiful green

2. *Lokao, or Chinese Green,* is a green pulverulent deposit from the decoction of the bark of *Rhamnus chlorophorus* and *Rhamnus utilis,* both indigenous to China. Kayser, who has investigated the lokao, states that the coloring matter is *lokaonic acid,* $C_{42}H_{48}O_{27}$, which is combined in the commercial preparation as the alumina lake. This lokaonic acid is decomposed by acids into *lokanic acid,* $C_{36}H_{36}O_{21}$, and *lokaose,* an inactive sugar. Lokao has been used for cotton- and silk-dyeing, but is practically displaced by the cheaper artificial colors.

E. Brown Dyes.

1. *Catechu* (or *Cutch*).—This has already been spoken of as one of the raw materials of the tanning industry. (See p. 359.) It finds, however, an equally extended use in dyeing as an adjective color. The explanation of this is that catechu contains two principles, *catechin,* $C_{21}H_{20}O_9 + 5H_2O$, a yellow dye forming brown precipitates with copper, alumina, and tin mordants, and *catechutannic acid,* $C_{13}H_{12}O_5$. The former is present in amount from twenty to thirty per cent., the latter, however, from forty-eight to fifty-two per cent. The best variety of catechu is the Pegu catechu, and after this the Bombay and the Bengal catechu. Catechu is extensively used in both cotton- and silk-dyeing for browns and for composite shades.

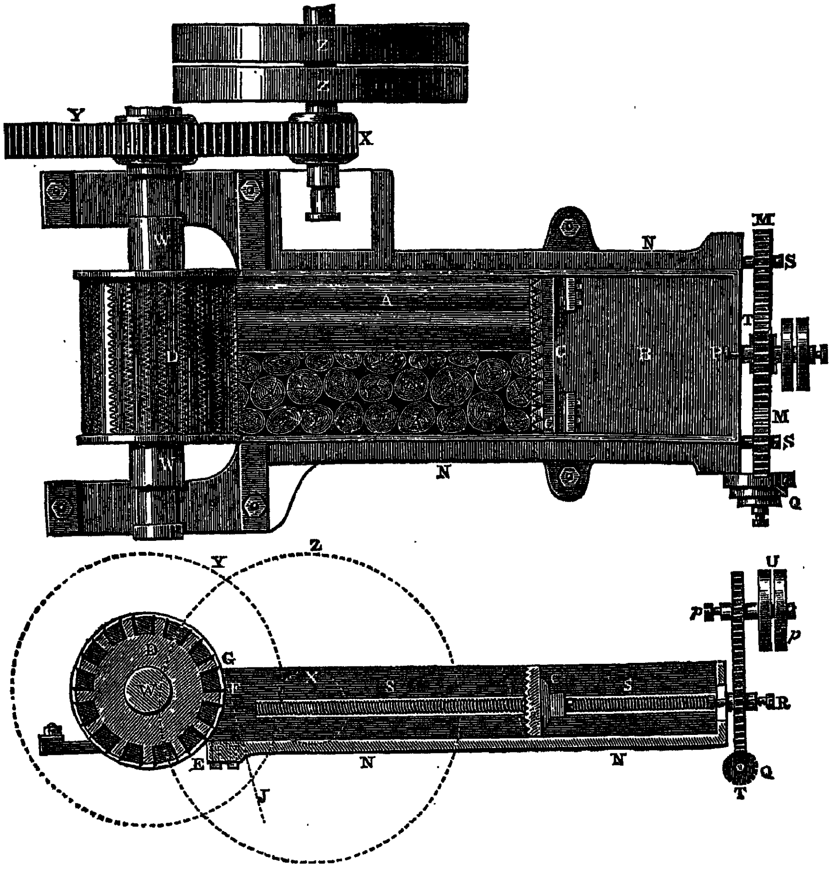
2. *Kino* is a natural dyestuff very similar to catechu and comes from a variety of sources, as *Butea frondosa* and *Butea superba,* yielding the Bengal kino; *Pterocarpus erinaceus,* yielding the West African kino; *Eucalyptus corymbosa* and other Eucalyptus species, yielding the Australian kino. The important principles are *kinoïn,* $C_{14}H_{12}O_6$, and its anhydride, *kino-red,* $C_{28}H_{22}O_{11}$. It is used like catechu for dyeing.

II. Processes of Treatment.

1. Cutting of Dye-woods.—Whether the dye-woods are to be used for the manufacture of extracts or used as wood by the dyer, they must be reduced to powder or cut into chips of small size. This process varies with different manufacturers. In America, it is usually one of cutting with powerful knives, in which whole logs are brought with their ends against rapidly-revolving cylinders, on the circumference of which are heavy steel knives, which cut off flat chips directly across the grain about one-eighth inch in thickness. This method is a very rapid one, as but little previous splitting of the logs is necessary. In Europe, where labor is cheaper, the logs are frequently sawed and split into billets about two feet long, and two to three inches in thickness, and these are then brought by hand diagonally against toothed knives on a rapidly-revolving cylinder, by which means the wood is torn or rasped into a much finer condition, or these billets are put into a machine which presses them in this way against the revolving knives. Such a machine of German design is shown in Fig. 113, where a rotating drum, *D*, carrying on its circumference a series of knife-blades, is continuously cutting

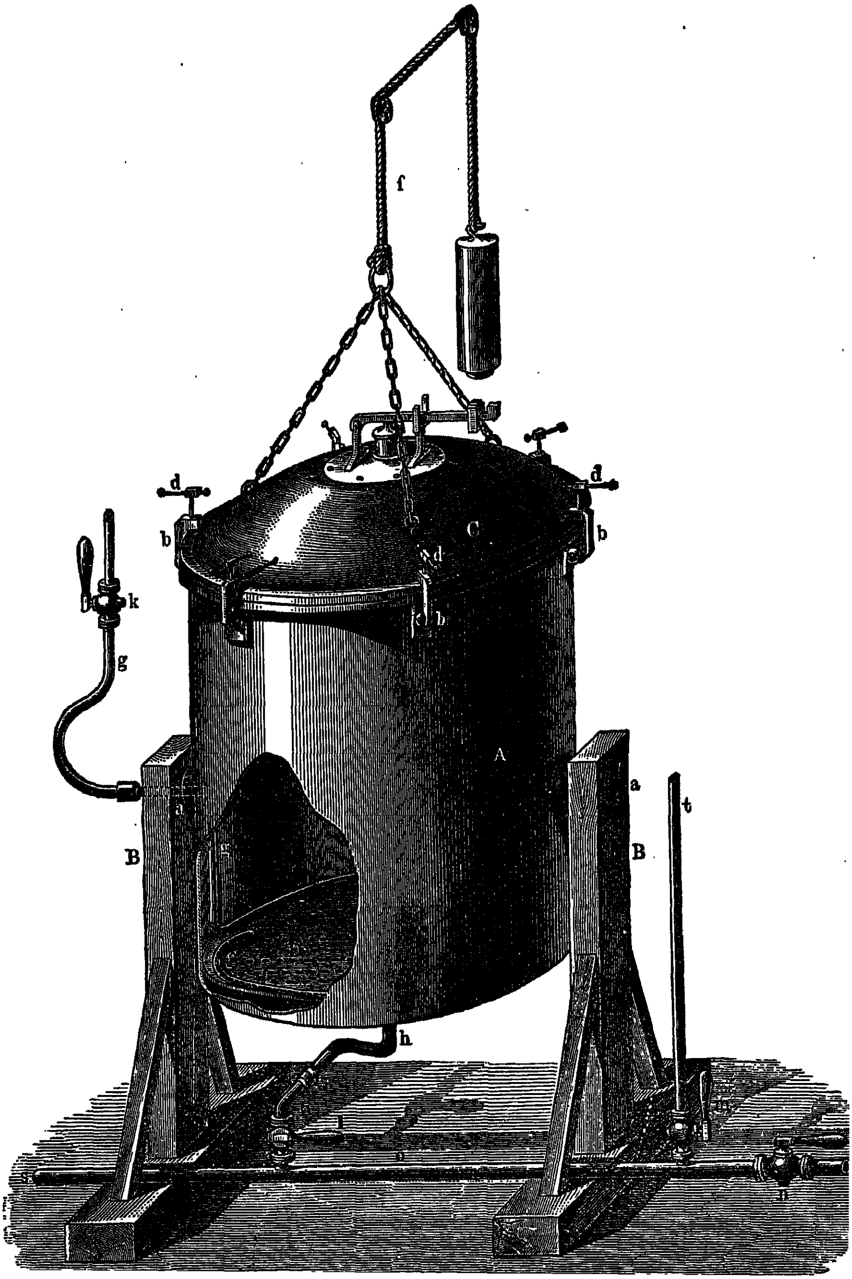
2. Fermentation or Curing of Dye-woods.—As has already been stated in several cases, the dye-woods in the fresh condition contain not the finished dye-color, but a chromogen capable of passing into the former under the influence of oxidizing or other agents. Notably is this the case with logwood, and the chips or rasped wood are therefore submitted to a curing treatment by moistening them with water and exposing them to the air in heaps some three feet in depth for from four to six weeks. The chips heat up, and the pile must then be turned with shovels to regulate the temperature and allow contact with the air. More water is then added, and the process continued until the chips assume a rich reddish-brown color or become coated with a bronze powder (hæmatëin). Various chemicals have been suggested to hasten the operation, such as ammonium carbonate and chloride, stale urine, sodium carbonate, potassium nitrate, chalk, and glue. None of these are known certainly to be of benefit. The alkalies give the chips a fine red color at first, but unless great care is taken they cause them to become black from

Fig. 113.



over-oxidation before the action can be checked. Glue has been used because it is said to combine with the tannin of the wood, and by remov-

Fig. 114.



ing it to open up the pores of the wood to the oxidizing influence and so facilitate the curing. But the existence of tannin in logwood has not been at all certainly established.

Curing is of value to the dyer because it enables him to rapidly obtain the color from the chips and gives him a liquor containing a more highly oxidized coloring matter, which "goes on" the goods more rapidly. It must be remembered, however, that curing the chips enables the manufacturer to sell twenty to thirty per cent. of water with them, while uncured chips contain only ten to fifteen per cent. of moisture.

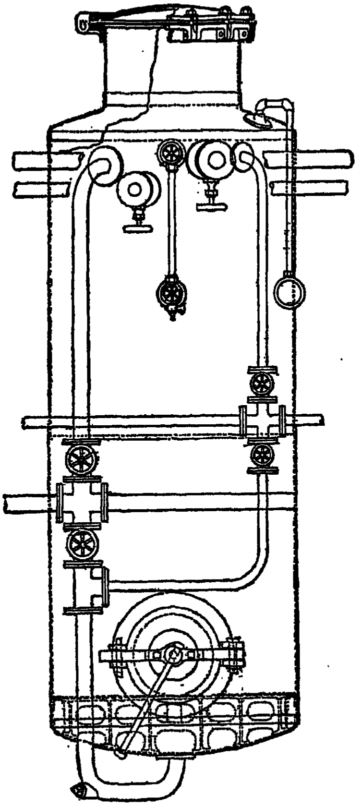
When the chipped logwood is intended for the manufacture of extract it is usually conveyed directly to the extractors without curing, which is, no doubt, the better procedure, since all oxidation in the first part of the process is objectionable.

3. Manufacture of Dye-wood Extracts.—As dye-woods contain generally only a tenth or less of their weight of dye-color, it becomes a matter of great economy in transportation and storage to prepare from them extracts, either as concentrated liquids or solids representing the active coloring principle. This is done by manufacturers who make a specialty of this extracting, and apply to it the best designed and most improved machinery.

The operation may be divided into two stages,—the extraction and the concentration. For extraction a rasped wood such as is made in France has many advantages over the chipped, since it yields its coloring to a smaller quantity of water and at a lower temperature than the chips. The extraction consists in heating the wood with water under various conditions and then drawing off the liquor into tanks for settling or treatment. The conditions refer to the kind of vessels, the amount and quality of the water, and the temperature. Many European manufacturers use open wooden vessels for extractors, so that the temperature does not get above 100° C. As this method was first used in France, it is known as the French process. The use of closed extractors, however, allows of increase in the pressure, and this within limits much facilitates the perfect extraction. A closed extractor of German design, in which a pressure not exceeding two atmospheres is used, is shown in Fig. 114. (See preceding page.) It will be seen that the vessel, *A*, is provided with a false bottom, *D*, to allow of the draining off the extract liquor, a perforated steam-pipe, *g*, to rapidly bring up the contents of the extractor to the required temperature, and a drainage-pipe, *h*, to draw off the thin extraction liquors.

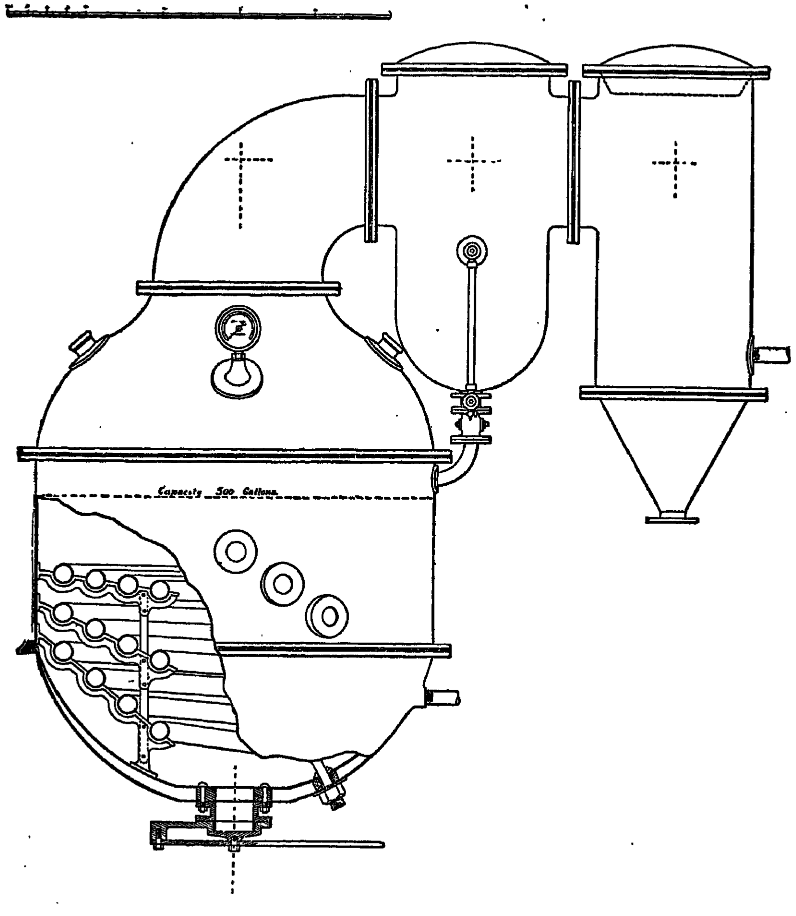
In America closed copper or iron vessels are used, arranged in battery form very much like the diffusion apparatus now used in the extraction of sugar. One cell of such an extraction battery is shown in Fig. 115. This method allows of continuous working, as one cell of the series can be emptied of exhausted dye-wood and loaded with fresh chips while the extraction liquors are passing successively through the other cells of the battery and acquiring the maximum strength. The temperature or pressure varies with different manufacturers, but most writers on the subject agree that a pressure not exceeding fifteen to twenty pounds excess over atmospheric pressure should be used. An increase in the pressure is always attended with an increase in the yield, and after a certain point with a decrease in the coloring value of the resulting extract. When the liquors from the extractors are run into large tanks and allowed to cool much wood-fibre and some resinous matter separates. The clear liquor is then drawn into the evaporators, which in this country almost invariably consist of vacuum-pans, but in Europe often consist of open pans or vessels in which heated disks revolve so as to favor the evaporation. While the liquor is still thin, double- or triple-effect pans are used, and of recent years the Yaryan evaporators (see Fig. 38, p. 144) have been applied with great success to the evaporation of dye-wood extracts. As the liquors become thicker the concentration is continued in vacuum-pans more analogous to the strike-pans of the sugar refinery. Such a vacuum-pan designed for use in the manufacture of dye-wood extracts is shown in Fig. 116. When the gravity of the liquid becomes 42° or 51° Tw., it is drawn off into barrels for shipment, or if the solid extract is desired the concentration is continued in a vacuum-pan.

Fig. 115.



Various methods of treatment have been suggested at different stages of the process with a view of improving the extract, but it is an open question whether anything better than pure water has yet been used. The addition of solutions of glue and of different salts to the wood before extraction has been frequently recommended. Chalk suspended in water and dilute limewater have also been recommended to be similarly used. Such processes could only result in an over-oxidized product. Borax has also been used, but without notable advantage in the case of logwood, although it serves very well in the case of the redwoods. The use of chlorine, hypochlorites, and chlorates has been patented in connection with logwood extract for addition either to the wood or the liquor after extraction, but it is doubtful if any of these are used on a large scale at the present time. That these substances and many others develop the color of logwood there can be no question, but to be of value to the dyer that development must take place in ture is said by Soxhlet* to be twenty or twenty-one per cent. of solid extract, while that by the French process is sixteen and a half per cent. The latter is superior in quality, and is therefore almost invariably reduced by the addition of such substances as molasses, glucose, and extract of chestnut. In America, in addition to the above, extract of hemlock and extract of quercitron (after the removal of the flavine) are considerably used to adulterate logwood extract.

FIG. 116.



4. MISCELLANEOUS PROCESSES.—(*a*) *Preparation of Guarancine and Madder Flowers.*—For the preparation of guarancine, the pulverized madder-root is warmed gently with dilute sulphuric acid (one part acid and two parts water) for some time, whereby the glucosides of the madder are decomposed. The sugary liquid is drained off and the resi-

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* Textile Colorist, viii, p. 125.

due heated with concentrated sulphuric acid, which decomposes the woody fibre and other organic substances present and decomposes any lime compounds that may have been in the madder. The whole mixture is now thrown into water, the precipitate collected, washed, and dried. The guarancine now contains the alizarin and purpurin in uncombined form. The yield is from thirty-four to thirty-seven per cent. For the preparation of "madder flowers" the powdered madder is set to ferment with warm water to which a little dilute sulphuric acid had been added. After some days, the liquid is filtered and the residue washed, pressed, and dried. The flowers of madder can be used more readily than crude madder in dyeing at low temperatures, and give finer and purer violets.

(*b*) *Preparation of Ammoniacal Cochineal and Carmine.*—Five parts of powdered cochineal are mixed with fifteen parts of ammonia-water, and the mixture is allowed to stand in a warm place with frequent stirring for some four weeks. Some two parts of alumina are then added, and the mixture carefully evaporated in a porcelain dish until the odor of ammonia has disappeared. The preparation so obtained, known as ammoniacal cochineal, yields its color more readily than cochineal and produces brighter shades of color.

Cochineal-carmine is a brilliant red pigment prepared from decoction of cochineal by the action of alum under certain conditions. The details of its preparation vary and are kept by different manufacturers as trade secrets. The following process has been published:* Five hundred grammes of finely-powdered cochineal are boiled for one-quarter of an hour with thirty times the weight of distilled water, thirty grammes of acid tartrate of potassium added, boiled for ten minutes longer, fifteen grammes of alum added and boiled for two minutes longer. The clear liquid is allowed to stand in shallow glass vessels, when the carmine separates in a very fine state. It is washed with water and dried in the shade. Or, by another process,† one pound of cochineal and one-half ounce of potassium carbonate are boiled with seven gallons of water for fifteen minutes. The heat having been withdrawn, one ounce of powdered alum is added, and the liquid stirred and allowed to settle. The clear liquid is decanted, one-half ounce of isinglass added, and heat applied until a coagulum forms, when the liquid is briskly stirred and allowed to settle.

(*c*) *Preparation of Flavine.*—As stated before (see p. 492), flavine is a preparation containing the coloring matter of the quercitron bark in purer and more concentrated form. The method for its preparation is not generally known, although it is found to contain quercetin as well as quercitrin, and frequently the former in larger amount.

A procedure that has been published ‡ is the following: Two hun-

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* Schützenberger, Die Farbstoffe, ii, p. 338.

† Allen, Commercial Organic Analysis, 2d ed., iii, p. 367.

‡ Gerb- und Farbstoffe-Extracte. Mierzinski. p. 208.

dred and fifty kilos. of the powdered quercitron are boiled for fifteen minutes with fifteen kilos. of crystallized soda and two hundred kilos. of water, there is then added to the liquid sixty-one kilos. of sulphuric acid of 66° B., and the boiling continued for three-quarters of an hour longer, when the whole is allowed to cool and settle, the liquid poured off, and the separated color drained and dried.

(*d*) *Preparation of Indigo-carmine, Soluble Indigo, etc.*—It was stated in an earlier section (see p. 495) that indigo-blue was soluble in strong sulphuric acid. The solubility depends, however, upon the chemical action of the acid, whereby sulphonic acids of indigo are formed. Two such acids, indigo-monosulphonic acid (sulpho-purpuric acid), $C_{16}H_9(HSO_3)N_2O_2$, and indigo-disulphonic acid (sulphindigotic acid), $C_{16}H_8(HSO_3)_2N_2O_2$, are formed. Of these, the first is insoluble in water or dilute acids, while the second is soluble with deep-blue color. Both are formed together in practice when indigo is dissolved in strong sulphuric acid, although if not more than four parts of sulphuric acid to one of indigo be used and too prolonged heating be avoided, the monosulphonic acid will be formed predominantly, while if some fifteen parts of ordinary concentrated sulphuric acid or seven parts of fuming sulphuric acid be taken to one of indigo and the heating be continued, the disulphonic acid will be the sole product. After treatment with the acid the dissolved mass of indigo is allowed to cool down and then strained to remove any lumps that may have escaped grinding; salt is thrown in, which precipitates the indigo-sulphonic acids, which are removed by filtration through felt. For finer grades of "indigo extract" the precipitate is redissolved in water and reprecipitated with salt several times, each precipitation removing a greater quantity of the objectionable green coloring-matter. Whatever be the process or proportion of acid used, the indigo must be very finely ground. This is done in indigo-mills, which are of various forms, known as "ball-mills," in which rotating cannon-balls gradually grind the color, as "cylinder-mills," in which heavy iron rolls accomplish the same work, and other forms. An illustration of such an indigo-mill with conical rolls, taken from a form in current use, is shown in Fig. 117. Indigo grinding for "extract" making is of little importance since the introduction of dry synthetic indigo. The direct use for dyeing of the product obtained by the action of sulphuric acid upon indigo is no longer common. The preparation and sale by the color manufacturers of pure preparations, known as *Indigo Extract, Soluble Indigo*, or *Indigo-carmine*, has replaced them. The sodium salt of the monosulphonic acid constitutes "indigo-purple" or "red indigo-carmine," the sodium salt of the disulphonic acid the true "indigo-carmine," which comes into commerce in paste form under that name or as a dry powder known as "Indigotin."

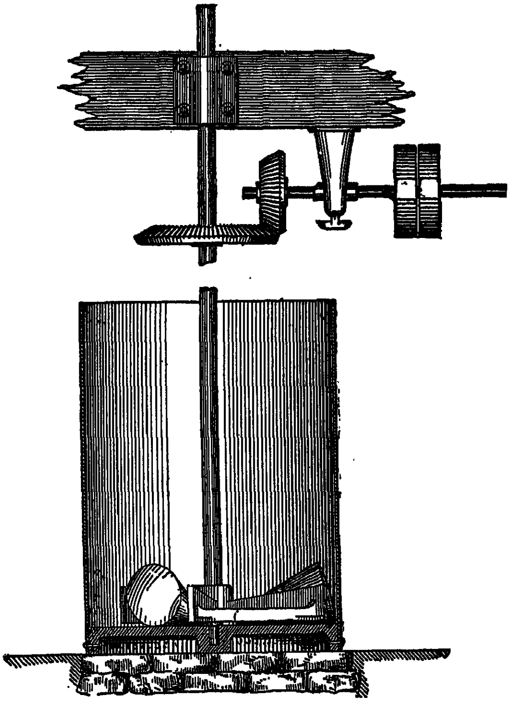
This indigo-disulphonic acid fixes itself on the animal fibre like other acid colors, and is dyed in an acid bath containing sulphuric acid

III. Products.

1. From Red Dyestuffs.—(*a*) *Brazil-wood Extracts* are made by the diffusion process, three varieties coming into commerce,—a liquid extract of 20° B., a liquid one of 30° B., and a solid one. One kilo. of the dry extract corresponds on the average to twelve kilos. of the wood. *Brasilin* is also manufactured on a large scale almost pure by Geigy, of Basle.

This brasilin often separates in the form of a crystalline crust on the surface of the commercial extract liquors. These crusts contain the brasilin mixed with the lime compound of the same. If this crude product is boiled with very dilute alcohol with the addition of zinc dust and hydrochloric acid, and the solution stood aside to crystallize, a very pure product is obtained.

Fig. 117.



Brasilin is relatively easily soluble in water, alcohol, and ether. In alkalies it is soluble with carmine-red color. Zinc dust will decolorize the solution, but on exposure to the air it speedily takes up the red color again. Acetate of lead precipitates a colorless crystalline compound which gradually turns red. Brasilëin bears the same relation to brasilin that hæmatëin bears to hæmatoxylin, and can be prepared by the oxidation of the alkaline solution of brasilin in the air.

but inferior in character. On wool mordanted with bichromate of potash they produce a fine brown.

The insolubility of the coloring matters in sandal-wood prevents their being used in the form of extracts.

(*b*) *Madder Preparations.*—We have already referred to *Guarancine* and *Flowers of Madder. Guaranceux* is the name applied to the impure purpurin recovered from the sediment of the waste-liquors in madder-dyeing.

Pincoffin (*Alizarine commerciale*) is a preparation from guarancine, in which the purpurin has been decomposed by superheated steam, leaving the alizarin unchanged. It has twenty-five per cent. less coloring power than the guarancine, but gives finer violets than can be obtained with the former.

(*c*) *Safflower Preparations.*—These are practically more or less pure preparations of carthamin, and the names *Safflower Extract, Safflower-carmine, Safflower-red,* and *Plate-red* refer to different concentrations of the carthamin solution. For the preparation of the pure safflower-red, the safflower-yellow must be removed by washing the crushed flowers with water until this runs off colorless. The residue is then treated with water and fifteen per cent. of its weight of crystallized soda salt. The solution is strained from the residue, filtered, and after acidulating with acetic or citric acid, cotton yarn is immersed in it to take up the color. The dyed cotton is stripped of the color by a five per cent. soda solution, and from this solution the color is again precipitated by citric acid. It is now drained, and comes into commerce as a paste known as "Safflower Extract." The color must be kept in sealed flasks, protected from the light. This paste dried upon plates at a gentle heat yields the so-called "plate-red." It then forms a red powder with greenish reflex, almost insoluble in water and ether, but easily soluble in alcohol. It is also soluble in alkalies with yellowish-red color. The "safflower-carmine," on the other hand, is prepared from the extract paste by washing the insoluble color and dissolving it in alcohol, which is then left to slowly evaporate. For dyeing purposes the safflower-carmine is dissolved by addition of soda, and the bath is then made slightly acid with citric acid; or the soda-extraction liquors from the flowers, which have been washed with water, may be used directly, acidifying the bath as before. Safflower-red is fixed in a weak acid bath both upon the animal fibre and upon the unmordanted cotton. On silk it produces a fine rose-red color.

(*d*) *Orseille Preparations.*—These come into commerce both as paste and liquor. The solid matter consists essentially of the impure orcëin in combination with ammonia. It is liable to be adulterated with the spent weeds from the manufacture of the orseille liquor or with other vegetable coloring matters. It is also at times adulterated with aniline dyes, such as magenta, acid magenta, and methyl violet. Various azo dyes, producing colors ranging from crimson to claret-red, are now sold as substitutes for the orseille extract, and, being cheaper, are used to adulterate it. These are known as "orchil extract," "orchil-red," "orselline," etc. They may be detected when so admixed by their behavior with salt solution and basic acetate of lead. The liquid extract is usually brought to 25° B., and is frequently adulterated with logwood or Brazil-wood extract. *Orseille Purple* (French Purple) is a pure orseille dye, obtained by extraction of the lichens with a fifteen per cent. ammonia solution, precipitation with hydrochloric or sulphuric acid, and redissolving in ammonia. This solution is then left exposed to the air in shallow vessels until it becomes dark purplish-violet. The color is then precipitated by addition of sulphuric acid, washed, and dried. *Orseille Carmine* is a similar preparation, in which the ammoniacal solution, after exposure to the air until it becomes cherry-red, is heated with alum or calcium chloride. *Cudbear,* or *Persio,* as before stated, is a dry powder obtained by evaporation of the extract, or prepared direct from the lichens by the action of ammonia or urine and then evaporated to the condition of a powder. It is often adulterated with common salt and other mineral matters, and is liable to much the same organic impurities or adulterants as orseille.

(*e*) *Cochineal Preparations.*—Ammoniacal cochineal and cochineal-carmine have already been referred to. *Ammoniacal Cochineal* is distinguished from carminic acid by giving a purple precipitate (instead of scarlet) with oxymuriate of tin. The crimson, purple, and mauve colors it yields with mordants are not affected by acids so readily as those produced directly by cochineal. Ammoniacal cochineal is used in admixture with ordinary cochineal for producing the bluer shades of pink. *Cochineal-carmine* requires for its production a decoction of cochineal itself and not of carminic acid, the nitrogenized matters being essential to its formation. Liebermann,* who has investigated carefully the nature of the cochineal coloring matter, found it to contain 3.7 per cent. of nitrogen, of which only .25 per cent. could be expelled by boiling with dilute alkali, the remainder existing apparently as proteids. He gives the following as the composition of the commercial sample of carmine examined by him: Water, seventeen per cent.; nitrogenous matter, twenty per cent.; ash, seven per cent.; coloring matter, fifty-six per cent.; wax, traces. Liebermann considers cochineal-carmine to be no ordinary compound of a coloring matter with alumina, but as an alumina-albuminate of the carmine coloring matter, comparable in some respects to the product from alizarin and alumina with "Turkey-red oil." Carmine forms red, porous, relatively light masses, which are easily rubbed up to a fine red powder. It is insoluble in water and alcohol, but readily soluble, when pure, in aqueous ammonia. Cochineal-carmine is liable to adulteration with starch, kaolin, vermilion, red-lead, chrome-red, etc. These admixtures may be detected by treating the sample with dilute ammonia, in which a pure sample should be completely and readily soluble.

M. Dechan † has published a series of analyses of commercial carmine, which are here given:

		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Moisture		22.1	16.1	2.0	22.3	20.2	23.5	8.5	10.0	21.2	13.0
Soluble in ether.	Coloring matter	46.1	69.2	34.1	65.7	60.8	69.5	26.1	72.0	18.4	67.5
	Alumina, lime, etc.	8.0	9.8	11.4	12.0	9.0	7.0	0.4	8.1	4.4	10.0
Insoluble in ether.	Organic matter	21.8	2.5	18.5	. . .	9.8	. . .	. . .	8.0	52.4	9.5
	Ash	2.0	2.4	34.0	Trace.	0.2	Trace.	14.6	1.9	3.6	Trace.
	Vermilion	. . .	. . .	. . .	. . .	. . .	. . .	50.4	. . .	. . .	. . .

Cochineal is not used in cotton-dyeing. In dyeing silk it has also been almost entirely superseded by aniline reds, and in wool-dyeing the azo colors have to a great extent replaced it. Two distinct shades of red are obtained with cochineal, according to the mordant used,—*cochineal-crimson* with cream of tartar and alum, and *cochineal-scarlet* with stannous chloride and cream of tartar or oxalic acid.

2. FROM YELLOW DYESTUFFS.—(*a*) *Old Fustic Extracts.*—Both a liquid extract of about 20° B. and a solid extract have been prepared. The latter forms large yellowish-brown blocks of a waxy lustre, which dissolve in water with yellow color. They are prepared from the wood by diffusion. The name *morin* has been given to a commercial product obtained by boiling the rasped wood with a two per cent. soda solution and evaporating the solution so obtained to a specific gravity of 1.041, when on cooling the morin and moritannic acid separate out.

(*b*) *Quercitron Extracts, etc.*—Both liquid and solid extracts are used commercially. The former of 20° and 30° B. respectively, and the latter as a dark-brown mass of waxy lustre. The extracts contain, as a rule, mixtures of quercitrin and quercetin. *Flavine* has already been referred to. It is a preparation in which the quercitrin of the bark has been extracted, and in large part changed by subsequent treatment with sulphuric acid into quercetin, which is superior in coloring power. The tannic acid of the bark extract has also been removed and the lime salts, so that it gives much purer colors than the original extract. Flavine is largely used in connection with cochineal or lac-dye for producing scarlet. A quercitron extract to which stannite of soda or sulphate of zinc has been added is said to be used under the name of "Fustic Substitute." It can be told from genuine extract of fustic by the test with ferric chloride, which produces a brown precipitate, turning olive-green with fustic, but a greenish-black with quercitron extract.

(*c*) *Persian Berries.*—A thick extract is prepared from Persian berries, soluble in water with yellow color shading into brown. The solution becomes clearer on addition of hydrochloric or nitric acids and deposits a dirty-yellow precipitate. Ammonia or caustic soda colors it a reddish-yellow, stannous chloride gives at once, and stannic chloride after the addition of carbonate of soda, a golden-yellow precipitate, iron salts a dark olive-green to greenish-black color.

3. FROM BLUE DYESTUFFS.—(*a*) *Commercial Indigo* occurs in lumps or fragments of a deep-blue color, usually showing a bronze or purple-red streak when rubbed with any hard substance, or in the case of the better kinds with the friction of the thumb only. The fracture of indigo is dull and earthy, it sticks to the tongue, is odorless and tasteless. The

specific gravity varies from 1.324 to 1.455. Helen Cooley * has given the following determinations of indigotin, ash, and specific gravity in a number of samples of commercial indigo:

DESCRIPTION.	Specific gravity.	Ash.	Indigotin.
Kurpah blue	1.129	17.54	55.11
Watson's best	1.292	6.50	59.53
Bengal red	1.391	6.41	54.03
Oude	1.427	7.02	52.90
Bengal blue	1.431	7.50	57.60
Kurpah red	1.529	21.20	45.28
Guatemala	1.559	14.49	47.04

Indigo preparations have been referred to under processes (see p. 504), and it was then noted that the salts of the indigo-sulphonic acids constituted the several so-called indigo extracts. *Indigo-carmine* is the potassium or sodium sulphindigotate ($C_{16}H_8(SO_3K)_2N_2O_2$). It comes into commerce in both paste and solid form. It is soluble in one hundred and forty parts of cold water, readily soluble in dilute sulphuric acid. It dyes animal fibres direct, but with a much lighter shade than indigo, and is not at all so fast to light, while to vegetable fibres it shows no affinity. An analysis of the several grades of carmine-paste by Mierzinski † gave:

DESCRIPTION.	Water.	Indigo.	Salt.
Carmine I.	89.0	4.96	5.7
Carmine II.	85.0	10.02	4.8
Carmine III.	73.7	12.04	13.9

Saxony Blue (*Chemic Blue*) is the free sulphindigotic acid, $C_{16}H_8N_2O_2(SO_3H)_2$, and forms a deep-blue solution. It is prepared as in the making of indigo-carmine, except the acid is not saturated with alkali. It was largely used in dyeing wool, but is not adapted for silk. *Indigo-purple* is a reddish-violet powder, which mixed with varying amounts of orseille can be used for dyeing wool directly without mordants. For its preparation, powdered indigo is covered with ordinary (not fuming) sulphuric acid, and having been cooled is left for half an hour. In this way is obtained a blue solution of sulphindigotic (indigo-disulphonic) acid, which can be worked up into indigo-carmine and a violet powder. This latter is the monosulphonic acid, which is washed first with water and then with dilute soda solution until the washings are no longer acid, then dried for use as above. A product of analogous composition, known as *Boiley's Blue*, is prepared by gradually adding one part of finely-powdered indigo to ten or twenty parts of acid sodium sulphate, $HNaSO_4$, in a state of fusion. The product is dissolved in water, precipitated with common salt, and washed with brine. Boiley's blue is a crystalline light-purplish mass, soluble in water with beautiful blue-violet color. Its solution in strong boiling acetic acid deposits on cool-

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ing large prismatic crystals exhibiting a coppery reflection. It is insoluble in alcohol or ether, but readily soluble in hot water. The light transmitted by the solution is red. With barium and strontium salts it yields violet precipitates.

The fact that indigo had been obtained artificially by several different methods was mentioned under the artificial dye-colors. (See p. 465.) A synthesis of indigo-carmine has also been effected within recent years. The process, due to B. Heymann,[*] is as follows: One part of phenyl-glycocoll ($C_6H_5.NHCH_2.COOH$) is rubbed up with ten to twenty times its volume of clean sand (which simply acts in the way of reducing the temperature of the reaction), and slowly added to fuming sulphuric acid, with eighty per cent. anhydride strength, warmed to 20° to 25° C. Care is to be taken that the temperature does not thereby exceed 30° C. After the solution of the phenyl-glycocoll, which takes place with evolution of sulphurous oxide, concentrated sulphuric acid of 66° B. is added to remove the excess of anhydride. It is then diluted with ice and common salt added, when indigo-carmine (indigo-disulphonic acid) at once separates out. Experiments on dyeing with the new product show it to be better and purer than the commercial indigo-carmine. Its identity was established in a number of ways. The yield amounts to sixty per cent. of the theoretical, but this may be improved by further study of the conditions of the reaction.

(*b*) *From Logwood.—Logwood Extracts* are prepared as liquids of 12°, 42°, and 51° Tw. (for equivalents of the Beaumé scale, see Appendix) and as a solid. This latter forms a dry black, lustrous and resin-like mass, which is quite brittle and easily powdered, taste sweetish astringent, and yields a reddish-brown solution. The specific gravity ranges from 1.45 to 1.51. The specific gravity is not a reliable indication of the strength of the fluid extract, as it is liable to be raised by the addition of salt, glucose, molasses, etc. The extracts are also sometimes adulterated with starch, dextrin, chestnut-bark extract, hemlock extract, etc. The following table by Brühl [†] gives the yields of extracts ob-

Description of Wood.	Yield of extract.	Soluble in ether.	Soluble in absolute alcohol.	Residue.
Yucatan	20.20	60.12	37.46	2.42
Yucatan, E. J.	17.34	58.34	38.51	3.15
Laguna	21.00	51.37	47.95	0.68
St. Domingo	14.02	44.95	53.47	1.58
St. Domingo, O.	19.30	43.81	50.32	5.87
Monte-Christo, 1884	18.75	32.00	60.32	7.68
Monte Christo, 1887	14.00	34.72	54.10	11.18
Fort Liberté, 1886	20.33	41.89	54.11	4.00
Fort Liberté, 1887	16.00	50.00	47.92	2.08
Fort Liberté, 1885–86	17.45	59.72	35.17	5.21
Fort Liberté, J. B., 1887	18.00	59.24	34.81	5.95
Jamaica	18.70	43.20	50.50	6.30
Jamaica	18.00	43.05	50.71	6.24
Jamaica wood roots	10.70	52.99	30.12	16.89

tained by himself from different woods and the percentage solubility of the resulting extracts in ether and alcohol. The portion dissolved by ether represents roughly the hæmatoxylin percentage, while that dissolved by absolute alcohol represents the hæmatëin and decomposition products of the hæmatoxylin.

Indigo Substitute (*Noir imperial,* or *Kaiserschwarz*).—Under these names are known oxidized logwood extracts, made by boiling logwood extract with copper, iron, or chromium salts with the addition of oxalic acid. They may be in liquid form, or pastes, or dry powders. The preparations are almost insoluble in water, but completely soluble in acids with yellowish-brown color. A commercial preparation of this class, known as "direct black," for cotton forms a brownish, viscid liquid, composed of fifty per cent. water, forty-five per cent. of a substance soluble in alcohol and ether (hæmatoxylin and hæmatëin), and 3.5 per cent. of copper sulphate. *Hœmatëin* (*Hématin*) is a commercial preparation of French origin, which claims to consist of nearly pure dyestuff. It forms a granular, reddish-brown powder, completely soluble in water, and dyes the same shades as those obtained from the wood. Fifteen kilos. of hæmatëin are said to be equivalent to one hundred kilos. of the logwood. *Hematine crystals* is a solid logwood extract made porous by the addition of nitrite of sodium just before solidifying.

(*c*) *Litmus,* as has been said, is a mixture of the lichen dye of that name with chalk or gypsum as inert material. It is made in different numbered grades, containing different amounts of the mineral matter. Litmus in the dry form has a violet-blue color, is quite friable, and dissolves in water and dilute alcohol, leaving a residue of chalk, gypsum, alumina, silica, etc.

4. FROM BROWN DYES.—(*a*) *Catechu* has been described already in part under the raw materials of the tanning industry. (See p. 359.) It is not unfrequently adulterated with starch, sand, clay, and blood. Good catechu should yield at least half its weight to ether and should be entirely soluble in boiling water, the latter solution depositing catechu on cooling. Catechu does not wholly dissolve in cold water unless it has been previously modified by age or exposure to damp. It should not yield more than five per cent. of ash. *Prepared Catechu* has been merely purified by mechanical means. For this purpose, the commercial catechu is fused on the water-bath, whereby sand, earth, and similar impurities settle out, and then it is strained to remove leaves, etc. The material so obtained is again melted on the water-bath, and to every one hundred parts of the catechu three-fourths per cent. of potassium bichromate is added, when it is allowed to cool down again.

IV. Analytical Tests and Methods.

1. FOR DYE-WOODS.—Here the question of adulteration does not come notably in play. The compact woods are not capable of much adulteration of any kind. When chipped or rasped, however, they may be adulterated quite considerably. The examination with the microscope or

A special case of cheapening is that of the cured or fermented logwood chips, which, as has already been stated, may take up as the result of this fermentative process as much as thirty to forty per cent. of water. In this case a moisture determination will show the change, allowance being made for the fourteen per cent., which is the average moisture of the unfermented wood.

To determine the comparative dyeing value of different samples of woods, the only thoroughly reliable test is an actual dyeing test made with definite weights of the wood, thoroughly extracted, and using definite amounts of mordants upon the wool or other fibre used. This test, as applied to logwood, for example, would be carried out as follows: Ten gramme portions of clean wool are separately mordanted for 1½ hours at the boil with 3 per cent. of potassium bichromate and 2½ per cent. of cream of tartar, washed, and dyed for 1 hour at the boil in the logwood bath, containing a definite amount of decoction or extract of each sample to be tested, afterwards washing and dyeing for the final comparison of shade. This method of logwood assay takes cognizance both of the actual and the potential coloring matter present (hæmatëin and hæmatoxylin), and is a more rational method of examination than any based on the color produced on cotton mordanted with alumina or tin salts. The dye test in other cases must be made upon a normal prepared extract of known strength and purity, and the result compared with those obtained with a corresponding weight of the supposed adulterated sample.

2. For Dye-wood and other Extracts.—(*a*) *Orseille Extract.*—This may be adulterated with logwood or Brazil-wood extract. They may be detected, according to Leeshing, as follows: A solution of orseille extract, much diluted and acidified with acetic acid, will, if pure, when boiled with a freshly prepared solution of stannous chloride, become pale yellow or almost colorless, while logwood extract solution under similar circumstances will show a violet color and Brazil-wood solution a red color. If, therefore, the orseille is adulterated with logwood extract a permanent grayish-blue color will show, if with Brazil-wood extract, a reddish color.

Orseille is also found frequently to have been adulterated with aniline dyes, especially magenta, acid magenta, and methyl violet. For the detection of magenta and methyl violet Knecht* employs cotton yarn dyed with chrysamin (p. 464). This does not take up the coloring matter of the orseille, but is dyed red by magenta and brownish-red by methyl violet. To detect the acid magenta, Kertesz† treats the orseille preparation with benzaldehyde and adds to the solution tin salt and hydrochloric acid, shaking up the mixture thoroughly. If acid magenta was present a red color will remain, while with pure orseille the solution remains colorless. One part of acid magenta in one thousand parts of orseille it is said can be thus detected. For other tests for the artificial dye-colors when present as adulterants in orseille,

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see Allen, "Commercial Organic Analysis," 2d ed., iii, pp. 322 and 323.

(*b*) *Quercitron Extracts.*—The dyeing value of the extract, as well as a possible adulteration of the same with dextrine, glue, etc., can be best determined by an actual dye test. For this purpose, wool is boiled with 1.5 per cent. of tin salt and three per cent. of oxalic acid, then washed. One gramme of the wool is now dyed with twenty cubic centimetres of a solution of ten grammes of the quercitron extract in one thousand cubic centimetres of water. Similarly several portions of one gramme each of mordanted wool are dyed with solutions of pure bark or pure extract of definite strength, and the results compared.

(*c*) *Annatto* (*Orlean*).—Annatto possesses only a slight importance as a dyeing agent, but special importance as the basis of most butter colorings. (See p. 299.) It is, therefore, a commercial article of common use and liable to be adulterated. The common adulterants are starch, dextrine, chalk, silica, alumina compounds and common salt, together with ochre, brick-dust. Most of these increase notably the percentage of ash, which in a pure sample it is said should not exceed ten to twelve per cent. Wynter Blyth gives the following two analyses as illustrating the nature of its adulteration:

DESCRIPTION.	Water.	Resin.	Extractive matter.	Ash.
Fair commercial sample . .	24.2	28.8	24.5	22.5
Adulterated sample	13.4	11.0	27.3	48.3 { Oxide of iron, alumina, silica, chalk, and salt.

For dyeing purposes the only satisfactory test is an actual dyeing test in comparison with an authentic unadulterated sample. For the analysis of the many butter-coloring mixtures containing annatto as the basis the reader is referred to Allen, "Commercial Organic Analysis," 2d ed., iii, pp. 353–356, and Wynter Blyth, "Foods, Composition and Analysis," p. 306.

(*d*) *Logwood Extract.*—Both the liquid and the solid extracts are liable to be adulterated, the former with glucose, molasses, dextrine, salt, and other extracts of lesser value, the latter with starch and inferior extracts. Notably are the French and German logwood extracts adulterated in the way just referred to. The following analyses of some of the commercial extracts as currently sold in France and Germany are given by V. H. Soxhlet: *

DESCRIPTION OF EXTRACT.	Molasses.	Dextrine	Chestnut extract.	Salt.
Guaranteed Pure, 30° B. . .	5 per cent.			
Prima, 30° B.	10 " "			
Secunda, 30° B.	20 " "	. . . . .	10 per cent.	10 per cent.
Secunda, Solid	20 " "	. . . . .	15 " "	
Sanford Brand, I.	25 " "	15 per cent.		
Sanford Brand, II	35 " "	10 " "	10 " "	

The Sanford Brand here referred to is a French extract made in imitation of the original American Sanford Extract.

The extracts may be tested for purity either by the colorimetric assay or by comparative dye tests. The colorimetric test is carried out, according to Henry Trimble,* as follows: A volume of solution corresponding to .001 gramme of the *dry* extract is treated with ten cubic centimetres of water naturally or artificially containing traces of calcium carbonate and a solution of .002 gramme of crystallized copper sulphate. The mixture is brought quickly to the boiling-point and diluted with distilled water to one hundred cubic centimetres. The color of this solution is then compared with one of pure hæmatoxylin similarly used, or with a standard sample of logwood extract.

The method of carrying out the dye test for logwood with bichromate of potassium mordant has already been given in speaking of dye-woods. The same test is, of course, equally applicable to the extracts. Cotton strips are sometimes used for these dye tests instead of wool. The cotton strips must be boiled in dilute soda solution and well washed. They may then be mordanted with nitrate of iron solution instead of the chromium salt, following the nitrate of iron with a rinsing in carbonate of soda solution and thorough washing. They are then put in the dye-bath cold, and this gradually heated to boiling. In this dye-testing with iron solution, the hæmatoxylin of the solution is oxidized by the ferric oxide to hæmatëin, so that the full coloring value of the logwood is obtained in the test.

For the discovery of adulterations like chestnut extract, which contain almost nothing soluble in ether, Houzeau proceeds as follows: One gramme of the extract to be investigated is dried at 110° C., exhausted with ether, and the weight of the dissolved material determined. The undissolved material is then exhausted with absolute alcohol, and the weight of the portion dissolved by this also determined. The comparison of the figures so obtained with those yielded when a pure extract is treated with the same solvents will show clearly the presence or absence of adulterating extract. Dye tests may also be carried out with the material which has been extracted by ether and alcohol respectively in the two cases, and the difference more fully established.

(*e*) *Catechu Extract.*—Catechu is frequently adulterated, not only with mineral matter like sand and clay, but with starch, dextrine, sugar, blood, etc. The mineral matters will, of course, remain in the ash. This in normal catechu should not exceed five per cent. The starch may be detected by extracting the sample with alcohol, boiling the insoluble residue with water, and testing the cooled liquid with iodine, which will show by the blue color any starch present. An addition of alcohol to the aqueous solution will show by the production of a turbidity any notable quantity of dextrine. Blood may be detected by treating the sample with alcohol, and drying and heating the residue in a tube, when ammonia and offensive decomposition products will be given off, or the coagulation of the blood albumen when the aqueous solution is boiled.

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* Journ. Soc. Dyers, etc., i, p. 92.

The value of catechu for dyeing purposes can only be determined by a dye test. For this purpose strips of cotton-stuff are immersed for half an hour in a catechu solution (for each gramme of the cotton fifty cubic centimetres of a catechu solution containing five grammes to the litre of water are taken and diluted with water if necessary). The strips are pressed out, and then the color developed by oxidizing in a hot solution of one to two grammes of potassium bichromate to the litre of water.

3. FOR COCHINEAL.—The adulteration of cochineal may be effected in various ways. A very common adulteration is to admix with the fresh cochineal insects others from which the coloring power has already been in large part extracted. To give the exhausted cochineal insects the appearance of fresh ones, they are shaken up with talc, barytes, and white lead, and thus given a coating resembling the silvery insects. Either a washing or an ash determination will serve to detect this adulteration. The valuation of the cochineal as to coloring power may be made by several methods. The one best known is that of Penny,* in which one gramme of the cochineal is treated with fifty grammes of dilute potassium hydroxide, twenty-five grammes of water added, and to this is then added drop by drop a solution of ferricyanide of potassium containing five grammes to the litre. The solution loses its purplish-red color and becomes brownish-yellow. The action of the ferricyanide of potassium solution is tested in comparison on the solution of one gramme of a cochineal of known purity. Liebermann † extracts the cochineal with boiling water, and determines the coloring matter by the addition of a slightly acid solution of lead acetate. After filtering and washing the lead precipitate, a lead determination is made in an aliquot portion, and from this the percentage of coloring matter calculated. Allen does not consider either of these methods to be perfectly satisfactory. An actual dye test is therefore in the end to be regarded as the most reliable method of valuation. For this purpose strips of woollen stuff of about five grammes in weight are put into the bath until the color is all taken up. A portion of the strips may then be dyed scarlet-red by immersing them in a tin solution (for one gramme of cochineal two grammes of cream of tartar, two grammes of tin salt, and as much water as is needed to thoroughly immerse the strips), and the other portion of the strips may be dyed a cherry-red by the use of an alum solution (for one gramme of cochineal, three-fourths gramme of cream of tartar and one and a half grammes of alum). These strips are then to be compared with others obtained from similar treatment of a normal or pure cochineal sample.

4. FOR INDIGO AND ITS PREPARATIONS.—Indigo may be of very varying value as it comes into commerce, partly because of the differences natural to such a product and dependent upon the differences in cultivation of the plant, care in extracting and drying the indigo, and the fact that the natural product is at best a mixture, and partly from intentional adulteration Thus starch colored with iodine Prussian blue

smalt, and logwood-powder are said to be used as adulterants of commercial indigo. In order to detect the starch, the suspected sample is rubbed up in a mortar with chlorine-water until it is completely decolorized, when a drop of potassium iodide is added. If starch be present the blue color of iodide of starch will be seen. To detect the smalt or Prussian blue, the sample is oxidized with nitric acid, when if a blue residue is shown in the yellowish solution adulteration is indicated. If the adulterant were Prussian blue, the color fades too after a time, if smalt, it is permanent. To detect logwood-powder, mix the sample with oxalic acid, place it upon filter-paper, and moisten it; in the presence of logwood the paper will be colored red, if the sample were pure it is unchanged.

In the assay of commercial indigo the *moisture* is generally to be determined. This should not exceed some seven per cent. in a genuine sample. The *ash* similarly is an important criterion of the quality of the indigo sample. In the purest kinds it is sometimes as low as two per cent., but from five to eight per cent. is more usual. Some of the inferior grades of indigo, such as Kurpah and Madras, may contain from twenty-five to thirty-five per cent. of ash.

The methods for the determination of the percentage of indigo-blue are, of course, the most important things to be considered in connection with indigo as a dyeing material. They are very numerous. We may summarize the more important of them under three heads,—viz., oxidation methods, reduction methods, and sublimation of the pure indigo-blue from the commercial product.

The oxidation of the indigo-blue takes place in acid solution, the indigo being previously dissolved in strong sulphuric acid. Potassium permanganate, bichromate, and ferricyanide have all been recommended and used in this connection. All the processes are open to the objection that the oxidizing agents act on the indigo-gluten and ferrous salts as well as on the indigo-blue and indigo-red, but the errors due to this cause may be practically avoided, as pointed out by Rawson, by previously precipitating the sulphindigotic acid in the form of the sodium salt by adding common salt to the solution. The method with permanganate of potassium, modified in this manner by the use of common salt, is as follows:* One gramme of the sample of indigo in the form of an impalpable powder is mixed in a small mortar with its own weight of ground glass. This mixture is gradually added with constant stirring to twenty cubic centimetres of concentrated sulphuric acid (specific gravity 1.845), which is then heated to about 85° C. for an hour. The product is then cooled, diluted with water to one litre, and filtered from indigo-brown and other soluble matter. Fifty cubic centimetres of the filtered solution are now taken, diluted with fifty cubic centimetres of water, and thirty-two grammes of common salt added, which quantity is almost sufficient to saturate the liquid. After standing for two hours, the solution is filtered, and the precipitate washed with about fifty cubic centimetres of brine of 1.2 specific gravity. This sodium sulphindi-

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* Allen, Commercial Organic Analysis, 2d ed., iii, p. 308.

gotate is dissolved in hot water, the solution cooled, mixed with one cubic centimetre of sulphuric acid, and diluted to three hundred cubic centimetres. This solution is then titrated in a porcelain dish with a solution of potassium permanganate containing .5 gramme of the solid salt per litre, the exact oxidizing power of which has been ascertained by experiment with a solution of pure indigotin. The oxidation is regarded as complete when the liquid which at first takes a greenish tinge changes to a light yellow with a faint pink color on the margin.

The reduction of indigo-blue may take place in alkaline solution or with a solution of the sulphindigotic acid or its salts. Ferrous hydroxide and hyposulphites are among the reducing agents used to effect the reduction in alkaline solutions. C. Rawson considers the hyposulphite reduction method the better one of the two. In carrying it out, one gramme of the finely-powdered sample is made into a paste with water and placed in a flask with about six hundred cubic centimetres of lime-water. The flask is closed by a cork having four perforations, two of which serve for the passage of coal-gas, a third carries a siphon, while to the fourth is fitted a tap-funnel. The contents of the flask are heated to 80° C. and one hundred to one hundred and fifty cubic centimetres of a strong solution of sodium hyposulphite ($NaHSO_2$) introduced through the tap-funnel. In a few minutes the liquid assumes a yellow tint, and is maintained at a temperature near the boiling-point for half an hour. After allowing the insoluble matters to subside, an aliquot portion of the solution should be removed, and a current of air drawn through it for about twenty minutes, when it is acidulated with hydrochloric acid. The precipitate, which consists of indigotin and indigo-red, is collected on a weighed filter, washed with hot water, dried at 100° C., and weighed. It is then exhausted with boiling alcohol whereby the indigo-red is dissolved out and the difference again weighed as indigo-blue. Rau reduces the indigo in alkaline solution with glucose, and L. M. Norton uses milk of lime and zinc-dust as reducing agent, and then takes an aliquot portion of the reduced solution to reduce a solution of iron-alum. The ferrous salt formed corresponds to the reduced indigo in the volume taken, and is determined by titration with a standard solution of potassium bichromate. (For details, see Helen Cooley's article, Amer. Journ. Anal. Chem., ii, p. 133.)

For the reduction of the indigo in acid solution, Bernthsen and Drew * recommend the use of hyposulphite of soda ($NaHSO_2$), and claim that the reaction is a quantitative one: $C_{16}H_8N_2O_2(SO_3H)_2 + NaHSO_2 + H_2O = C_{16}H_{10}N_2O_2(SO_3H)_2 + NaHSO_3$.

C. Rawson † considers that of all the volumetric methods which have been devised for estimating indigotin the hyposulphite process is capable of giving the most rapid and accurate results, but that considerable care and delicacy are required in its manipulation.

Lee ‡ has proposed the sublimation of the indigo-blue as a method for determining its percentage in commercial indigo. Other writers

REACTIONS OF THE MOST IMPORTANT NATURAL DYESTUFFS.

YESTUFFS.	Aqueous extract.	Caustic soda, 1 : 10.	Aluminum sulphate and sodium carbonate, 1 : 10.	Ferric chloride, 1 : 10.	Calcium chloride, 1 : 10.	Hydrochloric acid, 1 : 10.	Remarks.
ER	Dirty red.	Bluish red.	Red.	Dark brown precipitate.	Red precipitate.	Red precipitate.	. . . .
L-WOOD	No extraction.	Bluish-red extract.	Red.	Brown-black precipitate.	Red precipitate.	Red precipitate.	With alcohol, reddish extract.
OD	Bluish red.	Violet precipitate.	Reddish-violet solution.	Black solution.	Red precipitate in concentrated solution.	Yellowish-red color.	. . . .
USTIC	Reddish yellow.	Violet precipitate.	Yellow solution.	Black precipitate.	Red precipitate in concentrated solution.	Yellow-red color.	. . . .
FUSTIC	Red solution.	Bluish-red color.	Reddish-yellow solution.	Dark olive precipitate.	Red precipitate.	Bright yellow color.	. . . .
ITRON	Reddish yellow.	Red color.	Yellow precipitate.	Dark green precipitate.	Yellow precipitate.	Bright yellow color.	Flavine.
RIC	Yellow solution.	Red color.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Bright yellow color.	. . . .
TO	Yellow solution.	Yellow color.	Yellow solution when poured over.	Black precipitate, *turning blue with* sulphuric acid.	Red precipitate.	Red color.	Dyes cotton in alkaline solution.
IU	Turbid yellowish-brown solution.	Clear reddish-yellow color.	Yellow color.	Dark green precipitate.	Yellow precipitate.	Bright yellow precipitate.	With potassium bichromate, red-brown on heating.
RED CATECHU .	Clear yellowish-brown solution.	Reddish-brown precipitate.	Yellow color.	Bright olive color.	Yellow precipitate.	Bright yellow precipitate.	With potassium bichromate, yellow-brown.
UTS	Dirty yellow color.	Reddish-yellow precipitate.	Light yellow color.	Blue-black precipitate.	Turbidity.	Bright yellow precipitate.	. . . .
H	Dirty yellow color.	Reddish-yellow precipitate.	Yellow color.	Black precipitate.	Yellow precipitate.	Bright yellow precipitate.	. . . .
EAL	Bluish-red color.	Bluish-red solution.	Red color.	Black color.	Black precipitate.	Yellow-red color.	. . . .
N	Colorless.	Light yellow precipitate.	Light yellow precipitate.	Blue-black precipitate.	Turbidity.	Bright yellow precipitate.	. . . .
YE	Red color.	Bluish-red solution.	Red color.	Gray precipitate.	Red precipitate in concentrated solution.	Yellow color.	. . . .
AR	Bluish-red color.	Bluish-red solution.	Bright red color with aluminum sulphate.	Bright red color.	Red precipitate in concentrated solution.	Yellow-red color.	Orseille.

however, do not agree that, unless the indigo has previously been somewhat purified, the results can be depended upon.

C. Rawson * has given the following results with commercial samples, using the several processes just detailed:

METHOD USED.	Java.	Bengal.	Bengal.	Oude.	Kurpah.	Madras.
Water	2.99	5.22	6.17	7.50	8.05	5.71
Ash	1.99	3.91	4.86	8.21	25.72	33.62
Indigotin, by sublimation	60.84	57.50	49.36	41.60	41.92	39.56
Indigotin, volumetric, by hyposulphite	68.78	59.26	55.66	43.18	42.52	36.80
Indigotin, gravimetric, by ferrous sulphate and NaOH	68.24	58.84	54.34	44.50	41.50	34.50
Indigotin, gravimetric, by hyposulphite and lime	68.97 }	59.12 }	56.20 }	43.42 }	42.68 }	35.21 }
Indirubin, separated by alcohol .	4.23 }	3.50 }	2.80 }	3.65 }	2.45 }	3.98 }
Indigotin and indirubin, titration with $KMnO_4$ direct	76.18	66.71	62.66	50.04	47.15	39.50
Indigotin and indirubin titration after precipitation with salt . .	73.55	63.50	57.50	44.90	43.10	37.40

The table from Dammer's Chem. Technologie, Band iv, p. 591 (see opposite page), shows the characteristic reactions of the important natural dyestuffs.

V. Bibliography and Statistics.

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STATISTICS.

1. Indigo, Natural and Artificial.—The exportations of natural indigo from British India have decreased greatly owing to the introduction of synthetic indigo. The exports from British India were:

1896	169,500	cwt.	Value	43,700,000	rupees.
1901–02	89,750	"	"	18,522,554	"
1903–04	60,410	"	"	10,762,026	"
1904–05	49,256	"	"	8,346,073	"
1905–06	31,186	"	"	5,863,777	"
1906–07	35,102	"	"	7,004,773	"

The area under cultivation for the indigo plant in British India (Bengal, Madras, Agra, Oude, Punjab) was in:

1896	1,600,000 acres
1906	450,000 acres

The production of synthetic indigo has grown during the same period as follows:

1900	1873 tons	1904	8730 tons
1901	2673 tons	1905	11165 tons
1902	5284 tons	1906	12733 tons
1903	7233 tons		

2. Exportations of Dye-woods.—The exportations of several of the more important dye-woods from tropical American countries for the period given have been as follows:

1. *Logwood Exports:*

	From Haiti.		From Jamaica.	
	Pounds.	Value.	Pounds.	Value.
1882–83	152,288,713	$1,998,789	66,685,584	$434,632
1883–84	154,775,887	2,031,434	100,638,496	655,921
1884–85	142,986,254	1,876,695	126,795,200	743,774
1885–86	114,341,436	1,500,731	142,256,128	927,165
1886–87	105,000,065	1,378,125	132,009,472	932,089
1887–88	106,163,734	1,393,399	226,108,912	1,718,627
1888–89	57,021,431	748,406	258,616,960	1,826,035
1889–90	70,801,241	929,266	133,232,400	962,432
1890–91	56,743,891	744,764	244,794,592	1,861,395
1891–92	39,766,320	521,933	194,152,784	1,476,320
1892–93	....	....	207,472,832	1,633,947

2. *Fustic Exports:*

	From Mexico.		From Jamaica.	
	Pounds.	Value.	Pounds.	Value.
1882–83	30,746,240	$280,988	7,477,792	$48,738
1883–84	32,995,200	248,656	4,024,272	21,857
1884–85	17,471,509	128,019	2,078,160	13,093
1885–86	17,420,099	110,873	3,526,768	21,071
1886–87	24,942,407	178,621	9,366,000	61,044
1887–88	26,583,858	177,488	5,518,016	35,964
1888–89	18,224,030	133,952	2,777,216	10,425
1889–90	23,762,671	198,646	1,457,200	8,606
1890–91	16,927,020	119,631	2,128,112	12,714
1891–92	13,187,368	96,588	1,517,152	9,888
1892–93	....	....	14,472,976	102,190

3. *Exports of Brazil-wood from Bahia during recent years were.*

	To United States. Kilos.	To England. Kilos.	To Germany. Kilos.	To France. Kilos.	All other countries. Kilos.	Total Kilos.
1884	584,318	143,480	15,000	336,189	56,350	1,135,337
1885	232,912	292,212	49,568	703,497	......	1,278,189
1886	684,002	193,189	134,857	904,348	18,569	1,934,965
1887	783,616	152,453	46,640	1,374,543	......	2,357,252
1888	388,631	84,341	18,584	369,725	......	861,280
1889	149,063	82,156	753,457	....	......	984,676
1890	58,121	166,198	78,959	127,016	......	430,295
1891	251,873	....	....	670,857	21,321	944,051
1892	635,030	64,676	25,782	1,093,650	......	1,819,138
1893	615,158	517,937	147,177	548,734	8,970	1,837,976

3. IMPORTATIONS OF DYE-WOODS AND DYE-WOOD EXTRACTS INTO T UNITED STATES.

	1906.	1907.	1908.	1909.	1910.
Annatto extract (lbs.) ...	281,575	651,595	551,872	711,191	619,3
Valued at	$22,156	$51,128	$40,708	$48,839	$39,5
Cochineal (lbs.)	111,007	184,326	152,624	102,694	150,8
Valued at	$53,446	$84,911	$54,146	$33,875	$41,4
Fustic (tons)	5,783	3,483	4,452	2,466	5,8
Valued at	$89,513	$54,765	$53,884	$34,752	$82,8
Gambier (lbs.)	31,478,837	28,853,124	26,692,100	31,000,855	25,808,7
Valued at	$1,118,910	$977,000	$895,210	$1,313,990	$1,264,0
Indigo, crude (lbs.) ...	7,196,678	7,170,836	6,078,073	6,249,975	7,636,6
Valued at	$1,046,023	$1,233,515	$1,058,354	$1,400,000	$1,195,9
Indigo, extract (lbs.) ..	125,257	145,339	140,291	148,454	142,8
Valued at	$7,698	$8,013	$14,391	$17,897	$16,4
Logwood (tons)	36,624	37,901	21,809	17,873	31,2
Valued at	$498,602	$478,656	$248,578	$166,371	$353,3
Logwood and other dye-wood extracts (lbs.)	3,443,676	4,542,257	3,576,676	3,463,582	2,937,6
Valued at	$295,188	$368,704	$230,475	$231,612	$187,1
Madder, ground (lbs.) ...	45,991	62,633	50,856	37,910	30,7
Valued at	$4,600	$5,721	$5,249	$3,019	$2,3
Orchil, value	$33,980	$31,880	$29,924	$45,818	$38,7
Saffron, extract of, value	$59,964	$74,468	$70,569	$67,648	$80,7

(Commerce and Navigation of U. S., 1910.)

CHAPTER XIV.

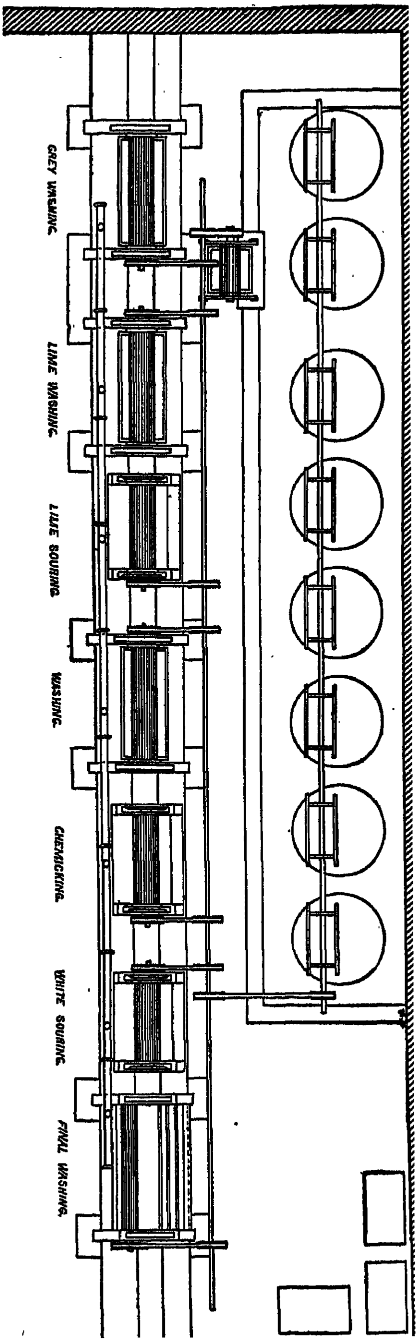
BLEACHING, DYEING, AND TEXTILE PRINTING.

PRELIMINARY.—Prior to the operation of bleaching, especially in cases where delicate shades are required, it is always necessary to thoroughly cleanse the fibre or fabric of grease and dirt. For *cotton*, which is generally handled as hanks, warps, and pieces, it is sufficient to boil it in a dilute solution of caustic soda or soda ash, followed by a good rinsing; it may, in some instances, be boiled in plain water, wrung out, and bleached or dyed; ordinarily, however, a boiling for two or three hours in a bath of eight to ten per cent. of crystallized soda and one to two per cent. of soap, calculated to the weight of the cotton, yields good result. The time for boiling out cotton is much reduced if it is immersed in a weak lukewarm bath of two per cent. sulphated oil strongly neutralized with ammonia or in a soap-bath containing ammonia. This is found to completely remove all natural oil on the fibres and thoroughly wet them. *Wool* is always thoroughly scoured both before and after it is manufactured into yarn. The soap solution generally employed contains from four to five ounces to the gallon of water, accompanied usually with a carbonated alkali (potash or ammonia) in about the following proportion: ten per cent. of soda and two per cent. of soap. The temperature of the bath is about 40° to 50° C. (See p. 343.) For *silk* (see p. 349) the boiling off contains about twenty-five to thirty pounds of Castile, Marseilles, or other *neutral soap* for each hundred pounds of silk, and a temperature at or near the boiling-point is taken for about two hours, turning the silk occasionally. For some colors a second boiling off can be employed to advantage, only one-half the quantity of soap being used as in the first bath. It is the practice to use the baths several times, care being taken to enrich them with fresh soap.

A. BLEACHING.—This highly-important operation results in a more or less complete destruction of the natural coloring matter which is found in all fibres of industrial importance. Owing to the somewhat powerful action of most of the agents employed for the purpose, it will appear that, unless care and discretion are applied to their use on the part of the bleacher, something more than a destruction of the coloring matter will occur,—a probable partial destruction of the fibre. The operation has been known since the earliest times; the white linens of the Egyptians and Phœnicians were much esteemed by the nations trading with them. In the early part of the eighteenth century immense fields were given up wholly to bleaching in the United Kingdom; the process as carried out required several months, consisting of a successive treatment of the cloth or fabric in alkaline solution—termed "*bucking*"—and washing, then exposing, while damp, and spread out on the grass to the sunlight for a few weeks (*crofting*), immersing in sour milk, washing again, and finally exposing on the grass, these several operations being repeated until the required degree of whiteness is obtained. Great improvements in the above tedious process resulted when the use of sulphuric acid was substituted for the sour milk, and chlorine gas replaced the lengthy field exposure, this latter being due to M. Berthollet; but the general use of this substance was not established until the manufacture of the now familiar "chloride of lime" or "bleach." Since then many other bleaching agents, notably, hydrogen peroxide, have appeared, but whether they will ever displace the above is an uncertainty.

1. *Cotton* in the *raw* or *unmanufactured* state is seldom bleached, except in the production of absorbent cotton; as *yarn*, however, it is continually. The hanks, which have been previously scoured, are worked in a solution of chloride of lime (*chemick*) from one to two hours, washed well in water, and passed through dilute sulphuric acid (1° Tw.) for about half an hour, and finally well washed. These operations can be easily conducted in the ordinary wooden tubs of the dye-house in places where much yarn does not have to be bleached, otherwise special arrangements should be provided. *Cotton warps* are similarly treated, the apparatus employed being a continuous (warp) dyeing-machine. *Cotton fabrics*

FIG. 118.



use in the bleached condition, and also those which are to be afterwards dyed or printed with delicate shades. The method of bleaching, which has reached a high state of perfection, is the so-called "madder-bleach," from the fact that it is employed on all piece goods to be printed with alizarin. The process detailed and illustrated below must not be accepted as the exact method followed in every establishment,—it being remembered that nearly every bleacher has his own modifications which he introduces, but all yield the same result. The operation of stamping or sewing on designating marks; sewing the pieces together and singeing,—a removal of the nap or down from the cloth by means of a gas flame or curved hot plate ("singeing plate"),—need not be detailed here; reference may be had to special works on textile manufacture.

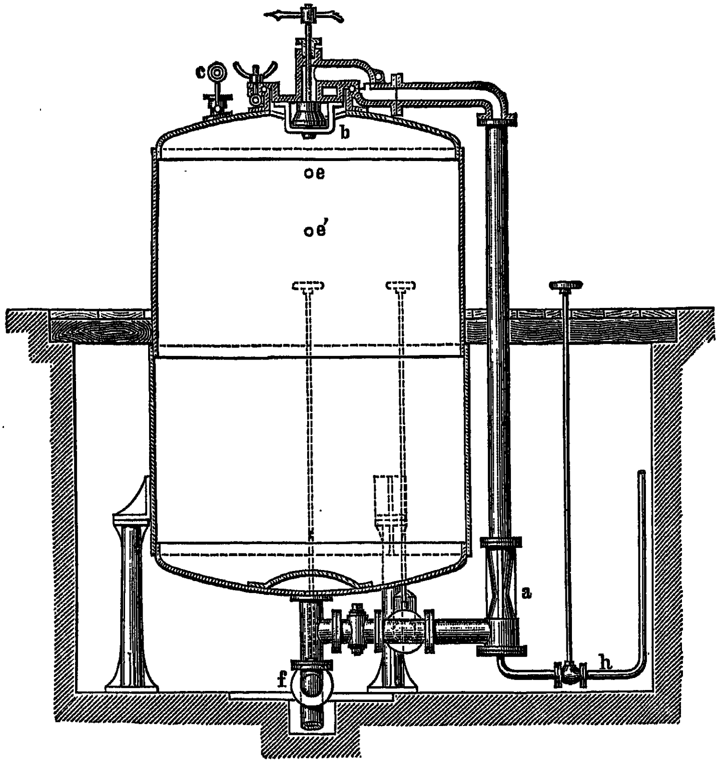
Fig. 118 is a plan of part of a bleach-house for cotton cloth. The goods being received, they are passed through the first washing-machine, on the left of the figure; this operation has for its object the removal of loose dirt, grease,—added to the fabric during weaving,—and other matters; usually the goods are stacked overnight in order to allow an incipient fermentation to take place, when they are passed several times through the *lime-wash* (milk of lime) in order to become thoroughly impregnated with about five per cent. of lime, this being accomplished by means of rollers immersed in and below the surface of the lime-bath and a pair of squeezing or "nipping rollers."

Following the liming operation is the boiling ("bowking") in kiers; these are strong, wrought-iron cylindrical vessels, provided with a series of pipes, and in some cases with injectors, which enable the liquids contained in them to circulate completely through the cloth, which is previously introduced in the form of a rope. Fig. 119 is a vertical section of a single injector-kier, and one well adapted for working at low pressures. Reference being had to the figure, the vessel being filled with the fabric, which is well laid in, the liquid is admitted, gradually finding its way to the false bottom, through which it passes to the injector at *a,* where it meets a steam current, which forces it upward through the large pipe, finally being admitted to the kier again through the valve *b,* repeatedly following the circuit.

Barlow's high-pressure kiers are usually worked in pairs, and the liquid is forced from one to the other by the aid of steam. This kier has a central perforated tube, through which the liquid passes to come in contact with the cloth. Several other forms of kiers are in use, even open kettles acting as such, the object being the same in each case.

The length of time the cloth remains in the kier varies considerably: in some establishments, where a high-pressure is used (forty to fifty pounds per square inch), less time is required,—five to six hours being deemed sufficient; again, where a low-pressure is used (eight to twelve pounds) the goods are allowed to remain in from ten to twelve hours. From this boiling the pieces are *washed* in water, and passed through dilute hydrochloric acid (specific gravity 1.01 = 2° Tw.),—the bath the lime is completely dissolved, when the goods are thoroughly washed, or until every trace of acid is removed, when a boiling with soap and soda follows in kiers exactly as in the boiling previously mentioned. For each hundred pounds of cloth a resin soap is used, made with five to six pounds of soda ash and one to two pounds of resin; the soda is dissolved in two gallons of water, the resin added, and the whole boiled for several hours; for each pound of cloth to be acted upon one gallon of water is used. The time required for this boil is nearly the same

FIG. 119.



as in the previous boiling. When the resin soap solution is run off, the goods are boiled for three or four hours with a one per cent. solution of soda, to remove the soap and any unconverted resin remaining, followed immediately by a wash. At this stage of the process occurs the real whitening, or bleaching, of the goods,—the so-called "*chemicking*,"—requiring much care, and is performed with a solution made by dissolving chloride of lime, allowing to settle and become clear, the supernatant liquor alone being used. The strength of the solution, varying from ¼° Tw. to 2° Tw. (specific gravity 1.001 to 1.01), being cloth better. Repeated passage of the goods through a weak solution is preferable to a shorter time in a strong solution, the danger from injury to the pieces being less. The next operation may be (not always) a wash, and then a *souring* in dilute (specific gravity 1.01) sulphuric acid,—termed a *white sour*,—after which the goods are allowed to remain for some time in a heap, but not long enough to become dry, as a tendering of the cloth will result; this is followed with a final wash to remove every trace of acid, passed through squeezing rollers, and over revolving cans heated by steam, to dry. The length of time required in the above process varies; if the goods are to receive a fine clear bleach, or are to receive delicate shades in dyeing and printing, four or five days may be necessary, but in the event of the goods being intended for full shades, half the time will answer.

Mather-Thompson's Process.—This is one of the newer processes, and is admirably suited for warps and piece-goods. The goods are sewed together, or tied, in the case of warps, subjected to the action of hot caustic alkali, washed, and transferred to wagons, the sides of which are of iron lattice-work (cages), and pushed into a horizontal kier, and for five hours acted upon by a solution of caustic soda (2° to 4° Tw. = specific gravity 1.01 to 1.02) delivered in a spray and at a pressure of four to five pounds. Without removing the goods from the kier they are washed with hot water, removed, and rinsed with cold water, completing the scouring. The bleaching is carried out in a continuous apparatus through the following stages:

1. Rinsing with warm water.
2. First chemick bath (chloride of lime solution, 1° Tw. = specific gravity 1.005).
3. Passage through atmosphere of carbonic acid gas.
4. Washing with cold water.
5. Worked through a one per cent. soda solution at 175° F.
6. Second washing.
7. Second chemick (chloride of lime solution .5° Tw.).
8. Second passage through carbonic acid gas.
9. Third wash.
10. Through one per cent. hydrochloric acid, or through one per cent. of a mixture of hydrochloric and sulphuric acid (2 : 1).
11. Final wash.

In this process the real bleaching is effected by the hypochlorous acid liberated by the action of the carbonic acid gas upon the calcium hypochlorite.

Lunge's Bleaching Process differs but slightly from others using chloride of lime, except that he increases the bleaching action by the use of a small quantity of some organic acid,—preferably acetic. Chloride of lime in contact with acetic acid forms calcium acetate, with evolution of free hypochlorous acid; this gives up oxygen during the bleaching, leaving hydrochloric acid, which acts on the calcium acetate, forming calcium chloride and regenerating the acetic acid. The hydrochloric acid never being in the free state cannot act on the fibre; acetic acid has no action, even at the high temperature or pressure used in bleaching.

Hermite Process for Electrolytic Bleaching.—This process is probably one of the most successful yet brought forward, embodying the use of electricity, effecting the bleaching by the decomposition of a four to five per cent. solution of *chloride of calcium* (not "chloride of lime," or "bleaching-powder"), of *magnesium,* or of *aluminum.* The electrolyzed solution of the salt employed is of especial service in causing the destruction of the coloring matter of vegetable fibres, but, owing to the peculiar effect of chlorine on wool or silk, it is impracticable with them. Electrolyzed salt solutions are replenished by the addition of a quantity of salt equal to that absorbed by the fibres or fabrics when withdrawn from the bleach-bath.

2. *Linen.*—This fibre is much more subject to the destructive action of bleaching agents than cotton, in consequence of which the same process is not applicable, and also on account of the greater amount of impurities present, chiefly pectic acid. For *yarns* the trade distinguishes three important grades of bleaching,—*half, three-quarters,* and *full white,* to obtain which several operations are necessary:

1. Boiling for three or four hours in a ten per cent. solution of soda ash, or in a six per cent. solution of caustic soda. Wash, rinse, and pass through squeezing rollers.
2. Pass through a .4° Bé. solution of chloride of lime, and work or *reel* one hour, and wash.
3. Transfer to dilute sulphuric acid for one hour (one part acid to two hundred parts water).
4. Boil again in a kier with two per cent. caustic soda.
5. Repeat the passage through chloride of lime and wash.
6. Final treatment with sulphuric acid as in No. 3.

The above will produce a *half-bleach,* and by repeating the three final operations a *full white* will be obtained. *Reeling* is a term particularly applicable to linen-bleaching, owing to the way the yarn is handled, the result being that the carbonic acid in the air acts upon and decomposes the chloride of lime, setting free hypochlorous acid, similarly to the use of the gas in the Mather-Thompson process.

Linen cloth, despite many trials, still requires much longer time to successfully bleach than yarn. It is quite possible to bleach the cloth in a comparatively short time, but the strength of the fibre would be weakened. The following outline of the general process indicates the successive stages:

1. Liming. Boil with eight to ten per cent. for fourteen hours and wash.
2. Allow to remain in dilute hydrochloric acid (specific gravity 1.012) for four to six hours and wash.
3. Boil with resin soap (two pounds caustic soda and two pounds resin) for ten hours, followed immediately by a boiling for six to eight hours with one pound caustic soda

5. "Chemick." Pass through chloride of lime solution of ½° Tw. for about five hours and wash.

6. "Sour." Steep in dilute sulphuric acid 1° Tw. for two to three hours and wash.

7. Boil for four to five hours with .5 to .75 per cent. of caustic soda, wash, and

8. Expose again for four to five days in the fields.

9. Second chemick. Same as No. 5, only ¼° Tw. for five hours.

10. If necessary, rub with a soft soap between "rubbing-boards"* to remove brown spots.

11. Expose again on the grass as before.

The frequent exposure of the goods on the grass to the combined action of moisture, air, and light necessarily dispenses with a certain amount of the chloride of lime, besides allowing of a less energetic action.

3. *Jute.*—A good white on this fibre is difficult to obtain. Prior to bleaching, jute is scoured with a five per cent. solution of sodium silicate (*soluble glass*) at 70° C., washed, and bleached with a solution of sodium hypochlorite containing about one per cent. of available chlorine, made by decomposing bleaching-powder with carbonate of soda, settling, and using the clear liquid. The goods are thoroughly washed, and treated in a dilute bath of hydrochloric acid (½° to 1° Tw.) and washed, or they can be further acted on by sulphurous acid by immersing in a bath of sodium bisulphite for two to three hours and dried. Jute can also be bleached by being worked in a solution containing one per cent. permanganate potash (calculated to the weight of its material) and exposing to the air until it becomes brown, when it is immersed in a solution of sulphurous acid and washed.

4. *Wool.*—For yarns, the oldest practical method of bleaching is "*stoving,*"—that is, an exposure of the damp goods to the vapors of burning sulphur, confined, usually, in a frame building; in the centre of the floor is mounted an iron pot in which roll sulphur is placed, and ignited by a piece of iron heated to redness. From six to eight per cent. of sulphur is consumed, and the time required is about eight hours, but for carpet yarns and goods of a similar grade twelve hours may be necessary. The yarn is removed and well washed, the water containing, possibly, a little carbonate of soda to neutralize any sulphurous acid remaining.

For piece-goods the same process is applicable, but it requires arrangements for passing the fabric over rollers inside the sulphur-house at a uniform rate. Piece-goods can also be bleached according to two somewhat lengthy processes, embodying the sulphuring in chambers, detailed in Sansone's "Dyeing," vol. i, p. 123.

The wool bleaching process based upon the action of the peroxides of sodium or hydrogen is the most important. No metal should be exposed in the wooden vats in which the bleaching is performed, and care

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* "*Rubbing boards*" are two fluted pieces horizontally placed, the upper of which is moved in opposite direction to the course of the cloth.

should be taken to see that no sediment is in the water-supply pipe, all such taking up oxygen from the reagent and thus weakening it. A solution of hydrogen peroxide (equal to about one per cent., and capable of destroying six cubic centimetres of decinormal potassium permanganate solution) is made up in the vat, and this is carefully neutralized with *silicate of soda* which has been previously diluted with *warm water;* the yarn or goods is immersed and kept below the surface of the liquid by means of a wooden lattice frame. The temperature must not be above the normal. In a few hours the wool will be bleached to a white or nearly so, and by keeping it immersed a "wool white" will be obtained, after which the material is lifted, and allowed to drain back into the vat, when the liquid is brought up to the original strength with fresh peroxide. The bath can be kept in use for six months. After draining, wash in water containing a trace of sulphuric acid, finally with water alone.

5. *Silk.*—The preliminary operations for treating this substance have already been mentioned. Ordinarily, silk is treated in a similar manner to wool, being hung on poles in an atmosphere of sulphurous acid for several hours (four to six), taken down and washed; or the silk can be worked in a bath of bisulphite of soda, followed by a weak alkaline wash and a final rinse. *Aqua regia* (hydrochloric acid and nitric acid, 5 : 1) of 3° to 4° Tw., and at 70° Fahr., is much used for small lots; the silk being constantly worked for about twenty minutes when the bleaching is finished. For very fine tints, the silk is entered into a soap-bath heated from 85° to 105° Fahr., wrung out, and bleached according to the peroxide process as indicated above for wool, but employing solutions of greater strength.

Tussah silk is always bleached with *hydrogen peroxide,* being immersed, as in the case of wool, for several hours, or even days. When the necessary degree of whiteness is obtained, the silk is rinsed and dried. Sansone mentions immersing the silk in strong peroxide, wringing out the excess, and steaming in a closed vessel. This method has yielded good results.

B. BLEACHING AGENTS AND ASSISTANTS. — *Chloride of Lime* ("Bleaching Powder"), the most important agent for bleaching purposes, is produced in immense quantities by acting on dry slaked lime with chlorine. It occurs in commerce as a white powder possessing a characteristic odor resembling that of chlorine, and if exposed rapidly absorbs moisture. The real strength depends upon the amount of available chlorine obtainable,—ranging between twenty-two and thirty-five per cent. Solutions of the above sold under fanciful names are met with in the trade varying in strength from five to eight per cent. "Chlor-ozone" is a product considerably used, and is essentially a solution of sodium hypochlorite.

Permanganate of Potash ($K_2Mn_2O_8$), although not strictly a bleaching agent, is mentioned on account of its very high oxidizing properties.

tank. The operation is conducted at as low a temperature as possible, and with continuous stirring; in about twelve hours the reaction is over, and the supernatant liquid drawn off and preserved. The residue, barium fluoride, is decomposed with sulphuric acid, and the hydrofluoric acid recovered. It is customary to refer to the strength of hydrogen peroxide as being of so many volume capacity, six, ten, etc.; this means that one volume of the peroxide will yield six, ten, etc., volumes of oxygen gas.

Sodium Peroxide, or *Sodium Dioxide* (Na_2O_2), is now an important substitute for hydrogen dioxide, as it is in many respects more convenient to use and can be kept, when properly sealed from the air, for a long time. It is a yellowish-white powder, and can be used in alkaline or acid solution.

Soda Ash (Na_2CO_3).—This is the commercial anhydrous carbonate of soda, used principally in scouring. It is generally contaminated with varying percentages of caustic soda, sodium chloride, sulphate, etc. Its value depends on the amount of Na_2O contained.

Sal Soda ($Na_2CO_3.10H_2O$) and *Concentrated Sal Soda* (Monohydrated, $Na_2CO_3.H_2O$) are much purer and more expensive carbonates; they contain no caustic soda, which renders them well suited to scouring.

Caustic Soda (NaOH).—It comes in trade in iron drums—solidly filled—or in a coarse powder. It is obtained by treating carbonate of soda with milk of lime, whereby the carbonate is decomposed with formation of calcium carbonate, when the clear liquid is drawn off and evaporated down to the solidifying point.

Carbonate of Potash (K_2CO_3) is not used in the dye and bleach works to the same extent as soda, although for silk- and wool-scouring it leaves the yarns, etc., with a better " feel," and when used in soaps, it does not cause colors to run or " bleed " to the same extent as soda. Its value depends upon the percentage of carbonate.

Acids.—The mineral acids are used in bleaching chiefly to neutralize alkalies, or to cause a disengagement of hypochlorous acid in the so-called " sours," and reference to their production is unnecessary. *Hydrochloric Acid* of commerce (also called *Spirit of Salt*, or *Muriatic Acid*) is yellow in color, due to impurities. The general strength is 21° Bé. (specific gravity 1.17). *Nitric Acid,* used in conjunction with the above for silk-bleaching, and largely in the preparation of some mordants, is bought with a gravity of 17.7° Bé. (specific gravity 1.140). *Sulphuric Acid* (H_2SO_4) is obtained by the burning of sulphur and conducting the gas into lead chambers, in contact with nitrous vapors and steam. It is a heavy, oily-looking liquid, and when pure is colorless. It is ordinarily sold at 66° Bé. (specific gravity 1.84).

Soaps.—The soaps employed in bleaching, etc., embrace *Tallow, Resin,* and *Olive Oil* (for silks), although others are used, but mainly for special purposes. Reference to them has been made in the chapter on Oils and Fats. (See p. 68.) In most large establishments soap-boiling appliances are in use.

mordanting is of the utmost importance, having for its object the precipitation of some substance upon the fibre which has an affinity for, and will effect a more or less complete fixation of, the coloring matter used for the dyeing. The nature of the mordanting substance used depends upon the character of the fibre, the kind of dye, and upon the effect sought; some shades require the use of several. Under ordinary circumstances *wool* is simply boiled in a solution of a metallic salt, for example, bichromate of potash ("chrome"), in the presence of a small quantity of some acid, in this case, preferably, sulphuric. Wool so treated is said to be *chromed,* and is in a condition to be dyed with logwood or with colors of the anthracene group. *Silk* is mordanted similarly, lower temperatures, however, being employed. If silk and wool are immersed for a time in a solution of a metallic salt, an absorption will take place, when the fibre can be washed in water, during which operation a deposition of a basic oxide will occur. *Cotton,* unlike wool or silk, has but little natural affinity for the majority of coloring matters, and of necessity must be specially prepared. It is well known that cotton has a strong tendency to combine with tannic acid, and this is made use of by steeping cotton in a solution of sumach extract, catechu, or other tannin-yielding material; if it is afterwards washed and worked in a bath of some soluble metallic salt, an insoluble compound will be formed, which *then* has the property of uniting with the dye. It is not always necessary to prepare the cotton with tannin, an immersion in the mordant, followed by an oxidation or *ageing,* being deemed sufficient.

Substantive Dyeing is where the coloring matter is taken up from its solution by the fibre without the assistance of any agent. Wool and silk are dyed with the coal-tar dyes in this manner, using some sulphate of soda and sulphuric acid in the case of the former, and with a soap-bath and a little acetic acid in the case of the latter. *Cotton,* when dyed with the benzidine colors, also comes under this head; it is possible a colored compound of cellulose and the base of the dye is formed. The use of salts in dyeing the above is merely to prevent a too rapid absorption of the dye by the fibre, thereby obviating uneven shades.

Adjective Dyeing necessitates the intervention of mordants, as above explained. Albumen, however, does not cause the formation of an insoluble precipitate on the fibre, but causes the cotton fibre to behave towards the dye in a manner similar to wool. Many coloring matters already fixed on cotton have the valuable property of serving as mordants for other dyes, a property much employed in the production of compound shades.

The following lists of mordants embrace only those of prominence and in general use; exact methods for their manufacture will be found in the works of Hummel, Sansone, Herzfeld, and others.

(*a*) *Mordants of Mineral Origin.—Tin Mordants.*—These are first in importance to the dyer and printer. They are used in two states of oxidation, *stannous* and *stannic.* The former salts have a great affinity with nitric acid, which are yellowish,—due, possibly, to an incomplete oxidation of the tin. The most prominent tin compound is *Stannous Chloride*,—when crystallized, "*tin crystals*," or as a liquid known as "*single muriate of tin*," or "*double muriate of tin*," according to the gravity. The crystals are obtained by dissolving feathered tin in commercial hydrochloric acid and evaporating; good samples contain about fifty per cent. of metal. The impurities are iron, lead, and sometimes copper. *Stannic Chloride* ($SnCl_4$) is of great importance not as a mordant but to the silk dyer as a *weighting* agent. It is produced in immense quantities, and sold under the name of "dynamite."

Tin Spirits, owing to the advent of the tar-colors, are much less used than formerly. Their composition was exceedingly variable, consisting usually of stannous chloride, with or without additions of sulphuric, oxalic, tartaric, and nitric acids, and they bore such names as *Amaranth Spirit, Yellow Spirit, Finishing Spirit*, etc. "Stannous Nitrate" (nitrate of tin) is essentially a solution of tin in nitric acid, the chemical composition of which is doubtful. "*Tin spirits*" is a collective name for a long list of *stannic* compounds, made, usually by the dyer, by the aid of hydrochloric and nitric acids, sodium and ammonium chlorides, etc. They are no longer used. *Stannate of Soda*, or *Preparing Salt*, is used in cotton- and woollen-printing; its value depends upon the amount of stannic oxide contained.

Alumina Mordants.—Sulphate of Aluminum, also known as *Patent Alum*, does not find much application in the dye-house, except in connection with the tin weighting process for silk, on account of its value in causing a plumping of the fibre. It is obtained from the mineral bauxite, and from cryolite. The brand manufactured for paper-makers is the purest, containing but little or no iron. By the addition of alkaline carbonates the normal aluminum sulphate is changed into a basic sulphate which yields alumina to the fibre more readily. Their application to cotton is followed by a treatment with ammonia or soap to fasten the alumina more fully, to wool generally with cream of tartar, and to silk by immersion overnight in the solution, followed by a washing, which causes the formation of a *basic* salt. *Aluminum Acetate*, or "Red Liquor,"—so called from the original use to which it was put, dyeing reds,—is obtained by the double decomposition of aluminum sulphate and *calcium* or *lead acetate* in the proper proportions, and using the supernatant liquid. Professors Liechti and Suida, and Köchlin have conducted elaborate researches into the action of the aluminum compounds as mordants, and their results have thrown much light upon the whole subject of mordanting. *Sulpho-acetate* of *Alumina* is obtained when an insufficient quantity of the acetate (lead or calcium) is added to decompose the alumina salt, and this forms the *red liquor* of trade. Ordinarily, the solutions have a dark-brown color and are characterized by a strong pyroligneous odor. The cotton-dyer and printer, especially the latter, make considerable use of this mordant, for reference to which, see p. 548. The remaining alumina compounds —viz., *chloride, nitrate, hyposulphite, oxalate*, etc.—are but little used, *Iron Mordants.*—Like tin, iron is employed in two states of o tion,—*ferrous* and *ferric*. *Ferrous Sulphate* ($FeSO_4.7H_2O$), *Cop* or *Green Vitrol,* occurs as a by-product from several chemical proc and is much used in cotton-dyeing, and in the preparation of mordants. *Ferrous Acetate*, also called *Pyrolignite of Iron* and *B iron Liquor,* is manufactured similarly to the acetate of alumina, c dissolving scrap-iron in crude acetic acid. It is applied in the general manner, and to the same fibres, as the alumina compound. remaining iron mordants are the *Nitrates* and the *Nitro-sulphates.* former are obtained by dissolving scrap-iron in nitric acid to the pr degree of saturation, and the latter, by treating copperas with n acid; as an iron mordant for black on silks and as a weighting a for black silks, this latter is probably the best, from the fact that iron exists in both states of oxidization.

Chromium Mordants comprise among the most important *Bichro of Potash* and *Bichromate of Soda,* both being products obtained f chromite. The former is well crystallized, the latter is quite deliq cent, frequently becoming fluid; in price it is cheaper than the po salt, and yields the same results. It is a valuable wool mordant, an also much used as an oxidizing agent. *Chrome Alum* (Potass Chromium Sulphate) is a residue from the manufacture of alizarin, is employed as the basis for producing many of the chromium morda *Chromium Acetate* is obtained by double decomposition of lead ace and chromium sulphate, and in commerce it is found of about 30° (specific gravity 1.15). It is used in printing. Other compounds u are the chloride, sulphate-acetate, and alkaline chromhydroxide solut

Copper Mordants are well represented by the *sulphate* (*blue-sto* and the *nitrate*. *Sulphate of Copper* is used in dyeing blacks, mo in conjunction with other mordants, and, owing to its cheapness, is u for the production of nearly all the copper compounds. *Nitrate Copper* is easily prepared by dissolving scrap-copper, not brass free from lead and solder as possible), in nitric acid, and diluting 1.4 specific gravity. In cold weather good crystals are obtained, they absorb moisture very rapidly. The *sulphide* and *acetate* find li application except in special cases.

Antimony Mordants.—*Tartar Emetic* (Antimonial Potassium T trate) is the best known of this group, and is much used for fixing tan in cotton-dyeing. *Oxychloride of Antimony* is another form, used the same purpose. These products have been practically displaced by *double fluorides of antimony* and potassium and of sodium which h been brought on the market as more convenient and desirable. T are well crystallized, easily soluble, and cheaper. The mode of appli tion is the same as for other antimony salts.

Other mordants besides those above mentioned are used, but not extensively, and enough has been said to indicate their general natu under the operations of dyeing the special uses to which they are appl will be mentioned.

and offers to the dyer a convenient mordant in place of many tannin-yielding substances, which, however, still hold their position on account of other properties. Tannin is much used by the cotton-dyer, and is applied generally in two ways: first, by *steeping*, and, second, by *padding*. For silk, tannin is extensively used in the production of blacks, and also for weighting. *Catechu*, or *Cutch* (see p. 497), is used in a similar manner to tannin, for the production of browns, drabs, blacks, and other shades, in combination with bichromate of potash, copper, iron, etc. Catechu is bought in mats weighing about one hundred and fifty pounds, and also as " cutch extract," or " prepared cutch," made by dissolving the crude cutch, straining from sticks, stone, etc., and evaporating to about 51° Tw. It is used for wool and for silk. *Sumach* (Shumach) is used in the dye-house in the ground state, and as an extract, which is, in some instances, grossly adulterated. *Nutgalls,* rich in tannin, find extensive application both in dyeing and printing, especially when light shades are to be fixed. They occur whole, " crushed," and as an extract, which comes usually of two qualities. *Myrobalans, kino, divi-divi* (see pp. 359 and 360), etc., are also employed.

D. DYEING.—The apparatus used by the dyer consists of vats, kettles, cisterns, etc., which are ordinarily constructed of wood, although they may be also of copper or similar metal, and even stone. Their capacity, in case of woollen yarn, is such that they can conveniently accommodate a hundred pounds of material, although the sizes vary according to circumstances. Wooden kettles are heated by a copper steam-coil inside and on the bottom, and are provided with a water-supply pipe, and a lifting plug-valve for emptying. Metal kettles are preferably heated with steam by a coil or double bottom. The shapes of the vat or kettle vary with the material to be dyed. For cotton, wool, and silk yarns they are mostly rectangular, and of varying depth, for loose material, mostly circular; in the case of indigo-vats for yarns, they are wine-pipes stood on end; this gives a great depth of liquid with a minimum of exposure. In hand-dyeing, the yarn is hung, and worked on sticks laid across the top of the kettles; piece-goods are worked by means of a movable winch. Loose material is dyed as such in circular tubs, warps are passed over a series of rollers immersed in the dye-liquor, and then between squeezing or nipping rollers. Machine or apparatus dyeing is rapidly gaining in favor. Two general systems are in use: (1) Pack system, where the material is tightly packed in a vessel and the dye-color forced through it, and (2) Loose system, where the material is moved through the dye-liquor.

Of primary importance in successful dyeing is a regular supply of pure water, and in the absence of this, various means must be resorted to to purify the water at hand, which may be contaminated with sewage, which may not render it unfit for use, or else it may contain *lime* or *magnesia,* usually as bicarbonates, which are soluble, or it may have *sulphates* or *chlorides.* Iron (when present it is as a bicarbonate) is very objectionable, and, for some operations, prevents the use of the water. Water which has flowed through limestone regions will invariably be *hard* from the *lime* dissolved, and that which flows or is pumped from granitic regions will be *soft,* due to the absence of lime, etc. In the event of water having suspended matter, this can be easily removed by suitable filtration, but if other impurities are present, chemical purification should be resorted to. A *hard water* is one which has bicarbonate of lime or magnesia dissolved, this solution being really a dissolving of *carbonate of lime* in carbonic acid contained in the water; besides the above, it may contain in solution *sulphates* of lime or magnesia. A water containing no sulphates, if boiled, would lose its hardness by the *bi*carbonate splitting off into carbonic acid gas and carbonate of lime or magnesia, which would be precipitated (temporary hardness); if sulphates were present, the boiling would have no effect on them (permanent hardness). A *soft water* is one containing no such impurities.

Chemical Purification for water embraces several processes, notably Dr. Clark's: decomposing the bicarbonate with a clear solution of calcium hydroxide, by this means the excess of carbon dioxide is combined with the lime added, which is precipitated and removed by settling. Only the temporary hardness is removed. The *Porter-Clark* process is similar to the above, with the exception that the precipitates are removed by the water being passed through a filter-press. *Caustic Soda* is also used as a purifying agent, which removes both the temporary and permanent hardness. The water will then be slightly alkaline. Alum and sulphate of alumina are extensively used in water purification for dyeing purposes. The alumina compound, if added to a water in suitable quantity, is completely eliminated by combining and separating with the impurities.

Solution of Coal-tar Colors requires a little care, because if imperfectly done the yarn or fabric will be spotted or striped: effects exceedingly difficult to remove. The colors are dissolved readily in warm water; some may require almost a boiling temperature, while others are injured when highly heated. They ought never be over a direct fire. In all cases it is well to strain through felt.

Cotton-dyeing.—Two operations are necessary, mordanting and dyeing, except in indigo-dyeing, where no mordant is required, and in the application of the substantive and primuline colors. In the case of *raw stock,* the operations are conducted in large circular or rectangular vats, heated as previously described, and provided with the necessary inlets and outlets for water, the outlet being covered with a gauze screen in order to keep the loose material from stopping it up. The material is "poled" or worked by long-handled rakes or by mechanical means. The *washing* can be done in a similar apparatus, or in one similar to a wool-scouring machine. For *yarns,* besides the open kettles mentioned on the preceding page, many mechanical devices are in use, and are well suited where large quantities of material are to be worked to one shade, but in cases where different shades are to be produced, hand-dyeing cannot be excelled. For *warps,* the apparatus referred to on page 523 pass through two or more different solutions. This arrangement is admirable for mordanting, dyeing, and washing, or in the event of using the primuline colors, requiring rapid treatment. The several baths can be maintained at different temperatures.

Cloth-dyeing Machinery.—The vats are either iron frames and wood or all wood, in some places small enough to stand on the floor of the dye-house, in others they must be sunk below that level, in all cases surmounted with a hand or power winch for working the pieces. *Drying* is accomplished by wringing out the yarn, centrifugating, and hanging on wooden sticks in a " dry-room," or in the case of piece-goods, squeezing through rollers, centrifugating, and carefully arranging on sticks as above.

Application of the Natural Coloring Matters.—Indigo, including synthetic indigo.—This dye is always applied in the cold, and by any of the several " vats " now known, among which the *lime* and *copperas* may be mentioned. This vat, or series (usually ten), is made up in various proportions, the amount of ground indigo ranging from thirty to thirty-eight pounds, copperas, fifty to eighty-five, lime, eighty to ninety. The vats being filled with water, the lime is added, followed by the ground indigo and the copperas, raking the whole up occasionally until the indigo has been reduced, which is known by the olive-colored appearance of the liquid. A good working vat is known by peculiar blue streaks or veins which appear when it is raked. The dyeing is performed by dipping the wetted yarns in the oldest (weakest) vat, then squeezed out, placed aside to oxidize, and passed through the next, and so on until the proper depth of shade is reached, the whole operation being conducted systematically. The lime which is precipitated on the yarn is removed by means of a weak acid and washing. Piece-goods are dyed in a similar solution by fastening the material to a large frame, which is dipped and re-dipped until the proper shade is obtained, or, in case of warps, also by passing over immersed rollers in a large vat, and finally over rollers exposed to the atmosphere; this is particularly suited for light shades.

Zinc-powder is much used in indigo-dyeing, supplanting copperas; for forty pounds of indigo about twenty pounds of zinc-dust are used. This vat is more economical than the preceding. Other vats are also employed,—viz., *hydrosulphite, German soda vat, urine, etc.,* but those detailed indicate sufficiently the character of the operation.

Logwood.—This dye-wood is used in the form of liquid or solid extracts, and as chips, and mainly for the production of blacks. The cotton is mordanted in a cold solution of acetate or nitrate of iron, squeezed, and the iron precipitated on the fibre by passing through a solution of carbonate of soda, and boiled in the logwood-bath; or the cotton is allowed to steep in a solution of tannin (sumach, galls, etc.) for several hours, then worked in dilute iron solutions as above,—this produces a tannate of iron,—followed by a passage through weak lime-water, and dye in a separate kettle. Acetate of alumina can be used with the iron, somewhat modifying the shade. A " chrome black " can be obtained by dyeing in a single bath of bichromate of potash, hydrochloric acid, and logwood; many modifications of this process are known. Gray shades can be obtained by first working in logwood, and afterwards in the copperas or bichromate of potash baths.

Of the *red dye-woods* little need be said, as they are now but seldom used; their coloring matters are fixed in the usual manner with tin, alumina, or iron mordants. Of the yellows, *Quercitron Bark* and *Fustic* are the most important; the former, used chiefly as an extract, is available for the production of greens, etc., in combination with other coloring matters. Fustic is used to shade logwood black. Turmeric is no longer used in dyeing.

*Application of the Artificial Coloring Matters to Cotton.**—In this section only the individual colors will be referred to, any attempt to discuss the production of *shades* by compounding would be beyond the scope of this publication.

Fuchsine is dyed upon tannin-prepared cotton, or upon cotton that has been worked in small quantities at a time in a bath of ten per cent. of neutral soap or Turkey-red oil, followed by an immersion in a warm bath of two hundred and fifty gallons water and one gallon acetate of alumina (9° Tw.). Work half an hour, wash, pass through a soap-bath for fifteen minutes, wash, squeeze, and dye. The color is added in successive portions until the required shade is obtained. *Safranine* is dyed upon a tannin mordant, or the tanned material is worked in a 3° Tw. bath of stannous chloride for an hour, washed, and passed through a two per cent. soap solution, and dyed at 140° F. *Methyl and allied Violets* can be dyed upon tannin as above, or pass the untanned cotton through a one per cent. olive-oil bath, squeeze, and dye at 100° F., or with the assistance of acetate of tin, or with alum and soda. The *basic greens*, including *Victoria Green, Methyl Green, Brilliant Green*, etc., are easily dyed upon cotton in the ordinary manner with a little (.5 per cent.) acetic acid.

The *Eosins*, with *Phloxin*, etc., are dyed in several ways: first, by passing the cotton through a two per cent. soap-bath, followed by an immersion for two hours in from two to three per cent. acetate of lead, washing well, and dyeing, cold, with a little acetic acid; or, second, by working in a dye-bath with eight to ten per cent. sulphate of soda, or the cotton can be worked in 5° Tw. bath of stannate of soda for an hour, worked for thirty minutes in a ten per cent. alum solution, rinsed, and dyed cold. *Rhodamin* is dyed on acetate of alumina exactly as for fuchsine. *Brilliant, Cotton,* and *Soluble Blues.* The cotton is tanned and dyed with five per cent. alum and one per cent. soda; or the tanned cotton can be worked in a 3° Tw. stannous-chloride bath for an hour, rinsed, and dyed at 150° F. If light shades are to be produced, work the cotton in a five per cent. soap-bath for an hour, squeeze, and work in a three per cent. tannin-bath, wring out, and dye with the assistance

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* Reference has been made in the preparation of this and subsequent sections on its application to several of the published trade circulars issued by the coal-

of tartaric acid and alum. *Victoria Blue.* Cotton is mordanted with tannin; dye with one per cent. acetate of alumina. *Methylene Blue.* This is an exceedingly valuable color to the cotton-dyer, as with it he can produce indigo shades. The cotton is mordanted with twenty-five per cent. sumach at 160° F. Give several turns, and allow to steep ten hours, wring out, and work for twenty minutes in two and one-half per cent. tartar emetic, wash, and dye in a bath prepared with acetic acid (three per cent.) at 75° F., gradually raising the temperature to 160° F. *Crocëin Scarlets* are dyed on cotton by working the untanned yarn in stannate of soda, wring, and pass for half an hour through sulphate of alumina, rinse, and dye. Cotton can also be dyed by passing first through stannic chloride, and then through acetate of alumina. Dye cold, or dye direct, with sulphate of alumina. *Auramin,* of considerable value, is dyed in the same manner as methylene blue. *Bismarck Brown* and *Chrysöidine.* Dye same as safranine; temperature 100° F. *Induline* and *Nigrosine.* Dye in same manner as for the cotton blues. *Paraphenylene Blue* is dyed upon tin or antimony, and tannin. The shades produced are very dark, and extremely fast; treated with bichromate of potash, the shade closely imitates, and is faster than, indigo. The substantive colors of the Congo and parallel groups are exceedingly valuable, for the reason that they are easily dyed upon unmordanted cotton, and that they are of exceptional fastness. The several *Congos, Benzo-* and *Delta-purpurin,* and *Rosazarin,* are dyed with two and one-half per cent. soap and ten per cent. sulphate of soda, or phosphate of soda, boil for one hour. *Hessian Purple* is dyed at a boil for half an hour with ten per cent. common salt, followed by a passage through dilute soda. *Chrysamin* is dyed with ten per cent. sulphate of soda and two and one-half per cent. soap at a boil. *Hessian Yellow* is dyed with ten per cent. of salt and a little Turkey-red oil. *Brilliant Yellow* and *Chrysophenin* are dyed with ten per cent. salt and two per cent. oxalic acid, work half an hour, squeeze, rinse, and dry. *Azo Blue,* and *Benzoazimine, Heliotrope,* etc., are dyed with ten per cent. sulphate or phosphate of soda and two and one-half pounds of soap, let stand, and skim the surface, add the dye, boil, and put in the yarn, and work for an hour, *boiling,* rinse the yarn, and dry at as low a temperature as possible. *Indigo shades* from *Benzoazimine* are obtained as above, but for every one hundred parts of color add three parts *Chrysamin.* All the substantive dyes act as mordants for a very large number of other colors, no other fixing agent being required. Diazotized and developed colors for cotton, of which primuline is the type are dyed in the usual way for a substantive color, then "diazotized" in a bath of nitrite of soda and a mineral acid, and afterwards "developed" by passing through a bath containing a developer, *e.g.,* β-naphthol, which develops and fixes the colors. Dark blues and blacks are largely dyed by this process specially for hosiery, on account of the fastness. (See p. 541.)

The important group of sulphur colors dye cotton various shades, the most important being the blacks, blues including indigo shades, cutch shades and olives. Cotton is dyed from alkaline dye baths prepared with sodium sulphide, common salt, and the necessary color. The shades are noted for their fastness except to chlorine.

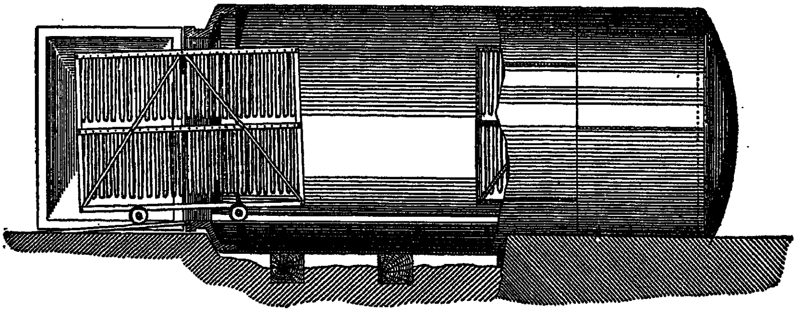
Another important group of cotton colors are the so-called "vat dyes" which dye cotton from baths containing the coloring matter in a reduced state, similar to indigo. The range of shades is very extensive, possessing very good fastness to general influences, including chlorine.

Aniline Black.—This color is produced directly upon the fibre during the dyeing by means of aniline oil in the presence of oxidizing agents; to obtain good results it is necessary that the oil used should be as pure as possible. Two methods are in general use,—*warm* (Grawitz patent) and the *cold.* In the former method, two thousand four hundred litres of water, thirty-two kilos. hydrochloric acid, sixteen kilos. bichromate of potash, and eight kilos. aniline oil are taken. The acid and aniline are each diluted with water and carefully mixed, the solution thus obtained being added to the main volume of water. The bichromate of potash is previously dissolved and added after the aniline. Immerse the cotton, and work for three-quarters of an hour in the cold, and then gradually raise the temperature to 60° or 70° C. In the cold method take eighteen kilos. hydrochloric acid, eight to ten kilos. aniline oil, twenty kilos. sulphuric acid, 66° Bé., fourteen to twenty kilos. bichromate of potash, and ten kilos. copperas. This bath is made up similarly to the previous one, with the exception that much less water is used. Aniline salts in solid form are often used instead of aniline oil and acid. The yarn is worked in one-half of the materials for an hour or so, after which the remainder is added, and the operation carried on for about one and a half hours longer, followed by a washing, and a boiling in a soap solution. In either case, the cotton after dyeing is subjected to a further oxidization with bichromate of potash, copperas, and sulphuric acid,—this having a tendency to prevent greening. Chlorate of soda is used considerably as an oxidizing agent in the dye-bath. Vanadium chloride, or vanadate of ammonia, has been recommended to be used with a chlorate in place of bichromate of potash; the proportion of the vanadium salt being to the displaced bichromate as 1: 4000. Another method is to produce the aniline black in powder form, purify it, liberate the base, which is dissolved in sulphuric acid, poured into water, and the precipitate formed thereby dissolved in caustic soda. This is reduced as in the case of indigo, and dyed in a similar manner.

Alizarin-dyeing, Turkey-red Process.—J. J. Hummel, in his "Dyeing of Textile Fabrics," 1886, p. 427, *et seq.*, details the *emulsion process,* which need not be described here. It may be stated, however, that beautiful results have been obtained from its use; the yarn passes through fourteen operations, as follows: boiling in soda and drying, worked in an emulsion of oil, dung, and carbonate of soda; passed through the previous process twice again; worked four times in carmordanted with alumina, dyed with alizarin (ten per cent.), sumach, and blood, cleared with carbonate of soda, final clearing with soap and tin crystals. To finish the dyeing requires about three weeks, but a real Turkey-red is produced. Except for some grades of goods, it is doubtful whether such a lengthy process would be profitable.

The following scheme of a process represents the type of a reasonably short one; it is well to remember that it can be modified to a considerable extent without altering its product. It is used in several establishments essentially as given. Boil the cotton for two hours in a 1.04 specific gravity solution of caustic soda, wash well in water, dry, and work in seven to ten per cent. solution of Turkey-red oil, squeeze, dry at about 115° to 120° F., steam in a chest, mordant with acetate of alumina (red liquor) at 80° Tw., and dry as before; work for an hour in a hot bath of five pounds of dung and eight to ten pounds of chalk, followed by a good wash, and pass to the dye-bath, made up of eight per cent. of alizarin, two per cent. Turkey-red oil, and about one per cent. of ground sumach, or equivalent in pure extract. Enter cold, and slowly increase the temperature to and maintain it at 160° F. for over half an hour. Dry, and steam in the chest as above. The final operation is a soaping with carbonate of soda and stannous chloride as in the above emulsion process.

FIG. 120.



An almost unlimited number of processes could be given, but it is hardly necessary, the principle remaining the same in every case. For full information reference is made to Hummel, Sansone, and Knecht, Rawson, and Löwenthal. The apparatus used for alizarin-dyeing is not special, with the exception of the machines for "padding," the material to be dyed with the oils and for working in the liquors; the most important is the steam-chest, which is essentially a large cylindrical wrought-iron drum with cast ends, one of which is provided with a well-closing door. The chest, or *steamer*, is provided with a steam-supply pipe, gauge, and safety-valve. The yarn or cloth is hung on sticks supported on rods inside, or, as shown in Fig. 120, mounted on iron carriages. Some chests are so built that the yarn contained can be turned while closed and with the steam pressure on, which seldom exceeds four or five pounds.

Ingrain Red, a color obtained from *primuline* or *polychromine,* is for some purposes a perfect substitute for Turkey-red, being fast to light, soap, and acids. Primuline is dissolved in warm water, common salt or sulphate of soda added, and the yarn worked in the bath until a good full yellow is obtained, when the material is washed, and immersed in a cold solution of nitrite of soda slightly acidulated with either hydrochloric or sulphuric acid, this causes a diazotizing of the yellow color, with the production of an unstable orange shade; the yarn is lifted out, washed rapidly, and at once dipped in a warm solution of *β-naphthol* in caustic soda, when a deep-red color is developed. The yarn is worked for a while, and afterwards well washed in water. If *phenol* or *resorcin* is substituted for the β-naphthol, a fast *yellow* or *orange* color, respectively, will be obtained. The diazotized yarn is very sensitive to the light: if it is not in a reasonable time developed, no color will be obtained; this fact is at the present time experimented upon with a view to its possible use in photography.

A more recent and still better substitute for Turkey-red is the azo-para-nitraniline obtained by diazotizing para-nitraniline C and developing with β-naphthol and red developer C. The cotton yarn is preferably first impregnated with the caustic soda solution of the developer, made with the addition of castor-oil soap, and then put in the diazotized solution.

Linen.—The uses to which fabrics made of this fibre are put demand colors that shall be fast to washing, light, and air; this requirement being satisfied by alizarin and indigo. The coal-tar colors, as a rule, are not applied, although they can be by treating the fibre in the same manner as cotton.

Jute, owing to its peculiar chemical structure, does not require any mordanting; all basic colors can be applied by simply boiling in a neutral bath. Some scarlets and a few of the acid colors are fixed with the assistance of a little acetic acid in the dye-bath, sometimes with a little sulphuric acid and alum.

Wool-dyeing.—Raw wool is dyed in the same manner as raw cotton, in open kettles, or in machines made for the purpose. *Woollen yarns* and *cloth* are similar in their manipulation to cotton, the apparatus being in both cases nearly the same. Dyeing-machines for carpet yarns are coming slowly into use, several forms being capable of handling a large quantity in comparison with hand labor.

Some classes of goods, *i.e.,* plushes, have cotton backs,—these being previously dyed in the hank and warp and then woven,—the face, or pile, is afterwards dyed in proper shade, care being taken to select such colors as will have no modifying effect upon the cotton color. For this purpose cottons dyed with aniline black, indigo, or alizarin are best suited.

Natural Coloring Matters applied to Wool.—Indigo, as extract, is now but little employed for dyeing wool on account of its fugitiveness, [illegible] used it is only for its cheapness. If other coloring matters pound shades, a *neutral* extract had better be used, and the dyeing done without the use of acid. *Wool* is dyed in a *vat,* where exceptionally fast and full shades are demanded, especially for army cloth. *Loose wool* is dyed in the so-called *fermentation-vat,* the wool being kept below the surface of the liquor, worked about by means of long rakes for a sufficient time, and taken out and put in large cord bags, or placed upon rope screens to drain and oxidize. It is finally dipped in very dilute acid to remove soluble impurities, well washed, and dried. *Woollen yarn* is worked in vats exactly as in the case of cotton. *Cloth* is worked in the vat below the surface of the liquid, by means of poles with hooks. The best indigo-dyed cloth is that made from wool which has been previously dyed in the raw state,—*dyed in the wool.*

Logwood.—This dyestuff is the real base of the blacks upon wool, the most generally followed method being with bichromate of potash as a mordant. Boil the wool in a bath of three per cent. bichromate and one per cent. sulphuric acid for an hour, lift out, rinse, and boil in a bath (made with a decoction of about forty per cent. chipped logwood) for an hour, lift the wool, and add a little extract of fustic, continue the boiling for a half-hour. Frequently blacks of the anthracene groups are used in combination with logwood to give increased fastness. To prevent a "greening," or development of greenish tinge on exposure of the goods to the light, a coal-tar color, such as "cloth red," is dyed on first, so as to neutralize the effect of the green shade which may form. For cheap work "*one-dip blacks*" are used,—these consist chiefly of a mixture of logwood and a mineral mordant, iron or copper. Wool can be mordanted with copperas, copper, and cream of tartar, etc., followed by dyeing in the logwood, or it can be worked in the logwood first, followed by a "development" in a bath of ferrous sulphate of iron and copper.

Logwood Blue, for some kinds of work, is an excellent substitute for indigo, full shades being obtained by direct dyeing, or by dyeing upon a light indigo bottom. Hummel gives the following method. Mordant the wool for one to one and a half hours at 100° C. with four per cent. of aluminum sulphate, four to five per cent. of cream of tartar; wash well, and dye in a separate bath for one to one and a half hours at 100° C., with fifteen to thirty per cent. of logwood and two to three per cent. of chalk. The addition of a little alizarin or tin crystals to the bath at the termination of the dyeing will cause the appearance of "bloom," peculiar to indigo.

The *red woods* are fast losing ground, although before the introduction of the artificial scarlets and cardinals they were much used. *Madder,* likewise, has been superseded by artificial alizarin. Wool was mordanted for browns with bichromate of potash as for logwood; for *reds,* mordant with alum, or sulphate of alumina, with cream of tartar (argols), and boil. Tin crystals and tartar produce a reddish-yellow. These colors were not brilliant, but the value of them depended upon their fastness. The use of *Cochineal* is mainly for the scarlets obtained therefrom. The wool is mordanted with tin crystals and cream of tar

tar, washed, and dyed in a bath with five to ten per cent. of cochineal (ground) for an hour. Another method is to boil the unmordanted wool in a bath of cochineal, tin crystals, and potassium oxalate for an hour. For *scarlets* with a bluish cast (*crimsons*) the wool is mordanted with aluminum sulphate and cream of tartar, or the wool can be mordanted in a bath containing tin crystals, tartar, and aluminum sulphate, followed by the dyeing in a separate bath. Copper, or iron, as a mordant will produce dark shades, and as impurities in the dye-baths will have a saddening effect upon the color obtained. *Fustic* is largely used in wool-dyeing, chiefly, however, in combination with other colors,—*i.e.*, indigo extract to produce greens, olives, sages, etc., and always upon mordanted wool, using tin crystals, sulphate of alumina, bichromate of potash, iron, and copper. *Quercitron Bark* is used for the same purpose as fustic and under the same conditions. *Flavin*, a production of the latter, is used in the same manner, its chief advantage is that it is much more concentrated. *Archil* (*Orchil*) as "extract," liquor, or paste is extensively used in the dyeing of carpet yarns; it is applied by simply boiling the yarn in a bath with the color, sulphuric acid, and sulphate of soda. It is exceedingly difficult to remove from yarn once dyed with it; a process which will economically accomplish this is much sought after by manufacturers.

Application of the Coal-tar Colors.—As a general rule, it may be stated that nearly all the soluble artificial colors can be dyed upon wool without any special treatment, by boiling in a bath with ten per cent. of sulphate of soda and two to four cent. of sulphuric acid. A few exceptions may be given: *Alkali Blue* (Nicholson's Blue). The color is dissolved in carbonate of soda, poured into the dye-bath, the wool entered, and the temperature raised to the boil, keep boiling for a while, lift, rinse well, and immerse in a bath of very dilute sulphuric acid, when the color will be at once developed. The *Violets* (Hofmann's, etc.) are dyed neutral, or with a little soap. *Methyl Green* is applied to wool with borax, after having been mordanted with hyposulphite of soda. and hydrochloric acid. *Auramine* is dyed both neutral and acid. The *Indulines* are dyed neutral, and then boiled in dilute sulphuric acid. *Gallëin* and *Cœrulëin* are dyed upon wool mordanted with potassium bichromate and a small quantity of acetic acid. The application of *Alizarin* to wool is exactly as for madder, the general mordant being sulphate of alumina and tartar for *reds;* tin crystals and tartar for *orange;* potassium bichromate and sulphuric acid for *red-browns;* iron and tartar yield *violet;* and copper, shades of *brown*. The addition of a little lime to the dye-bath is necessary in case none is naturally present in the water.

Nitro-alizarin (Alizarin Orange) produces with several metallic mordants, applied as above, a range of shades, which have not reached commercial importance. *Alizarin Blue* is dyed upon a chromium mordant, and yields a durable blue, of some value,—for wool, the price of bining alizarin or a derivative of the same with a base, such as aniline, give various fast shades, and are dyed nearly the same as the older alizarin blue and alizarin blue S, except that the bath may be exhausted with very little or no acid.

The constant tendency to do away with the mordanting processes for wool dyeing has caused the development of certain groups of dyestuffs, which yield shades of extreme fastness, and which are produced by dyeing the wool in the presence of the chrome salt, or by dyeing first and "fixing" the color by adding the chrome to the extracted dye baths, or after chroming in a separate dye bath. It is instructive to note that some of the dyes which produce such shades on wool are old and well known cotton substantive dyes.

The *mineral* colors are dyed upon fibres through the decomposition of metallic salts, for example, to dye *Prussian Blue,* the wool is worked in a bath of red prussiate of potash and sulphuric acid, and gradually brought to a boil, squeezed, rinsed, and dried.

Silk-dyeing.—Silk has a great affinity for the coal-tar colors, with which it can be dyed without any mordant, although it is customary to employ a soap-bath (boiled-off liquor) with or without the addition of a weak acid, usually acetic. If soap is not used the colors will appear streaky or spotted. For ribbons, fancy dress goods, plushes, etc., the above colors are solely employed, with the possible exception now and then of recourse to some natural coloring matter, the use of the latter being almost restricted to logwood for blacks and modified shades, including browns. Silk is dyed in skeins or hanks, warps, or pieces, this latter including plushes. The machinery is of the simplest kind, embracing the kettles, with and without winches, washing-machines, etc., and need not be especially described.

Silk is not dyed with indigo (vat process), but indigo shades are obtained by using indigo-carmine. Black is obtained by several processes. Work the silk in acetate of iron and wash, then in a warm soap solution, followed by an immersion in ferrocyanide of potash, washed, and worked again in the iron-bath, rinsed well, and steeped in a solution of catechu or gambir for ten or twelve hours and washed. This preliminary process is necessary in order to insure a good result if systematically carried out and not forced. The material is dyed in a logwood decoction containing soap.

To obtain heavily weighted goods, for blacks, the process of dipping in iron solution and then in tannin-containing liquors is often repeated several times. A method giving excellent results, and which is considerably used, is as follows: Wash the goods, and pass through a bath of nitrosulphate of iron, wash, and then through a solution of carbonate of soda. These two operations are repeated several times, each time causing the precipitation of more iron upon the fibre, and consequently "weighting" the silk. Work for some time in a bath of ferroprussiate of potash and then in a bath of catechu, followed with a little "muriate of tin" or tin crystals, wash, and transfer to the logwood-bath, which may contain a little extract of fustic to modify the shade required, then to a soap-bath. Every locality is not suited to black silk-dyeing on account of impurities in the water, careful purification of which is a special requisite. *Seal plushes* are dyed, first in a dye-bath in the ordinary manner, a dark-brown shade, followed by the application of a black, blue-black, or other color, in the form of a paste thickened with starch, gum, or other medium, the application of this being done on a machine provided with revolving brushes, and so regulated that only the *tip* or face of the piece of goods is coated. One important feature in plushes of this character, and also in other kinds of silk goods which have been heavily iron-mordanted, is that the natural lustre of the fibre is somewhat destroyed; this loss is supplied by means of a mixture of vegetable oils made into a paste with starch or other substance, applied as in the case of the *tip,* and steamed in an apparatus similar to that used for alizarin red (p. 540). The oil, usually a definite amount, is absorbed by the silk fibre under the influence of steam, imparting a permanent lustre. The goods, when removed from the steamer, are washed to remove the starch, excess of oil, etc., when they are ready for other operations.

"Dynamited" silk is silk weighted with stannic chloride (dynamite) and fixed with silicate and phosphate of soda, and for full fibres with sulphate of alumina. Weighting may be as high as 400 per cent.

A class of fabrics similar to plush, but with the *pile* of two or even three colors, much used for carriage-robes, etc., and dyed to imitate the skins of animals, are prepared in the following manner: The material (cotton in black with silk *pile,* the former previously dyed a fast color) is dyed, say a brown, in the ordinary manner; upon the fibre is then applied a discharge made of stannous chloride solution and permanganate of potash. This is so controlled that only one-half of the fibre is acted upon. When the effect is produced the excess is washed off, rinsed, dried, and, if necessary, a *tip* is applied, which only dyes the very face of the pile. In this manner three colors are obtained on each thread of the face. After treating as above, the whole may be dyed a very light shade, thereby producing modified effects.

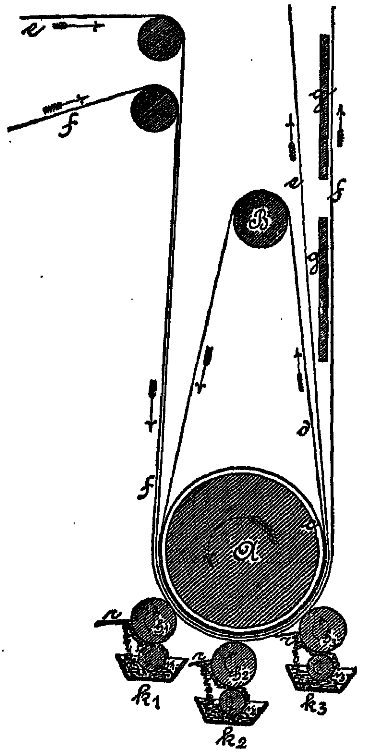
The artificial coloring matters are applied to silk as previously stated. *Nicholson's Blue* (Alkali Blue) is applied as directed for wool, and seldom for the production of mixed shades. *Picric Acid* is much used for compounding, especially for greens, faster colors can be obtained by using naphthol yellow and indigo-carmine. The *Eosins* yield beautiful colors, and are applied in a soap-bath followed by a brightening in dilute acid. The *Azo* dyes are applied with a neutral soap-bath.

The use of *Alizarin* with silk is only in cases where fastness is of more importance than brilliant shades. *Alizarin Black* is being much used in dyeing *mohair goods* (astrachans), and is applied in the ordinary manner.

E. Printing Textile Fabrics.—A brief outline of the more important "*styles*" in use is all that will be attempted in this section, two main groups, differing in the manner of applying the colors,—namely, *Direct Printed Colors* and *Dyed Colors.*

Direct Printing is done by mixing the desired color with the proper fixing agents and applying directly to the fabric by means of blocks engraved with the design, or in a machine provided with a cylinder upon which the design is likewise engraved; for each color to be applied a separate cylinder is needed. From the above it is obvious that the color so applied will appear only on those portions of the fabric brought in contact with the design.

FIG. 121.



Dyed Colors are obtained by printing different mordants upon the cloth, as above, and fixing as for ordinary cloth, and then dyeing the whole, or, by printing upon the cloth *resists,* substances which will prevent the dye from becoming fixed at those places so printed, or, again, by dyeing the whole pieces first, and then producing patterns or designs by means of substances which will destroy the ground-color whenever brought in contact; these substances are called *discharges.* This broad definition is deemed sufficient for the purpose intended; the principle of each style will be apparent upon following the methods hereafter given.

The operations conducted in a print-works embrace as a preliminary *bleaching,* the details of which are referred to on p. 524. Then the preparation of the colors, which is always done in copper pans mounted in such a manner that they can be emptied easily, and that their contents can be boiled by steam, and cooled by water, facilities for this being done by means of steam and water trunnions connecting with the double bottom of each pan. From five to eight pans are supplied in a "battery," although it is often convenient to have one or more pans separately mounted, and without steam taps. The agitation of the contents is performed either by means of wooden paddles or, preferably, by mechanical agitation, which can be raised clear above the top of the pan, and without interfering with the working of the others. As the majority of colors used are made with either starch or flour for thickening, it is necessary, to insure good results, that they are strained or filtered; for this purpose it is well to have wooden frames made, over which is tacked brass or copper wire cloth (iron is inadmissible). The most important piece of apparatus is the printing-machine, an idea of the construction and operation of which may be had from Fig. 121. *A* is a cylindrical " bowl " or drum, covered with several thicknesses of felt cloth, *c;* around this drum, and passing over a smaller one, *B*, is an endless band, *d* (full width of the machine); over this band, and acting as a guide to the fabric to be printed, is another band, *e*, which serves to keep *d* clean, being, in fact, a piece of cloth yet to be bleached and printed; the piece being printed is indicated by *f*. The means for applying the color are shown in the figure below the large drum,—viz., the printing rollers or engraved cylinders h_1, h_2, h_3, which are fed with color through coming in contact with the wooden rollers n_1, n_2, n_3, which dip in the color contained in the troughs k_1, k_2, k_3. Pressing against each of the rollers, *h*, is shown a small strip of metal, *r*, technically termed the " doctor," the purpose of which is to remove the excess of color from the face of the printing-rollers before they come in contact with the cloth. These " doctors " are best made of bronze or gun-metal, or some of the newer aluminum-copper alloys,—capable of better resisting weak acid. Before the cloth is printed upon it passes over a "lint doctor," the office of which is to remove any loose hair or fibres from the cloth. Printing-machines are built with any number of color boxes and rollers up to twelve or fourteen, each being for a separate color. Sansone mentions one for use with twenty colors. Great nicety is required in adjusting the machines in working to have no overlapping of colors or mordants,—perfect " registration " being sought.

For drying the printed goods revolving cylinders, or " cans " of large diameter, are used, or the goods are passed over heated plates, in no case allowing the printed face to come in contact with any part of the apparatus. Steaming follows to fix the colors, the apparatus being a steamer, as shown on p. 540, or one constructed of brick and iron, acting continuously, thereby turning out much more work than the former. The dyeing- and washing-machines are similar to those already described.

Mordants, Resists, Discharge, etc.—All the various substances used in printing must be applied in the form of pastes, the consistency of which must be such that whenever applied they will not run or spread, which impairs the sharpness of outline of the printed pattern. For the purpose the color-mixer has recourse to the starches and gums, the most important of which are *corn* or *wheat starch*, and *flour*, usually made up into ten per cent. pastes. The gums include *gum arabic*, *dextrine* (*British gum*), and *tragacanth*. The first is used in several degrees of consistency, from a fifty to a one hundred and fifty per cent. solution, dextrine the same, and the last in a ten per cent. paste. The proportions are by no means uniform, but they represent the average strengths used in the color house. *Blood albumen* is considerably used, large quantities being manufactured cheaply in Chicago and other Western localities. The mordants used embrace the acetates of alumina of various strengths, basic sulphate, and others of less importance. The acetates and nitrates of iron are the most prominent salts of this element, to the great number of recipes published for preparing mordants, and of the difficulty in selecting those which may be called representative, only a few will be given of the more important.

Acetate of Alumina, or "Red Liquor" (Crookes).—

Water	45 gallons.	45 gallons.
Alum	100 pounds.	200 pounds.
Acetate of lead	100 "	200 "
Soda crystals	10 "	10 "

Or the same result can be had by substituting acetate of calcium for the lead salt. In either case the alumina salt is dissolved in about half the quantity of water, and the acetate in the remainder, when the two solutions are mixed and allowed to settle, the precipitated lime or lead sulphate being removed. The addition of soda is to neutralize any free acetic acid.

Acetate of Iron, or "Black Iron Liquor," can be obtained either by double decomposition as above, or by dissolving scrap-iron or precipitated oxide of iron in crude acid. In the former method sulphate of iron and acetate of lead are used as follows: Water, forty pounds, sulphate of iron, twenty-four pounds, acetate of lead, twenty-four pounds. Dissolve each separately, mix, and filter. The oxide of iron above mentioned is obtained by precipitating a solution of copperas with ammonia or soda, filtering and washing, and dissolving the moist precipitate in ordinary acetic acid to make a twenty-five per cent. solution. In the event of using soda, much longer washing is required.

Nitrate of Iron is made as above; copperas and nitrate of lead being used for the decompositions in equal proportions. Nitrates made by direct solution are obtained by several methods, the best being nitric acid nearly saturated with scrap-iron and diluted to about 80° Tw. Some of the so-called nitrates of iron are mixtures of sulphate and nitrate of iron and some are composed entirely of sulphate of iron, while others are waste liquors, such as are obtained by dissolving iron out of "tin scrap" by means of sulphuric acid. Others may contain hydrochloric acid, with or without the addition of copperas. *Chromium Acetate* is similarly prepared with chrome alum and lead acetate, or by precipitating chrome alum with an alkali, and dissolving the washed precipitate in acetic acid, or in nitric acid if the nitrate is wanted. This latter mordant can be made by using lead nitrate and chrome alum.

The tin mordants are used to brighten the color with madder and cochineal dyeing. The first is *Stannous Chloride,* $SnCl_2 + 2H_2O$. It is made by dissolving tin in hydrochloric acid and evaporating the solution. It is used somewhat in wool-dyeing, but more largely in calico-printing. Stannic chloride, $SnCl_4$, is also used, and its combination with sal ammoniac known as "Pink Salt," and *Sodium Stannate,* Na_2SnO_3, known as "Preparing Salt."

The principal styles of printing tissues are given in the following

PRINTED (DIRECT) COLORS.

1. *Steam or Extract Styles.*
   - (*a*) *Coal-tar Colors.*
     - *Alizarin, Basic Aniline Colors, Acid Colors, and Neutral Azo Colors.*
   - (*b*) *Dyewood Extracts* (natural organic coloring matters).
     - *Logwood, Quercitron Bark, Sapan and other Red Woods, Catechu, Annatto, Cochineal.*
   - (*c*) *Steam Mineral Colors.*
2. *Pigment Styles* (fixed by albumen).
3. *Oxidation Colors.*
4. *Direct Indigo-printing* (alkaline styles).

DYED COLORS.

5. *Alizarin Dyed Styles.*
6. *Turkey-red Styles.*
7. *Indigo Styles.*
8. *Manganese Bronze Styles.*

1. *Steam Styles.*—Here the colors and proper mordants are mixed, and applied to the fabric in one operation, followed by air drying and steaming, or by immediate steaming, drying, and again steaming, the object in each case being to fix and develop the colors. Several conditions are to be noted in this style, chiefly the humidity of the steam, temperature, pressure, and the duration of the steaming, in order that the same shades may be again obtained with the same colors. Before being printed the cloth is passed through a solution of stannate of soda, also called "preparing salt," and then through sulphuric acid (1.005 to 1.015 specific gravity), washed, and dried. The colors best suited are the basic,—that is, those which form insoluble lakes with tannin in combination with a metal, and the general method of applying the same is given in the following extract from Sansone ("Printing"), p. 208: "A color is formed consisting of thickening, the solution of coloring matter, and acetic acid. The acetic acid is added in the preparation of the color in order to prevent the tannic acid from combining with the dyestuff; in other words, the acetic acid keeps both the coloring matter and the tannin in solution in the thickened color, and prevents their combining with each other; but when the color is printed and the cloth is dried and steamed, the acetic acid is expelled, and the coloring matter and the tannin then go into combination to form the insoluble colored lake. This lake, however, not being sufficiently fast to stand by itself, a metallic mordant is necessary to give additional fastness to the colors; for this reason the cloth, after printing, dyeing, and steaming, is passed into a solution containing tartar emetic." The antimony of which at once unites with the "tannate" of the color already on the fabric, thereby producing a more insoluble body. The steaming operation must be conducted with such a volume of steam that the acetic acid volatilized can be carried away, or else the colors may be injured. Of

Alizarin, without exception, is the most important coloring matter used in cotton-printing, for which purpose the goods are previously treated with alizarin oil and dried. With alizarin in printing, as in dyeing, the color obtained depends upon the selection of the mordant, which can, however, be a mixture; for *reds,* alumina, with or without tin; *purples,* iron; *browns,* with either ferricyanide of potassium or acetate of iron, and acetate of alumina, or with chromium mordants. When the fabrics have been printed they are steamed for one or two hours, and passed through a heated chalk-bath, washed, and soaped. The following indicate the methods of preparing several colors:

Red. (Standard.)

Alizarin paste (fifteen per cent.)	6	pounds.
Starch paste	2	gallons.
Acetate of alumina (11° Bé.)	1¼	pints.
Acetate of lime (15° Bé.)	1	pint.
Nitrate of alumina (13° Bé.)	¾	"

Purple. (Standard.)

Alizarin	2	pounds.
Starch paste	1	gallon.
Acetate of iron (13° Bé.)	1	quart.
Acetate of lime (13° Bé.)	1	pint.
Acetic acid	1	"

Brown. (Standard.)

Alizarin (fifteen per cent.)	4	pounds.
Starch paste	1	gallon.
Nitro-acetate of chromium (25° Bé.)	3	pounds.
Acetate of lime (13° Bé.)	¼	pound.

Since the introduction of the alizarin greens and violets, their use in connection with chromium in cotton-printing has been most rapid.

Dye-woods, with the exception of logwood, have been nearly superseded by the tar colors. The method of applying the color is nearly the same as for other steam colors,—viz., print, dry in the air, steam, and wash, and is made up with chromium as the mordant, and an oxidizing agent, with or without the presence of another coloring matter to modify the shade.

The following recipes illustrate the color as made for blacks:

Steam Logwood Black. (Sansone.)

Water	1	gallon.
Acetic acid (6° Tw.)	1	"
Logwood extract (30° Tw.)	1	"
Quercitron bark extract (30° Tw.)	2	pounds.
Starch	5	"
Dextrine	2.5	"
Olive oil	.5	pound.
Chlorate of potash or soda	.75	"
Boil, stir until cold, then add		
Acetate of chromium (20° Tw.)	1	gallon.

Steam Logwood Black. (Sansone.)

Starch	6	pounds.
Flour	6	“
Acetic acid (6° Tw.)	2.5	gallons.
Logwood extract (20° Tw.)	3.5	“
Acetate of iron (15° Tw.)	3.5	“
Olive oil	1.5	pounds.

Of the other natural coloring matters there may be mentioned *Cochineal*, applied with *tin* or *alumina; Sapan,* in the same manner, an *Quercitron Bark,* with *alumina* or *chromium. Catechu,* most used fo *browns,* may be applied with acetate of chromium or with logwood an fuchsine.

The *Mineral Colors* are to some extent made use of, their applicatio depending upon the principle of double decomposition upon its fibr when subjected to steaming. The following examples will make th principle clear: Yellows are obtained by the decomposition of nitrat of lead and a soluble chromate, the insoluble *chromate of lead* (“ chrom yellow ”) being formed. For Blues, both prussiates of potash are used Brown is obtained by means of chloride of manganese and bichromat of potash.

2. *Pigment Styles.*—For this style effects are produced by means o insoluble color lakes and the mineral colors, which are fixed upon th cloth by steaming, the action of which coagulates the albumen wit which the colors are invariably mixed for printing. The colors are generally supplied to the color-mixer in a dry condition, and include *Ultramarine* of various qualities, *Vermilion* (sulphide of mercury), the *Chromates of Lead and Barium, Cadmium Yellow* (cadmium sulphide) *Chrome Green* (oxide of chromium), the *Ochres,* yellow and red, an *Lamp-black.* A familiar example of this style is seen in cheap flags an decorative muslins.

3. *Oxidation Colors.*—The most important of this class is *Anilin Black,* and will be briefly outlined as follows: Aniline oil is made into paste with a chlorate (soda generally) and a metallic salt, with th proper amount of starch paste. This is printed upon the fabric “ aged ” for forty-eight hours, or passed through a “ steam ager,' then passed through a warm bath of bichromate of potash, washed well and finally worked through a soap-bath. The metallic salt mentione acts as a carrier of oxygen, and for the purpose vanadate of ammonium sulphide of copper, bichromate of potash, etc., are used. For the preparation of the color paste the following methods are given:

1. Water	1	gallon.
Aniline salt	2	pounds.
Aniline oil	2	“
Starch	2	“
Dextrine	½	pound.

The paste is made first with the starch and dextrine, then the aniline is added.

2. Chlorate of soda (8° Bé.)	1	gallon.
Starch	2	pounds.
Dextrine	½	pound.
Chloride of ammonium	½	"

These are made separately, but when wanted are mixed, and two pounds of *sulphide of copper* paste are added, and the whole well mixed and strained. (Crookes.)

The use of vanadium is shown by the following method (Sansone, "Printing," p. 275):

Water	1	gallon.
Starch	1½	pounds.
Dextrine	¾	pound.
Boil, cool down to 120° F., then add		
Aniline oil	1½	pounds.
previously neutralized with		
Hydrochloric acid (32° Tw.)	1½	pounds.
Stir until cold, then add a cold solution of		
Chlorate of soda	¾	pound.
Boiling water	1	"
Before printing add further		
Vanadium solution	½	"

Print, dry not too hard, age two days, then pass through two per cent. solution of bichromate of potash at 160° F., wash and soap.

The vanadium solution is made with vanadate of ammonia, hydrochloric acid, glycerine, and water, and contains about .15 gramme per litre.

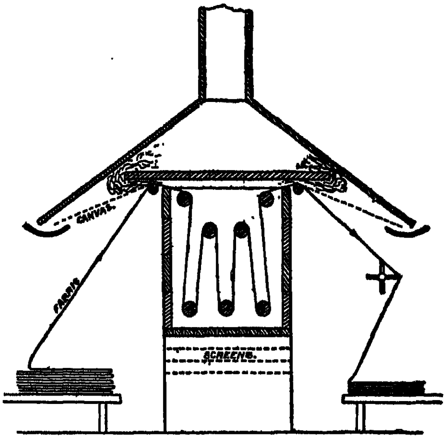
Other colors are produced by oxidation,—namely, Brown (with phenylendiamine, Sansone), by simply printing with a chlorate, drying, and steaming, Yellow, Grays, Olives, Blues, etc. To obtain white patterns on goods printed with aniline black, a "*resist*" or "*reserve*" is first applied of the desired pattern, consisting of white arsenic as the base, with caustic soda, and the proper thickening. For *discharging* the aniline black after it is printed, permanganate of potash is used; the goods are afterwards passed through a solution of oxalic acid.

4. *Indigo-printing.*—Indigo is printed upon cotton fabics in two ways, one of which is known as the "Glucose," and the other the "Reduced Indigo" Process. The former is carried out as follows: Indigo is finely ground, and made into a paste with water, to which is added caustic soda; this is now kept in a closed vessel in order to prevent as much as possible the absorption of carbonic oxide from the atmosphere. When used in printing, it is thickened with dextrine and starch; the following table (from Sansone, "Cotton-Printing," p. 284) showing the proportions used for several shades:

Light calcined starch	3	parts.	3	parts.	3	parts.
Indian corn starch	1½	"	1½	"	1½	"
Water	3¾	"	3¾	"	3¾	"
Caustic soda lye (70° Tw.) .	16	"	28	"	40	"
Indigo paste	30	"	18	"	6	"

The cloth, before being printed upon, is worked through a twenty-five per cent. solution of glucose and dried. After printing, the cloth must be again dried and passed through an atmosphere of wet steam, in an apparatus shown in Fig. 122, to effect the reduction of the indigo, which now takes place. The cloth is now washed in water, being repeatedly, during the washing, exposed to the air, when the *reduced* indigo is oxidized and its real color appears. The reason for rapidly steaming is to act upon the caustic alkali while it is still in that state, as if it should become carbonated through delay little reduction will take place. This method is employed in printing indigo upon alizarin-dyed goods and in other combinations with resists, etc.

FIG. 122.



The "*Reduced Indigo Process*" is based upon the fact that indigo, when finely ground and mixed with lime and thiosulphate of soda in suitable thickening agents, is reduced; if, with this reduced indigo paste, patterns are printed upon cotton fabrics, and then exposed to the air, the indigo is oxidized with a regeneration of the blue color. The pieces are then washed and dried.

Instead of using indigo in printing, one of the newer colors, *Immedial Blue,* is now very extensively used and printed with suitable mordants directly upon the goods.

5. *Dyed Alizarin.*—This process differs from all those previously mentioned in that the colors are produced by first *printing* upon the fabric the thickened mordants suited to alizarin, *ageing,* during which the mordants so printed are decomposed and more firmly fixed upon

discharges, which may or may not be made so as to yield colored patterns. The base is citric or tartaric acid, thickened with a suitable paste, and if for colors, containing a salt of lead if for a yellow discharge, or ferro-prussiate of potash for a blue discharge, or iron and logwood for a black discharge. After printing on the discharges, the goods are passed through a bath of bleaching-powder, well washed, and then, if lead has been printed on, passed through a bath of bichromate of potash, when chrome yellow will be produced. If the prussiate of potash has been printed, a blue color will be developed. Green is obtained by mixing both discharges first.

7. *Indigo Styles* are similar to the above; resists are printed on the cloth, which is then dyed in the vat in the ordinary manner, when, upon a removal of the resist by suitable means, white patterns are had upon a blue ground. By the system of discharges various colors may be put on by means of lead and other metallic salts. Vermilion is applied directly with albumen. For a discharge which has to be afterwards dyed red with alizarin, bromide of manganese and an aluminum salt are used.

8. *Manganese Bronze Style,* or *Bistre Style.*—This process has for its object the production of hydrated peroxide of manganese upon the fibre, and the subsequent printing of colors by means of discharges. The goods are worked in a solution of manganous chloride, dried, and worked in soda lye, washed and passed through a solution of chloride of lime until a brown color is produced. Wash, dry, and the goods are ready for printing. A discharge for white is made with muriate of tin (120° Tw.); for blue, yellow prussiate of potash with an organic acid; for yellow, a lead salt, developed with bichromate of potash. Green and black as in the previous style.

Woollen- and Silk-printing.—*Wool,* either as yarn or fabric, is generally printed with the tar colors, and according to the steam style previously described. The goods are dried after printing, steamed for one hour, and well washed. *Silk* is printed in the same style after being prepared by suitable agents, such as tin with or without an acid. Previous to being printed both silk and wool must be entirely free from grease. Silk warps for ribbon and veiling are often printed by hand blocks, and with aniline colors dissolved and thickened with Irish moss. After printing, the warps are simply air dried—being neither washed nor steamed. Such colors are not fast, but they are much used for so-called " Dresden " and " Persian effects."

The following table from Rupe's "Chemie der Natürlichen Farbstoffe" Braunschweig, 1900) shows the artificial dye-colors which have replaced or are in practical use competing with the natural dyestuffs named:

NATURAL DYESTUFFS.	Is displaced for cotton.	Is displaced for wool and silk.
QUERCITRON	Mainly by substantive dye-colors: *Diamine fast yellow B A* (C.), *Chloramine yellow* (C.), *Chrysophenine* (C.), *Auramine* (H. G.), *Diamine yellow* (H.), *Chrysamine* (H.), *Thioflavine* (G.). For printing along with logwood it is still used as before.	Is not much used now, the different mordant coloring yellows having taken its place. In addition, *Naphthol yellow S* (H.), *Tartrazine, Quinoline yellow* (H.).
PERSIAN BERRIES . .	Are still much used in cotton-printing and in connection with tin salts. For direct printing compete: *Auramine, Thioflavine T* (C.), the latter exclusively for discharges; in addition, *Chrysophenine* (H.), *Chloramine yellow* (H.), *Oriol* (G.). Important are also the yellow salicylic acid azo colors, such as *Alizarin yellow* (H.), etc.	Little used for wool, For silk replaced by *Tartrazine, Fulling yellow* (C.), *Naphthol yellow S* (H.).
WELD	Is hardly ever used for cotton.	Is little used for wool, but, on the other hand, largely for silk. Is replaced by *Naphthol yellow S, F[illegible] yellow* (C.), *Tartrazine, Fulling yellow* (C.), [illegible] (G.), *[illegible]mine* (G. H.), [illegible] *yellow* (G.), *Alizarin yellow* (H.).
FUSTIC	Almost entirely displaced by the substantive yellow dyes, as with quercitron. In addition, *Sun yellow* (G.), *Diphenyl fast yellow* (G.), *Cresotin yellow* (G.), also by *Alizarin yellow* and its homologues (H.). For printing in connection with logwood it is still unreplaced.	Is still much used in wool-dyeing, although strongly pushed by the different mordant-attracting yellows: *Anthracene yellow C* (C. G.), *Chrome yellow* (C. G.), *Mordant yellow* (C. G.), *Fulling yellow* (C.), *Azo yellow* (H.), *Fast yellow* (H.), *Alizarin yellow* (H.).
LOGWOOD	In cotton dyeing (for black) is about given up. For better goods is replaced by *Aniline black, Diaminogen black* (C.), for cheaper goods by the direct dyeing and diazotizable blacks: *Diamine black* (C.), *Oxydiamine black* (C.), *Columbia black* (C.), *Direct deep black* (C.), also by *Vidal black, Immedial black* (G. H.), and similar sulphated products.	With wool the case is the same as with cotton. It is still used for dyeing, but is losing ground rapidly. The substitutes are: *Naphthol* and *Naphthylamine black* (C. G. H.), *B[illegible] black* (C. G.), *Diamond black* (C. G. H.), [illegible] *black* (C.), *Alizarin black* (G. H.), *Anthracene black* (C. G.), *Azo acid black* (H.), *Chromotrope S* (H.). For silk, still used enormously and with no substitute.
BRAZIL-WOOD	For cotton scarcely used now, being replaced by the substantive dyeing reds: *Diamine fast red F* (C.), *Congorubine* (C.), *Diamine bordeaux* (C.), *Benzopurpurine* (G. H.), *Diamine red* (H.), also by *Fuchsine* (G. H.), *Hessian purple* (G.), *Safranine*, (H.), *Paranitraniline red* (H.), *Alizarin red* (H.).	Also for wool and silk almost entirely replaced by *Cloth red* (C.), *Wool red* (C.), *Acid fuchsine* (G.), *Fast red* (H.), *Archil substitute* (G.), *Ponceau* (H.), *Apollo red* (G.), *Rocellin* (G.); in the fulling industry by *Alizarin red* (C. H.), *Diamine fast red* (C.), *Chromotrope* (H.).
COCHINEAL	. . . .	Is still used somewhat for wool and silk, but is being displaced by vivid acid wool colors, such as *Azoeosin* (G.), *Chromazon red* (G.), *Palatine scarlet* (H. C.), *Brilliant crocëin* (H.), *Brilliant cochineal* (C.), and the different *Ponceaux*, etc.
ARCHIL	. . . .	Has practically been entirely displaced for wool and silk by the readily levelling red acid wool dyes: *Acid fuchsine* (C.), *Azocarmine* (C. G. H.), *Archil substitute* (C. G. H.), *Azofuchsine* (C. G. H.), *Lanafuchsine* (C.), *Azorubine* (C.), *Azo acid fuchsine* (H.), *Rosinduline* (G.), *Apollo red* (G.), *Chromotrope* (H.).
ANNATTO	For cotton is replaced by the different artificial orange colors, as	. . . .

NATURAL DYESTUFFS.	Is displaced for cotton.	Is displaced for wool and silk.
SAFFLOWER	Was first replaced for cotton by the *Eosines*, *Phloxine* (C. G.); later these were displaced by *Rhodamine* (C. G.), *Erica* (C.), *Diamine rose* (C.), *Geranine* (C.), *Safranine* (H.), etc.	. . . .
BERBERINE	. . . .	Is not used for wool, but still somewhat for silk. Substitutes are the same as those mentioned for Weld.
CATECHU	Still used for cotton, although a whole series of excellent substantive dyes have appeared. Especially have the *Diamine* colors, *Benzo* and *Congo* colors with supplementary treatment with chrome and copper, recently competed successfully (C.), and *Chrysoidine* (H.), *Vesuvine* (H.), etc. For calico-printing, catechu is still very largely used, although the different *Alizarin* colors are seeking to displace it in part (C.).	Still used for silk in combination with logwood in large amount without any competing products (C.). For weighting of silk.
INDIGO	Despite the many seriously competing products is still much used for cotton. These competing products are: *Synthetic indigo*, *Indoin* (C. G. H.), *Naphthindon* (C.), *Fast cotton blue* (C.), *Methylene blue* (C. H.), *Indamine blue* (H.), *Janus blue* (H.), and the direct coloring and diazotizable blues of the Diamine, Diphenyl, and Benzo color groups. [*Diamine blue* and related colors (H.), *Diaminogen blue* (C. H.).] A new product, *Immedial blue* (C. H.), belonging to the sulphated colors, which has recently appeared, seems to be among the most important substitutes. In calico-printing, Indigo has been in part replaced by the *Synthetic indigo* preparations and by the different basic blues, including *Nitroso blue*, *Alizarin blue*, etc. (C.).	On wool, is replaced on the one hand by *Alizarin blue* (C. G. H.), *Synthetic indigo*, *Alizarin cyanine* (C. G. H.), *Anthracene blue* (G. H.), *Chromotrope F B* (H.), *Gallamine blue* (G.), *Gallocyanine* (G.), and on the other hand by *Sulphocyanine* (C.) and *Lanacyl blue*. However, the application of Indigo to wool still holds out relatively well.

The communications upon which this table is based were from the firms of Leopold Casella & Co., of Frankfurt-am-Main (C.), Joh. Rud. Geigy & Co., of Basel (G.), and Farbwerke, vormals Meister, Lucius and Brüning, of Höchst (H.).

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APPENDIX.

I. The Metric System.

THE French *metric* system is based upon the idea of employing, as ie unit of all measures, whether of length, capacity, or weight, a uni-orm unchangeable standard, adopted from nature, the multiples and ibdivisions of which should follow in decimal progression. To obtain ich a standard, the length of one-fourth part of the terrestrial meridian, xtending from the equator to the pole, was ascertained. The tenillionth part of this arc was chosen as the unit of measures of length, ad was denominated *meter*. The cube of the tenth part of the meter as taken as the unit of measures of capacity, and denominated *liter*. he weight of distilled water, at its greatest density, which this cube is ipable of containing, was called *kilogram*, of which the thousandth part as adopted as the unit of weight, under the name of *gram*. The multiles of these measures, proceeding in a decimal progression, are distinuished by employing the prefixes, *deca, hecto, kilo,* and *myria,* taken rom the Greek numerals; and the subdivisions, following the same order, y *deci, centi, milli,* from the Latin numerals. Since the introduction f this system it has been adopted by the principal nations of Europe, xcepting Great Britain, and in many of them its use is compulsory. t is in general use in France, Germany, Austria, Italy, Spain, Norway, weden, Netherlands, Switzerland, Greece and British India. It was egalized in Great Britain in 1864, and in the United States by an act f Congress in 1866.

The *meter*, or unit of length, at 32°, = 39.370432 inches.
The *liter*, or unit of capacity, = 33.816 fluidounces. *U. S.*
The *gram*, or unit of weight, = 15.43234874 Troy grains.

Upon this basis the following tables have been constructed:

MEASURES OF LENGTH.

		English inches.			English inches.
Iillimeter (mm.)	=	.03937	Decameter (Dm.)	=	393.70432
entimeter (cm.)	=	.39370	Hectometer (Hm.)	=	3937.04320

MEASURES OF CAPACITY.

		English cubic inches.			English cubic inches.
Milliliter (ml.)	=	.061028	Decaliter (Dl.)	=	610.280000
Centiliter (cl.)	=	.610280	Hectoliter (Hl.)	=	6102.800000
Deciliter (dl.)	=	6.102800	Kiloliter (Kl.)	=	61028.000000
Liter (l.)	=	61.028000	Myrialiter (Ml.)	=	610280.000000

MEASURES OF WEIGHT.

		Troy grains.			Troy grains.
Milligram (mg.)	=	.0154	Decagram (Dg.)	=	154.3234
Centigram (cg.)	=	.1543	Hectogram (Hg.)	=	1543.2348
Decigram (dg.)	=	1.5432	Kilogram (Kg.)	=	15432.3487
Gram (gm.)	=	15.4323	Myriagram (Mg.)	=	154323.4874

EQUIVALENT WEIGHTS AND MEASURES.

1 kilometer = 1093.61 yards
or 0.621 statute mile
1 square meter = 10.764 square feet
1 cubic meter = 35.3 cubic feet
1 liter = 1 quart and ½ gill U.S. measure
or 1 pint and 3 gills Imperial measure
1 cubic centimeter = .061 cubic inch
or 0.03381 fluidounce
1 hectoliter = 26.4 U. S. gallons
or 22.01 Imperial gallons
1 kilogram = 2.204 lbs. avd.
or 2 lbs. 3 ozs. 4⅜ drams
1 inch = 25.4 millimeters

1 foot = 0.3048 meter
1 yard = 0.9144 meter
1 square foot = 0.0929 square meter
1 cubic inch = 16.3872 cubic centimeters
1 cubic foot = 0.02832 cubic meter
1 pound avd. = 453.5925 grams
1 ounce avd. = 28.3495 grams
1 grain = 0.0648 gram
1 U. S. gallon = 3.78543 liters
1 Imperial gallon = 4.54346 liters
1 U. S. quart = 0.94636 liter
1 fluidounce = 28.396 cubic centimeters

I. Tables for Determination of Temperature.

RELATIONS BETWEEN THERMOMETERS.

In *Fahrenheit's* thermometer, the freezing-point of water is placed at 32°, and the boiling-point at 212°, and the number of intervening degrees is 180.

The *Centigrade* or *Celsius's* thermometer, which is now recognized in the U S. Pharmacopœia and has been adopted generally by scientists, marks the freezing-point *zero*, and the boiling-point 100°.

From the above statement, it is evident that 180 degrees of Fahrenheit are equal to 100° of the Centigrade, or one degree of the first is equal to $\frac{5}{9}$ of a degree of the second. It is easy, therefore, to convert the degrees of one into the equivalent number of degrees of the other; but in ascertaining the corresponding points upon the different scales, it is necessary to take into consideration their different modes of graduation. Thus, as the zero of Fahrenheit is 32° below the point at which that of the Centigrade is placed, this number must be taken into account in the calculation.

1. If any degree on the *Centigrade* scale, either above or below zero, be multiplied by 1.8, the result will, in either case, be the number of degrees above or below 32°, or the freezing-point of *Fahrenheit.*

2. The number of degrees between any point of *Fahrenheit's* scale

THERMOMETRIC EQUIVALENTS.

According to the Centigrade and Fahrenheit Scales.

C.°	F.°	C.°	F.°	C °	F.°	C.°	F.°	C.°	F°.
—39.4	—39	—17.2	1	5	41	27.2	81	49.4	121
—39	—38.2	—17	1.4	5.5	42	27.7	82	50	122
—38.8	—38	—16.6	2	6	42.8	28	82.4	50.5	123
—38.3	—37	—16.1	3	6.1	43	28.3	83	51	123.8
—38	—36.4	—16	3.2	6.6	44	28.8	84	51.1	124
—37.7	—36	—15.5	4	7	44.6	29	84.2	51.6	125
—37.2	—35	—15	5	7.2	45	29.4	85	52	125.6
—37	—34.6	—14.4	6	7.7	46	30	86	52.2	126
—36.6	—34	—14	6.8	8	46.4	30.5	87	52.7	127
—36.1	—33	—13.8	7	8.3	47	31	87.8	53	127.4
—36	—32.8	—13.3	8	8.8	48	31.1	88	53.3	128
—35.5	—32	—13	8.6	9.	48.2	31.6	89	53.8	129
—35	—31	—12.7	9	9.4	49	32	89.6	54	129.2
—34.4	—30	—12.2	10	10	50	32.2	90	54.4	130
—34	—29.2	—12	10.4	10.5	51	32.7	91	55	131
—33.8	—29	—11.6	11	11	51.8	33	91.4	55.5	132
—33.3	—28	—11.1	12	11.1	52	33.3	92	56	132.8
—33	—27.4	—11	12.2	11.6	53	33.8	93	56.1	133
—32.7	—27	—10.5	13	12	53.6	34	93.2	56.6	134
—32.2	—26	—10	14	12.2	54	34.4	94	57	134.6
—32	—25.6	—9.4	15	12.7	55	35	95	57.2	135
—31.6	—25	—9	15.8	13	55.4	35.5	96	57.7	136
—31.1	—24	—8.8	16	13.3	56	36	96.8	58	136.4
—31	—23.8	—8.3	17	13.8	57	36.1	97	58.3	137
—30.5	—23	—8	17.6	14	57.2	36.6	98	58.8	138
—30	—22	—7.7	18	14.4	58	37	98.6	59	138.2
—29.4	—21	—7.2	19	15	59	37.2	99	59.4	139
—29	—20.2	—7	19.4	15.5	60	37.7	100	60	140
—28.8	—20	—6.6	20	16	60.8	38	100.4	60.5	141
—28.3	—19	—6.1	21	16.1	61	38.3	101	61	141.8
—28	—18.4	—6	21.2	16.6	62	38.8	102	61.1	142
—27.7	—18	—5.5	22	17	62.6	39	102.2	61.6	143
—27.2	—17	—5	23	17.2	63	39.4	103	62	143.6
—27	—16.6	—4.4	24	17.7	64	40	104	62.2	144
—26.6	—16	—4	24.8	18	64.4	40.5	105	62.7	145
—26.1	—15	—3.8	25	18.3	65	41	105.8	63	145.4
—26	—14.8	—3.3	26	18.8	66	41.1	106	63.3	146
—25.5	—14	—3	26.6	19	66.2	41.6	107	63.8	147
—25	—13	—2.7	27	19.4	67	42	107.6	64	147.2
—24.4	—12	—2.2	28	20	68	42.2	108	64.4	148
—24	—11.2	—2	28.4	20.5	69	42.7	109	65	149
—23.8	—11	—1.6	29	21	69.8	43	109.4	65.5	150
—23.3	—10	—1.1	30	21.1	70	43.3	110	66	150.8
—23	—9.4	—1	30.2	21.6	71	43.8	111	66.1	151
—22.7	—9	—0.5	31	22	71.6	44	111.2	66.6	152
—22.2	—8	0	32	22.2	72	44.4	112	67	152.6
—22	—7.6	0.5	33	22.7	73	45	113	67.2	153
—21.6	—7	1	33.8	23	73.4	45.5	114	67.7	154
—21.1	—6	1.1	34	23.3	74	46	114.8	68	154.4
—21	—5.8	1.6	35	23.8	75	46.1	115	68.3	155
—20.5	—5	2	35.6	24	75.2	46.6	116	68.8	156
—20	—4	2.2	36	24.4	76	47	116.6	69	156.2
—19.4	—3	2.7	37	25	77	47.2	117	69.4	157
—19	—2.2	3	37.4	25.5	78	47.7	118	70	158
—18.8	—2	3.3	38	26	78.8	48	118.4	70.5	159
—18.3	—1	3.8	39	26.1	79	48.3	119	71	159.8

Thermometric Equivalents.—Continued.

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
72	161.6	95.5	204	118.8	246	142.2	288	166	330.8
72.2	162	96	204.8	119	246.2	142.7	289	166.1	331
72.7	163	96.1	205	119.4	247	143	289.4	166.6	332
73	163.4	96.6	206	120	248	143.3	290	167	332.6
73.3	164	97	206.6	120.5	249	143.8	291	167.2	333
73.8	165	97.2	207	121	249.8	144	291.2	167.7	334
74	165.2	97.7	208	121.1	250	144.4	292	168	334.4
74.4	166	98	208.4	121.6	251	145	293	168.3	335
75	167	98.3	209	122	251.6	145.5	294	168.8	336
75.5	168	98.8	210	122.2	252	146	294.8	169	336.2
76	168.8	99	210.2	122.7	253	146.1	295	169.4	337
76.1	169	99.4	211	123	253.4	146.6	296	170	338
76.6	170	100	212	123.3	254	147	296.6	170.5	339
77	170.6	100.5	213	123.8	255	147.2	297	171	339.8
77.2	171	101	213.8	124	255.2	147.7	298	171.1	340
77.7	172	101.1	214	124.4	256	148	298.4	171.6	341
78	172.4	101.6	215	125	257	148.3	299	172	341.6
78.3	173	102	215.6	125.5	258	148.8	300	172.2	342
78.8	174	102.2	216	126	258.8	149	300.2	172.7	343
79	174.2	102.7	217	126.1	259	149.4	301	173	343.4
79.4	175	103	217.4	126.6	260	150	302	173.3	344
80	176	103.3	218	127	260.6	150.5	303	173.8	345
80.5	177	103.8	219	127.2	261	151	303.8	174	345.2
81	177.8	104	219.2	127.7	262	151.1	304	174.4	346
81.1	178	104.4	220	128	262.4	151.6	305	175	347
81.6	179	105	221	128.3	263	152	305.6	175.5	348
82	179.6	105.5	222	128.8	264	152.2	306	176	348.8
82.2	180	106	222.8	129	264.2	152.7	307	176.1	349
82.7	181	106.1	223	129.4	265	153	307.4	176.6	350
83	181.4	106.6	224	130	266	153.3	308	177	350.6
83.3	182	107	224.6	130.5	267	153.8	309	177.2	351
83.8	183	107.2	225	131	267.8	154	309.2	177.7	352
84	183.2	107.7	226	131.1	268	154.4	310	178	352.4
84.4	184	108	226.4	131.6	269	155	311	178.3	353
85	185	108.3	227	132	269.6	155.5	312	178.8	354
85.5	186	108.8	228	132.2	270	156	312.8	179	354.2
86	186.8	109	228.2	132.7	271	156.1	313	179.4	355
86.1	187	109.4	229	133	271.4	156.6	314	180	356
86.6	188	110	230	133.3	272	157	314.6	180.5	357
87	188.6	110.5	231	133.8	273	157.2	315	181	357.8
87.2	189	111	231.8	134	273.2	157.7	316	181.1	358
87.7	190	111.1	232	134.4	274	158	316.4	181.6	359
88	190.4	111.6	233	135	275	158.3	317	182	359.6
88.3	191	112	233.6	135.5	276	158.8	318	182.2	360
88.8	192	112.2	234	136	276.8	159	318.2	182.7	361
89	192.2	112.7	235	136.1	277	159.4	319	183	361.4
89.4	193	113	235.4	136.6	278	160	320	183.3	362
90	194	113.3	236	137	278.6	160.5	321	183.8	363
90.5	195	113.8	237	137.2	279	161	321.8	184	363.2
91	195.8	114	237.2	137.7	280	161.1	322	184.4	364
91.1	196	114.4	238	138	280.4	161.6	323	185	365
91.6	197	115	239	138.3	281	162	323.6	185.5	366
92	197.6	115.5	240	138.8	282	162.2	324	186	366.8
92.2	198	116	240.8	139	282.2	162.7	325	186.1	367
92.7	199	116.1	241	139.4	283	163	325.4	186.6	368
93	199.4	116.6	242	140	284	163.3	326	187	368.6
93.3	200	117	242.6	140.5	285	163.8	327	187.2	369
93.8	201	117.2	243	141	285.8	164	327.2	187.7	370
94	201.2	117.7	244	141.1	286	164.4	328	188	370.4

Thermometric Equivalents.—Continued.

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
189	372.2	211.6	413	233.8	453	256.1	493	278.3	533
189.4	373	212	413.6	234	453.2	256.6	494	278.8	534
190	374	212.2	414	234.4	454	257	494.6	279	534.2
190.5	375	212.7	415	235	455	257.2	495	279.4	535
191	375.8	213	415.4	235.5	456	257.7	496	280	536
191.1	376	213.3	416	236	456.8	258	496.4	280.5	537
191.6	377	213.8	417	236.1	457	258.3	497	281	537.8
192	377.6	214	417.2	236.6	458	258.8	498	281.1	538
192.2	378	214.4	418	237	458.6	259	498.2	281.6	539
192.7	379	215	419	237.2	459	259.4	499	282	539.6
193	379.4	215.5	420	237.7	460	260	500	282.2	540
193.3	380	216	420.8	238	460.4	260.5	501	282.7	541
193.8	381	216.1	421	238.3	461	261	501.8	283	541.4
194	381.2	216.6	422	238.8	462	261.1	502	283.3	542
194.4	382	217	422.6	239	462.2	261.6	503	283.8	543
195	383	217.2	423	239.4	463	262	503.6	284	543.2
195.5	384	217.7	424	240	464	262.2	504	284.4	544
196	384.8	218	424.4	240.5	465	262.7	505	285	545
196 1	385	218.3	425	241	465.8	263	505.4	285.5	546
196.6	386	218.8	426	241.1	466	263.3	506	286	546.8
197	386.6	219	426.2	241.6	467	263.8	507	286.1	547
197.2	387	219.4	427	242	467.6	264	507.2	286.6	548
197.7	388	220	428	242.2	468	264.4	508	287	548.6
198	388.4	220.5	429	242.7	469	265	509	287.2	549
198.3	389	221	429.8	243	469.4	265.5	510	287.7	550
198.8	390	221.1	430	243.3	470	266	510.8	288	550.4
199	390.2	221.6	431	243.8	471	266.1	511	288.3	551
199.4	391	222	431.6	244	47. 2	266.6	512	288.8	552
200	392	222.2	432	244 4	472	267	512.6	289	552.2
200.5	393	222.7	433	245	473	267.2	513	289.4	553
201	393.8	223	433.4	245.5	474	267.7	514	290	554
201.1	394	223.3	434	246	474.8	268	514.4	290.5	555
201.6	395	223.8	435	246.1	475	268.3	515	291	555.8
202	395.6	224	435.2	246.6	476	268.8	516	291.1	556
202.2	396	224.4	436	247	476.6	269	516.2	291.6	557
202.7	397	225	437	247.2	477	269.4	517	292	557.6
203	397.4	225.5	438	247.7	478	270	518	292.2	558
203.3	398	226	438.8	248	478.4	270.5	519	292.7	559
203.8	399	226.1	439	248.3	479	271	519.8	293	559.4
204	399.2	226.6	440	248.8	480	271.1	520	293.3	560
204.4	400	227	440.6	249	480.2	271.6	521	293.8	561
205	401	227.2	441	249.4	481	272	521.6	294	561.2
205.5	402	227.7	442	250	482	272.2	522	294.4	562
206	402.8	228	442.4	250.5	483	272.7	523	295	563
206.1	403	228.3	443	251	483.8	273	523.4	295.5	564
206.6	404	228.8	444	251.1	484	273.3	524	296	564.8
207	404.6	229	444.2	251.6	485	273.8	525	296.1	565
207.2	405	229.4	445	252	485.6	274	525.2	296.6	566
207.7	406	230	446	252.2	486	274.4	526	297	566.6
208	406.4	230.5	447	252.7	487	275	527	297.2	567
208.3	407	231	447.8	253	487.4	275.5	528	297.7	568
208.8	408	231.1	448	253.3	488	276	528.8	298	568.4
209	408.2	231.6	449	253.8	489	276.1	529	298.3	569
209.4	409	232	449.6	254	489.2	276.6	530	298.8	570
210	410	232.2	450	254.4	490	277	530.6	299	570.2
210.5	411	232.7	451	255	491	277.2	531	299.4	571
211	411.8	233	451.4	255.5	492	277.7	532	300	572
211.1	412	233.3	452	256	492.8	278	532.4		

III. Specific Gravity Tables.

1. *Baumé's Scale for Liquids Lighter than Water.*

The following table is calculated for a temperature of 17.5° C. (63.5° F.), and is based on the formulas $\frac{140}{\text{B.}^\circ + 130} = \text{specific gravity}$ and $\frac{140}{\text{specific gravity}} - 130 = \text{B.}^\circ$.

Degree Baumé.	Specific gravity.	Degree Baumé.	Specific gravity.	Degree Baumé.	Specific gravity.	Degree Baumé.	Specific gravity.
10	1.0000	33	0.8588	56	0.7526	79	0.6698
11	0.9929	34	0.8536	57	0.7486	80	0.6666
12	0.9859	35	0.8484	58	0.7446	81	0.6635
13	0.9790	36	0.8433	59	0.7407	82	0.6604
14	0.9722	37	0.8383	60	0.7368	83	0.6573
15	0.9655	38	0.8333	61	0.7329	84	0.6542
16	0.9589	39	0.8284	62	0.7290	85	0.6511
17	0.9523	40	0.8235	63	0.7253	86	0.6482
18	0.9459	41	0.8187	64	0.7216	87	0.6452
19	0.9395	42	0.8139	65	0.7179	88	0.6422
20	0.9333	43	0.8092	66	0.7142	89	0.6393
21	0.9271	44	0.8045	67	0.7106	90	0.6363
22	0.9210	45	0.8000	68	0.7070	91	0.6335
23	0.9150	46	0.7954	69	0.7035	92	0 6306
24	0.9090	47	0.7909	70	0.7000	93	0.6278
25	0.9032	48	0.7865	71	0.6965	94	0.6250
26	0.8974	49	0.7821	72	0.6931	95	0.6222
27	0.8917	50	0.7777	73	0.6896	96	0.6195
28	0.8860	51	0.7734	74	0.6863	97	0.6167
29	0.8805	52	0.7692	75	0.6829	98	0.6140
30	0.8750	53	0.7650	76	0.6796	99	0.6113
31	0.8695	54	0.7608	77	0.6763	100	0.6087
32	0.8641	55	0.7567	78	0.6731		

The coefficient of expansion of petroleum oils for increase or decrease of 1° C. in temperature has been determined for both Russian and American oils. For the latter the following figures have been given (*Iron Age*, xxxviii, No. 7):

Specific gravity at 15° C. (59° F.).	Coefficient of expansion for 1° C.
Under 0.700	0.00090
0.700 to 0.750	0.00085
0.750 to 0.800	0.00080
0.800 to 0.815	0.00070
Over 0.815	0.00065

As stated in the text (p. 39), it is customary in practice to take as

2. *Comparison of Various Baumé Hydrometers for Liquids Heavier than Water with Specific Gravities.* (*Lunge's Technical Methods of Chemical Analysis,* vol. i, p. 935.)

Degrees.	Rational Hydrometer $d=\frac{144.3}{144.3-n}$	Baumé's Hydrometer according to Gerlach's scale.	Baumé American scale $d=\frac{145}{145-n}$	Degrees.	Rational Hydrometer $d=\frac{144.3}{144.3-n}$	Baumé's Hydrometer according to Gerlach's scale.	Baumé American scale $d=\frac{145}{145-n}$
1	1.007	1.0068	1.005	34	1.308	1.3015	1.309
2	1.014	1.0138	1.011	35	1.320	1.3131	1.317
3	1.022	1.0208	1.023	36	1.332	1.3250	1.334
4	1.029	1.0280	1.029	37	1.345	1.3370	1.342
5	1.037	1.0353	1.036	38	1.357	1.3494	1.359
6	1.045	1.0426	1.043	39	1.370	1.3619	1.368
7	1.052	1.0501	1.050	40	1.383	1.3746	1.386
8	1.060	1.0576	1.057	41	1.397	1.3876	1.395
9	1.067	1.0653	1.064	42	1.410	1.4009	1.413
10	1.075	1.0731	1.071	43	1.424	1.4134	1.422
11	1.083	1.0810	1.086	44	1.438	1.4281	1.441
12	1.091	1.0890	1.093	45	1.453	1.4421	1.451
13	1.100	1.0972	1.100	46	1.468	1.4564	1.470
14	1.108	1.1054	1.107	47	1.483	1.4710	1.480
15	1.116	1.1138	1.114	48	1.498	1.4860	1.500
16	1.125	1.1224	1.122	49	1.514	1.5012	1.510
17	1.134	1.1310	1.136	50	1.530	1.5167	1.531
18	1.142	1.1398	1.143	51	1.540	1.5325	1.541
19	1.152	1.1487	1.150	52	1.563	1.5487	1.561
20	1.162	1.1578	1.158	53	1.580	1.5652	1.573
21	1.171	1.1670	1.172	54	1.597	1.5820	1.594
22	1.180	1.1763	1.179	55	1.615	1.5993	1.616
23	1.190	1.1858	1.186	56	1.634	1.6169	1.627
24	1.200	1.1955	1.201	57	1.652	1.6349	1.650
25	1.210	1.2053	1.208	58	1.671	1.6533	1.661
26	1.220	1.2153	1.216	59	1.691	1.6721	1.683
27	1.231	1.2254	1.231	60	1.711	1.6914	1.705
28	1.241	1.2357	1.238	61	1.732	1.7111	1.727
29	1.252	1.2462	1.254	62	1.753	1.7313	1.747
30	1.263	1.2569	1.262	63	1.774	1.7520	1.767
31	1.274	1.2677	1.269	64	1.796	1.7731	1.793
32	1.285	1.2788	1.285	65	1.819	1.7948	1.814
33	1.297	1.2901	1.293	66	1.842	1.8171	1.835

What is known as the " Rational " Baumé scale is calculated by taking water at the temperature chosen at 0° B. and sulphuric acid of 1.842 specific gravity at 66° B. and using the formula $\frac{144.3}{144.3-n^\circ}=d.$ (See Lunge's " Sulphuric Acid and Alkali," vol. i., p. 20.)

3. *Twaddle's Scale for Liquids Heavier than Water.*

Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.
0	1.000	29	1.145	58	1.290	87	1.435	116	1.580	145	1.725	173	1.865
1	1.005	30	1.150	59	1.295	88	1.440	117	1.585	146	1.730	174	1.870
2	1.010	31	1.155	60	1.300	89	1.445	118	1.590	147	1.735	175	1.875
3	1.015	32	1.160	61	1.305	90	1.450	119	1.595	148	1.740	176	1.880
4	1.020	33	1.165	62	1.310	91	1.455	120	1.600	149	1.745	177	1.885
5	1.025	34	1.170	63	1.315	92	1.460	121	1.605	150	1.750	178	1.890
6	1.030	35	1.175	64	1.320	93	1.465	122	1.610	151	1.755	179	1.895
7	1.035	36	1.180	65	1.325	94	1.470	123	1.615	152	1.760	180	1.900
8	1.040	37	1.185	66	1.330	95	1.475	124	1.620	153	1.765	181	1.905
9	1.045	38	1.190	67	1.335	96	1.480	125	1.625	154	1.770	182	1.910
10	1.050	39	1.195	68	1.340	97	1.485	126	1.630	155	1.775	183	1.915
11	1.055	40	1.200	69	1.345	98	1.490	127	1.635	156	1.780	184	1.920
12	1.060	41	1.205	70	1.350	99	1.495	128	1.640	157	1.785	185	1.925
13	1.065	42	1.210	71	1.355	100	1.500	129	1.645	158	1.790	186	1.930
14	1.070	43	1.215	72	1.360	101	1.505	130	1.650	159	1.795	187	1.935
15	1.075	44	1.220	73	1.365	102	1.510	131	1.655	160	1.800	188	1.940
16	1.080	45	1.225	74	1.370	103	1.515	132	1.660	161	1.805	189	1.945
17	1.085	46	1.230	75	1.375	104	1.520	133	1.665	162	1.810	190	1.950
18	1.090	47	1.235	76	1.380	105	1.525	134	1.670	163	1.815	191	1.955
19	1.095	48	1.240	77	1.385	106	1.530	135	1.675	164	1.820	192	1.960
20	1.100	49	1.245	78	1.390	107	1.535	136	1.680	165	1.825	193	1.965
21	1.105	50	1.250	79	1.395	108	1.540	137	1.685	166	1.830	194	1.970
22	1.110	51	1.255	80	1.400	109	1.545	138	1.690	167	1.835	195	1.975
23	1.115	52	1.260	81	1.405	110	1.550	139	1.695	168	1.840	196	1.980
24	1.120	53	1.265	82	1.410	111	1.555	140	1.700	169	1.845	197	1.985
25	1.125	54	1.270	83	1.415	112	1.560	141	1.705	170	1.850	198	1.990
26	1.130	55	1.275	84	1.420	113	1.565	142	1.710	171	1.855	199	1.995
27	1.135	56	1.280	85	1.425	114	1.570	143	1.715	172	1.860	200	2.000
28	1.140	57	1.285	86	1.430	115	1.575	144	1.720				

The uniform division of the Twaddle scale makes the degrees very easily convertible into specific gravity readings It is only necessary to multiply the degree as read off by five and add this to 1.000 in order to obtain the specific gravity.

Again, as the gallon of distilled water at ordinary temperatures weighs ten pounds avoirdupois, it is possible to determine the weight of a gallon of an acid or lye by the aid of the Twaddle scale. Thus, if an acid shows 50° Twaddle, corresponding to the specific gravity 1.250, it weighs twelve and a half pounds per gallon. Or, as a liter of distilled water weighs one thousand grams, a liter of a liquid showing 20° Twaddle will weigh eleven hundred grams.

4. *Comparison of the Twaddle Scale with the Rational Baumé Scale.*

Twaddle.	Baumé.	Specific gravity.	Twaddle.	Baumé.	Specific gravity.	Twaddle.	Baumé.	Specific gravity.	Twaddle.	Baumé.	Specific gravity.
0	0	1.000	44	26.0	1.220	88	44.1	1.440	131	57.1	1.655
1	0.7	1.005	45	26.4	1.225	89	44.4	1.445	132	57.4	1.660
2	1.4	1.010	46	26.9	1.230	90	44.8	1.450	133	57.7	1.665
3	2.1	1.015	47	27.4	1.235	91	45.1	1.455	134	57.9	1.670
4	2.7	1.020	48	27.9	1.240	92	45.4	1.460	135	58.2	1.675
5	3.4	1.025	49	28.4	1.245	93	45.8	1.465	136	58.4	1.680
6	4.1	1.030	50	28.8	1.250	94	46.1	1.470	137	58.7	1.685
7	4.7	1.035	51	29.3	1.255	95	46.4	1.475	138	58.9	1.690
8	5.4	1.040	52	29.7	1.260	96	46.8	1.480	139	59.2	1.695
9	6.0	1.045	53	30.2	1.265	97	47.1	1.485	140	59.5	1.700
10	6.7	1.050	54	30.6	1.270	98	47.4	1.490	141	59.7	1.705
11	7.4	1.055	55	31.1	1.275	99	47.8	1.495	142	60.0	1.710
12	8.0	1.060	56	31.5	1.280	100	48.1	1.500	143	60.2	1.715
13	8.7	1.065	57	32.0	1.285	101	48.4	1.505	144	60.4	1.720
14	9.4	1.070	58	32.4	1.290	102	48.7	1.510	145	60 6	1.725
15	10.0	1.075	59	32.8	1.295	103	49.0	1.515	146	60 9	1.730
16	10.6	1.080	60	33.3	1.300	104	49.4	1.520	147	61.1	1.735
17	11.2	1.085	61	33.7	1.305	105	49.7	1.525	148	61.4	1.740
18	11.9	1.090	62	34.2	1.310	106	50.0	1.530	149	61.6	1.745
19	12.4	1.095	63	34.6	1.315	107	50.3	1.535	150	61 8	1.750
20	13.0	1.100	64	35.0	1.320	108	50.6	1.540	151	62.1	1.755
21	13.6	1.105	65	35.4	1.325	109	50.9	1.545	152	62.3	1.760
22	14.2	1.110	66	35.8	1.330	110	51.2	1.550	153	62.5	1.765
23	14.9	1.115	67	36.2	1.335	111	51.5	1.555	154	62.8	1.770
24	15.4	1.120	68	36.6	1.340	112	51.8	1.560	155	63.0	1.775
25	16.0	1.125	69	37.0	1.345	113	52.1	1.565	156	63.2	1.780
26	16.5	1.130	70	37.4	1 350	114	52.4	1.570	157	63.5	1.785
27	17.1	1.135	71	37.8	1.355	115	52.7	1.575	158	63.7	1.790
28	17.7	1.140	72	38.2	1.360	116	53.0	1.580	159	64.0	1.795
29	18.3	1.145	73	38.6	1.365	117	53.3	1.585	160	64.2	1.800
30	18.8	1.150	74	39.0	1.370	118	53.6	1.590	161	64.4	1.805
31	19.3	1.155	75	39.4	1.375	119	53.9	1.595	162	64.6	1.810
32	19.8	1.160	76	39.8	1.380	120	54.1	1.600	163	64.8	1.815
33	20.3	1.165	77	40.1	1.385	121	54.4	1.605	164	65.0	1.820
34	20.9	1.170	78	40.5	1.390	122	54.7	1.610	165	65.2	1.825
35	21.4	1.175	79	40.8	1.395	123	55.0	1.615	166	65.5	1.830
36	22.0	1.180	80	41.2	1.400	124	55.2	1.620	167	65.7	1.835
37	22.5	1.185	81	41.6	1.405	125	55.5	1.625	168	65.9	1.840
38	23.0	1.190	82	42.0	1.410	126	55.8	1.630	169	66.1	1.845
39	23.5	1.195	83	42.3	1.415	127	56.0	1.635	170	66.3	1.850
40	24.0	1.200	84	42.7	1.420	128	56.3	1.640	171	66.5	1.855
41	24.5	1.205	85	43.1	1.425	129	56.6	1.645	172	66.7	1.860
42	25.0	1.210	86	43.4	1.430	130	56.9	1.650	173	67.0	1.865
43	25.5	1.215	87	43.8	1.435						

5. *Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix (as used for sugar solutions).*

Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.
0.0	1.00000	0.00	5.0	1.01970	2.84	10.0	1.04014	5.67
0.1	1.00038	0.06	5.1	1.02010	2.89	10.1	1.04055	5.72
0.2	1.00077	0.11	5.2	1.02051	2.95	10.2	1.04097	5.78
0.3	1.00116	0.17	5.3	1.02091	3.01	10.3	1.04139	5.83
0.4	1 00155	0.23	5.4	1.02131	3.06	10.4	1.04180	5.89
0.5	1.00193	0.28	5.5	1.02171	3.12	10.5	1.04222	5.95
0.6	1.00232	0.34	5.6	1.02211	3.18	10.6	1.04264	6.00
0.7	1.00271	0.40	5.7	1.02252	3.23	10.7	1.04306	6.06
0 8	1.00310	0.45	5.8	1.02292	3.29	10.8	1.04348	6.12
0.9	1.00349	0.51	5.9	1.02333	3.35	10.9	1.04390	6.17
1.0	1.00388	0.57	6.0	1.02373	3.40	11.0	1.04431	6.23
1.1	1.00427	0.63	6.1	1.02413	3.46	11.1	1.04473	6.29
1.2	1.00466	0.68	6.2	1.02454	3.52	11.2	1.04515	6.34
1.3	1.00505	0.74	6.3	1.02494	3.57	11.3	1.04557	6.40
1.4	1.00544	0.80	6.4	1.02535	3.63	11.4	1.04599	6.46
1.5	1.00583	0.85	6.5	1.02575	3.69	11.5	1.04641	6.51
1.6	1.00622	0.91	6.6	1.02616	3.74	11.6	1.04683	6.57
1.7	1.00662	0.97	6.7	1.02657	3 80	11.7	1.04726	6.62
1.8	1.00701	1.02	6.8	1.02697	3.86	11.8	1.04768	6.68
1.9	1.00740	1.08	6.9	1.02738	3.91	11.9	1.04810	6.74
2.0	1.00779	1.14	7.0	1.02779	3.97	12.0	1.04852	6.79
2.1	1.00818	1.19	7.1	1.02819	4.03	12.1	1.04894	6.85
2.2	1.00858	1.25	7.2	1.02860	4.08	12.2	1.04937	6.91
2.3	1.00897	1.31	7.3	1.02901	4.14	12.3	1.04979	6.96
2.4	1.00936	1.36	7.4	1.02942	4.20	12.4	1.05021	7.02
2.5	1.00976	1.42	7.5	1.02983	4.25	12.5	1.05064	7.08
2.6	1.01015	1.48	7.6	1.03024	4.31	12.6	1.05106	7.13
2.7	1.01055	1.53	7.7	1.03064	4 37	12.7	1.05149	7.19
2.8	1.01094	1.59	7.8	1.03105	4.42	12 8	1.05191	7.24
2.9	1.01134	1.65	7.9	1.03146	4.48	12.9	1.05233	7.30
3.0	1.01173	1.70	8.0	1.03187	4.53	13.0	1.05276	7.36
3.1	1.01213	1.76	8.1	1.03228	4.59	13.1	1.05318	7.41
3.2	1.01252	1.82	8.2	1.03270	4.65	13.2	1.05361	7.47
3.3	1.01292	1 87	8.3	1.03311	4.70	13.3	1.05404	7.53
3.4	1.01332	1.93	8.4	1.03352	4.76	13.4	1.05446	7.58
3.5	1.01371	1.99	8.5	1.03393	4.82	13.5	1.05489	7.64
3.6	1.01411	2.04	8.6	1.03434	4.87	13.6	1.05532	7.69
3.7	1.01451	2.10	8.7	1.03475	4.93	13.7	1.05574	7.75
3.8	1.01491	2.16	8.8	1.03517	4.99	13.8	1.05617	7.81
3.9	1.01531	2.21	8.9	1.03558	5.04	13.9	1.05660	7.86
4.0	1.01570	2.27	9.0	1.03599	5.10	14.0	1 05703	7.92
4.1	1.01610	2.33	9.1	1.03640	5.16	14.1	1.05746	7.98
4.2	1.01650	2.38	9.2	1.03682	5.21	14.2	1.05789	8.03
4.3	1.01690	2.44	9.3	1.03723	5.27	14.3	1.05831	8.09
4.4	1.01730	2 50	9.4	1.03765	5.33	14.4	1.05874	8.14
4.5	1.01770	2.55	9.5	1.03806	5.38	14.5	1.05917	8.20
4.6	1.01810	2.61	9.6	1.03848	5.44	14.6	1.05960	8.26
4.7	1 01850	2.67	9.7	1.03889	5.50	14.7	1.06003	8 31
4.8	1.01890	2.72	9.8	1.03931	5.55	14.8	1 06047	8.37

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.
15.0	1.06133	8.48	20.0	1.08329	11.29	25.0	1.10607	14.08
15.1	1.06176	8.54	20.1	1.08374	11.34	25.1	1.10653	14.13
15.2	1.06219	8.59	20.2	1.08419	11.40	25.2	1.10700	14.19
15.3	1.06262	8.65	20.3	1.08464	11.45	25.3	1.10746	14.24
15.4	1.06306	8.71	20.4	1.08509	11.51	25.4	1.10793	14.30
15.5	1.06349	8.76	20.5	1.08553	11 57	25.5	1.10839	14.35
15.6	1.06392	8.82	20.6	1.08599	11.62	25.6	1.10886	14.41
15.7	1.06436	8.88	20.7	1.08643	11 68	25.7	1.10932	14.47
15.8	1.06479	8.93	20.8	1.08688	11.73	25.8	1.10979	14.52
15.9	1.06522	8.99	20.9	1.08733	11.79	25.9	1.11026	14.58
16.0	1.06566	9.04	21.0	1.08778	11.85	26.0	1.11072	14.63
16.1	1.06609	9.10	21.1	1.08824	11.90	26.1	1.11119	14.69
16.2	1.06653	9.16	21.2	1.08869	11.96	26.2	1.11166	14.74
16.3	1.06696	9.21	21.3	1.08914	12.01	26.3	1.11213	14.80
16.4	1.06740	9.27	21.4	1.08959	12.07	26.4	1.11259	14.85
16.5	1.06783	9.33	21.5	1.09004	12.13	26.5	1.11306	14.91
16.6	1.06827	9.38	21.6	1.09049	12.18	26.6	1.11353	14.97
16.7	1.06871	9.44	21.7	1.09095	12.24	26.7	1.11400	15.02
16.8	1.06914	9.49	21.8	1.09140	12 29	26.8	1.11447	15.08
16.9	1.06958	9.55	21.9	1.09185	12.35	26.9	1.11494	15.13
17.0	1.07002	9.61	22.0	1.09231	12.40	27.0	1.11541	15.19
17.1	1.07046	9.66	22.1	1.09276	12.46	27.1	1.11588	15.24
17.2	1.07090	9.72	22.2	1.09321	12.52	27.2	1.11635	15.30
17.3	1.07133	9.77	22.3	1.09367	12.57	27.3	1.11682	15.35
17.4	1.07177	9.83	22.4	1.09412	12.63	27.4	1.11729	15.41
17.5	1.07221	9.89	22.5	1.09458	12.68	27.5	1.11776	15.46
17.6	1 07265	9.94	22.6	1.09503	12.74	27.6	1.11824	15.52
17.7	1.07309	10.00	22.7	1.09549	12.80	27.7	1.11871	15.58
17 8	1.07353	10.06	22.8	1.09595	12.85	27.8	1.11918	15.63
17.9	1.07397	10.11	22 9	1.09640	12.91	27.9	1.11965	15.69
18.0	1.07441	10.17	23.0	1.09686	12.96	28.0	1.12013	15.74
18.1	1.07485	10.22	23.1	1.09732	13.02	28.1	1.12060	15.80
18.2	1.07530	10.28	23.2	1.09777	13.07	28.2	1.12107	15.85
18.3	1.07574	10.33	23.3	1.09823	13.13	28.3	1.12155	15.91
18.4	1.07618	10.39	23.4	1.09869	13.19	28.4	1.12202	15.96
18.5	1 07662	10.45	23.5	1.09915	13.24	28.5	1.12250	16.02
18.6	1.07706	10.50	23.6	1.09961	13.30	28.6	1.12297	16.07
18.7	1.07751	10.56	23.7	1.10007	13.35	28.7	1.12345	16.13
18.8	1.07795	10.62	23.8	1.10053	13.41	28.8	1.12393	16.18
18.9	1.07839	10.67	23.9	1.10099	13.46	28.9	1.12440	16.24
19.0	1.07884	10.73	24.0	1.10145	13.52	29.0	1.12488	16.30
19.1	1.07928	10.78	24.1	1.10191	13.58	29.1	1.12536	16.35
19.2	1.07973	10.84	24.2	1.10237	13.63	29.2	1.12583	16.41
19.3	1.08017	10.90	24.3	1.10283	13.69	29.3	1.12631	16.46
19.4	1.08062	10.95	24.4	1.10329	13.74	29.4	1.12679	16.52
19.5	1.08106	11.01	24.5	1.10375	13.80	29.5	1.12727	16.57
19.6	1.08151	11.06	24.6	1.10421	13.85	29.6	1.12775	16.63
19.7	1 08196	11.12	24.7	1.10468	13.91	29.7	1.12823	16.68

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.
30.0	1.12967	16.85	35.0	1.15411	19.60	40.0	1.17943	22.33
30.1	1.13015	16.90	35.1	1.15461	19.66	40.1	1.17995	22.38
30.2	1.13063	16.96	35.2	1.15511	19.71	40.2	1.18046	22.44
30.3	1.13111	17.01	35.3	1.15561	19.76	40.3	1.18098	22.49
30.4	1.13159	17.07	35.4	1.15611	19.82	40.4	1.18150	22.55
30.5	1.13207	17.12	35.5	1.15661	19.87	40.5	1.18201	22.60
30.6	1.13255	17.18	35.6	1.15710	19.93	40.6	1.18253	22.66
30.7	1.13304	17.23	35.7	1.15760	19.98	40.7	1.18305	22.71
30.8	1.13352	17.29	35.8	1.15810	20.04	40.8	1.18357	22.77
30.9	1.13400	17.35	35.9	1.15861	20.09	40.9	1.18408	22.82
31.0	1.13449	17.40	36.0	1.15911	20.15	41.0	1.18460	22.87
31.1	1.13497	17.46	36.1	1.15961	20.20	41.1	1.18512	22.93
31.2	1.13545	17.51	36.2	1.16011	20.26	41.2	1.18564	22.98
31.3	1.13594	17.57	36.3	1.16061	20.31	41.3	1.18616	23.04
31.4	1.13642	17.62	36.4	1.16111	20.37	41.4	1.18668	23.09
31.5	1.13691	17.68	36.5	1.16162	20.42	41.5	1.18720	23.15
31.6	1.13740	17.73	36.6	1.16212	20.48	41.6	1.18772	23.20
31.7	1.13788	17.79	36.7	1.16262	20.53	41.7	1.18824	23.25
31.8	1.13837	17.84	36.8	1.16313	20.59	41.8	1.18887	23.31
31.9	1.13885	17.90	36.9	1.16363	20.64	41.9	1.18929	23.36
32.0	1.13934	17.95	37.0	1.16413	20.70	42.0	1.18981	23.42
32.1	1.13983	18.01	37.1	1.16464	20.75	42.1	1.19033	23.47
32.2	1.14032	18.06	37.2	1.16514	20.80	42.2	1.19086	23.52
32.3	1.14081	18.12	37.3	1.16565	20.86	42.3	1.19138	23.58
32.4	1.14129	18.17	37.4	1.16616	20.91	42.4	1.19190	23.63
32.5	1.14178	18.23	37.5	1.16666	20.97	42.5	1.19243	23.69
32.6	1.14227	18.28	37.6	1.16717	21.02	42.6	1.19295	23.74
32.7	1.14276	18.34	37.7	1.16768	21.08	42.7	1.19348	23.79
32.8	1.14325	18.39	37.8	1.16818	21.13	42.8	1.19400	23.85
32.9	1.14374	18.45	37.9	1.16869	21.19	42.9	1.19453	23.90
33.0	1.14423	18.50	38.0	1.16920	21.24	43.0	1.19505	23.96
33.1	1.14472	18.56	38.1	1.16971	21.30	43.1	1.19558	24.01
33.2	1.14521	18.61	38.2	1.17022	21.35	43.2	1.19611	24.07
33.3	1.14570	18.67	38.3	1.17072	21.40	43.3	1.19663	24.12
33.4	1.14620	18.72	38.4	1.17122	21.46	43.4	1.19716	24.17
33.5	1.14669	18.78	38.5	1.17174	21.51	43.5	1.19769	24.23
33.6	1.14718	18.83	38.6	1.17225	21.57	43.6	1.19822	24.28
33.7	1.14767	18.89	38.7	1.17276	21.62	43.7	1.19875	24.34
33.8	1.14817	18.94	38.8	1.17327	21.68	43.8	1.19927	24.39
33.9	1.14866	19.00	38.9	1.17379	21.73	43.9	1.19980	24.44
34.0	1.14915	19.05	39.0	1.17430	21.79	44.0	1.20033	24.50
34.1	1.14965	19.11	39.1	1.17481	21.84	44.1	1.20086	24.55
34.2	1.15014	19.16	39.2	1.17532	21.90	44.2	1.20139	24.61
34.3	1.15064	19.22	39.3	1.17583	21.95	44.3	1.20192	24.66
34.4	1.15113	19.27	39.4	1.17635	22.00	44.4	1.20245	24.71
34.5	1.15163	19.33	39.5	1.17686	22.06	44.5	1.20299	24.77
34.6	1.15213	19.38	39.6	1.17737	22.11	44.6	1.20352	24.82
34.7	1.15262	19.44	39.7	1.17789	22.17	44.7	1.20405	24.88

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.
45.0	1.20565	25.04	50.0	1.23278	27.72	55.0	1.26086	30.37
45.1	1.20618	25.09	50.1	1.23334	27.77	55.1	1.26143	30.42
45.2	1.20672	25.14	50.2	1.23389	27.82	55.2	1.26200	30.47
45.3	1.20725	25.20	50.3	1.23444	27.88	55.3	1.26257	30.53
45.4	1.20779	25.25	50.4	1.23499	27.93	55.4	1.26314	30.58
45.5	1.20832	25.31	50.5	1.23555	27.98	55.5	1.26372	30.63
45.6	1.20886	25.36	50.6	1.23610	28.04	55.6	1.26429	30.68
45.7	1.20939	25.41	50.7	1.23666	28.09	55.7	1.26486	30.74
45.8	1.20993	25.47	50.8	1.23721	28.14	55.8	1.26544	30.79
45.9	1.21046	25.52	50.9	1.23777	28.20	55.9	1.26601	30.84
46.0	1.21100	25.57	51.0	1.23832	28.25	56.0	1.26658	30.89
46.1	1.21154	25.63	51.1	1.23888	28.30	56.1	1.26716	30.95
46.2	1.21208	25.68	51.2	1.23943	28.36	56.2	1.26773	31.00
46.3	1.21261	25.74	51.3	1.23999	28.41	56.3	1.26831	31.05
46.4	1.21315	25.79	51.4	1.24055	28.46	56.4	1.26889	31.10
46.5	1.21369	25.84	51.5	1.24111	28.51	56.5	1.26946	31.16
46.6	1.21423	25.90	51.6	1.24166	28.57	56.6	1.27004	31.21
46.7	1.21477	25.95	51.7	1.24222	28.62	56.7	1.27062	31.26
46.8	1.21531	26.00	51.8	1.24278	28.67	56.8	1.27120	31.31
46.9	1.21585	26.06	51.9	1.24334	28.73	56.9	1.27177	31.37
47.0	1.21639	26.11	52.0	1.24390	28.78	57.0	1.27235	31.42
47.1	1.21693	26.17	52.1	1.24446	28.83	57.1	1.27293	31.47
47.2	1.21747	26.22	52.2	1.24502	28.89	57.2	1.27351	31.52
47.3	1.21802	26.27	52.3	1.24558	28.94	57.3	1.27409	31.58
47.4	1.21856	26.33	52.4	1.24614	28.99	57.4	1.27467	31.63
47.5	1.21910	26.38	52.5	1.24670	29.05	57.5	1.27525	31.68
47.6	1.21964	26.43	52.6	1.24726	29.10	57.6	1.27583	31.73
47.7	1.22019	26.49	52.7	1.24782	29.15	57.7	1.27641	31.79
47.8	1.22073	26.54	52.8	1.24839	29.20	57.8	1.27699	31.84
47.9	1.22127	26.59	52.9	1.24895	29.26	57.9	1.27758	31.89
48.0	1.22182	26.65	53.0	1.24951	29.31	58.0	1.27816	31.94
48.1	1.22236	26.70	53.1	1.25008	29.36	58.1	1.27874	32.00
48.2	1.22291	26.75	53.2	1.25064	29.42	58.2	1.27932	32.05
48.3	1.22345	26.81	53.3	1.25120	29.47	58.3	1.27991	32.10
48.4	1.22400	26.86	53.4	1.25177	29.52	58.4	1.28049	32.15
48.5	1.22455	26.92	53.5	1.25233	29.57	58.5	1.28107	32.20
48.6	1.22509	26.97	53.6	1.25290	29.63	58.6	1.28166	32.26
48.7	1.22564	27.02	53.7	1.25347	29.68	58.7	1.28224	32.31
48.8	1.22619	27.08	53.8	1.25403	29.73	58.8	1.28283	32.36
48.9	1.22673	27.13	53.9	1.25460	29.79	58.9	1.28342	32.41
49.0	1.22728	27.18	54.0	1.25517	29.84	59.0	1.28400	32.42
49.1	1.22783	27.24	54.1	1.25573	29.89	59.1	1.28459	32.52
49.2	1.22838	27.29	54.2	1.25630	29.94	59.2	1.28518	32.57
49.3	1.22893	27.34	54.3	1.25687	30.00	59.3	1.28576	32.62
49.4	1.22948	27.40	54.4	1.25744	30.05	59.4	1.28635	32.67
49.5	1.23003	27.45	54.5	1.25801	30.10	59.5	1.28694	32.73
49.6	1.23058	27.50	54.6	1.25857	30.16	59.6	1.28753	32.78
49.7	1.23113	27.56	54.7	1.25914	30.21	59.7	1.28812	32.83

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.
60.0	1.28989	32.99	65.0	1.31989	35.57	70.0	1.35088	38.12
60.1	1.29048	33.04	65.1	1.32050	35.63	70.1	1.35155	38.18
60.2	1.29107	33.09	65.2	1.32111	35.68	70.2	1.35214	38.23
60.3	1.29166	33.14	65.3	1.32172	35.73	70.3	1.35277	38.28
60.4	1.29225	33.20	65.4	1.32233	35.78	70.4	1.35340	38.33
60.5	1.29284	33.25	65.5	1.32294	35.83	70.5	1.35403	38.38
60.6	1.29343	33.30	65.6	1.32355	35.88	70.6	1.35466	38.43
60.7	1.29403	33.35	65.7	1.32417	35.93	70.7	1.35530	38.48
60.8	1.29462	33.40	65.8	1.32478	35.98	70.8	1.35593	38.53
60.9	1.29521	33.46	65.9	1.32539	36.04	70.9	1.35656	38.58
61.0	1.29581	33.51	66.0	1.32601	36.09	71.0	1.35720	38.63
61.1	1.29646	33.56	66.1	1.32662	36.14	71.1	1.35783	38.68
61.2	1.29700	33.61	66.2	1.32724	36.19	71.2	1.35847	38.73
61.3	1.29759	33.66	66.3	1.32785	36.24	71.3	1.35910	38.78
61.4	1.29819	33.71	66.4	1.32847	36.29	71.4	1.35974	38.83
61.5	1.29878	33.77	66.5	1.32908	36.34	71.5	1.36037	38.88
61.6	1.29938	33.82	66.6	1.32970	36.39	71.6	1.36101	38.93
61.7	1.29998	33.87	66.7	1.33031	36.45	71.7	1.36164	38.98
61.8	1.30057	33.92	66.8	1.33093	36.50	71.8	1.36228	39.03
61.9	1.30117	33.97	66.9	1.33155	36.55	71.9	1.36292	39.08
62.0	1.30177	34.03	67.0	1.33217	36.60	72.0	1.36355	39.13
62.1	1.30237	34.08	67.1	1.33278	36.65	72.1	1.36419	39.19
62.2	1.30297	34.13	67.2	1.33340	36.70	72.2	1.36483	39.24
62.3	1.30356	34.18	67.3	1.33402	36.75	72.3	1.36547	39.29
62.4	1.30416	34.23	67.4	1.33464	36.80	72.4	1.36611	39.34
62.5	1.30476	34.28	67.5	1.33526	36.85	72.5	1.36675	39.39
62.6	1.30536	34.34	67.6	1.33588	36.90	72 6	1.36739	39.44
62.7	1.30596	34.39	67.7	1.33650	36.96	72.7	1.36803	39.49
62.8	1.30657	34.44	67.8	1.33712	37.01	72.8	1.36867	39.54
62.9	1.30717	34.49	67.9	1.33774	37.06	72.9	1.36931	39.59
63.0	1.30777	34.54	68.0	1.33836	37.11	73.0	1.36995	39.64
63.1	1.30837	34.59	68.1	1.33899	37.16	73.1	1.37059	39.69
63.2	1.30897	34.65	68.2	1.33961	37.21	73.2	1.37124	39.74
63.3	1.30958	34.70	68.3	1.34023	37.26	73.3	1.37188	39.79
63.4	1.31018	34.75	68.4	1.34085	37.31	73.4	1.37252	39.84
63.5	1.31078	34.80	68.5	1.34148	37.36	73.5	1.37317	39.89
63.6	1.31139	34.85	68.6	1.34210	37.41	73.6	1.37381	39.94
63.7	1.31199	34.90	68.7	1.34273	37.47	73.7	1.37446	39.99
63.8	1.31260	34.96	68.8	1.34335	37.52	73.8	1.37510	40.04
63.9	1.31320	35.01	68.9	1.34398	37.57	73.9	1.37575	40.09
64.0	1.31381	35.06	69.0	1.34460	37.62	74.0	1.37639	40.14
64.1	1.31442	35.11	69.1	1.34523	37.67	74.1	1.37704	40.19
64.2	1.31502	35.16	69.2	1.34525	37.72	74.2	1.37768	40.24
64.3	1.31563	35.21	69.3	1.34648	37.77	74.3	1.37833	40.29
64.4	1.31624	35.27	69.4	1.34711	37.82	74.4*	1.37898	40.34
64.5	1.31684	35.32	69.5	1.34774	37.87	74.5	1.37962	40.39
64.6	1.31745	35.37	69.6	1.34836	37.92	74.6	1.38027	40.44
64.7	1.31806	35.42	69.7	1.34899	37.97	74.7	1.38092	40.49
64.8	1.31867	35.47						

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.
75.0	1.38287	40.64	80.0	1.41586	43.11	85.0	1.44986	45.54
75.1	1.38352	40.69	80.1	1.41653	43.61	85.1	1.45055	45.59
75.2	1.38417	40.74	80.2	1.41720	43.21	85.2	1.45124	45.64
75.3	1.38482	40.79	80.3	1.41787	43.26	85.3	1.45193	45.69
75.4	1.38547	40.84	80.4	1.41854	43.31	85.4	1.45262	45.74
75.5	1.38612	40.89	80.5	1.41921	43.36	85.5	1.45331	45.78
75.6	1.38677	40.94	80.6	1.41989	43.41	85.6	1.45401	45.83
75.7	1.38743	40.99	80.7	1.42056	43.45	85.7	1.45470	45.88
75.8	1.38808	41.04	80.8	1.42123	43.50	85.8	1.45539	45.93
75.9	1.38873	41.09	80.9	1.42190	43.55	85.9	1.45609	45.98
76.0	1.38939	41.14	81.0	1.42258	43.60	86.0	1.45678	46.02
76.1	1.39004	41.19	81.1	1.42325	43.65	86.1	1.45748	46.07
76.2	1.39070	41.24	81.2	1.42393	43.70	86.2	1.45817	46.12
76.3	1.39135	41.29	81.3	1.42460	43.75	86.3	1.45887	46.17
76.4	1.39201	41.33	81.4	1.42528	43.80	86.4	1.45956	46.22
76.5	1.39266	41.38	81.5	1.42595	43.85	86.5	1.46026	46.26
76.6	1.39332	41.43	81.6	1.42663	43.89	86.6	1.46095	46.31
76.7	1.39397	41.48	81.7	1.42731	43.94	86.7	1.46165	46.36
76.8	1.39463	41.53	81.8	1.42798	43.99	86.8	1.46235	46.41
76.9	1.39529	41.58	81.9	1.42866	44.04	86.9	1.46304	46.46
77.0	1.39595	41.63	82.0	1.42934	44.09	87.0	1.46374	46.50
77.1	1.39660	41.68	82.1	1.43002	44.14	87.1	1.46444	46.55
77.2	1.39726	41.73	82.2	1.43070	44.19	87.2	1.46514	46.60
77.3	1.39792	41.78	82.3	1.43137	44.24	87.3	1.46584	46.65
77.4	1.39858	41.83	82.4	1.43205	44.28	87.4	1.46654	46.69
77.5	1.39924	41.88	82.5	1.43273	44.33	87.5	1.46724	46.74
77.6	1.39990	41.93	82.6	1.43341	44.38	87.6	1.46794	46.79
77.7	1.40056	41.98	82.7	1.43409	44.43	87.7	1.46864	46.84
77.8	1.40122	42.03	82.8	1.43478	44.48	87.8	1.46934	46.88
77.9	1.40188	42.08	82.9	1.43546	44.53	87.9	1.47004	46.93
78.0	1.40254	42.13	83.0	1.43614	44.58	88.0	1.47074	46.98
78.1	1.40321	42.18	83.1	1.43682	44.62	88.1	1.47145	47.03
78.2	1.40387	42.23	83.2	1.43750	44.67	88.2	1.47215	47.08
78.3	1.40453	42.28	83.3	1.43819	44.72	88.3	1.47285	47.12
78.4	1.40520	42.32	83.4	1.43887	44.77	88.4	1.47356	47.17
78.5	1.40586	42.37	83.5	1.43955	44.82	88.5	1.47426	47.22
78.6	1.40652	42.42	83.6	1.44024	44.87	88.6	1.47496	47.27
78.7	1.40719	42.47	83.7	1.44092	44.91	88.7	1.47567	47.31
78.8	1.40785	42.52	83.8	1.44161	44.96	88.8	1.47637	47.36
78.9	1.40852	42.57	83.9	1.44229	45.01	88.9	1.47708	47.41
79.0	1.40918	42.62	84.0	1.44298	45.06	89.0	1.47778	47.46
79.1	1.40985	42.67	84.1	1.44367	45.11	89.1	1.47849	47.50
79.2	1.41052	42.72	84.2	1.44435	45.16	89.2	1.47920	47.55
79.3	1.41118	42.77	84.3	1.44504	45.21	89.3	1.47991	47.60
79.4	1.41185	42.82	84.4	1.44573	45.25	89.4	1.48061	47.65
79.5	1.41252	42.87	84.5	1.44641	45.30	89.5	1.48132	47.69
79.6	1.41318	42.92	84.6	1.44710	45.35	89.6	1.48203	47.74
79.7	1.41385	42.96	84.7	1.44779	45.40	89.7	1.48274	47.79

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar according to Balling or degree Brix.	Specific gravity.	Degree Baumé.
90.0	1.48486	47.93	94.0	1.51359	49.81	98.0	1.54290	51.65
90.1	1.48558	47.98	94.1	1.51431	49.85	98.1	1.54365	51.70
90.2	1.48629	48.02	94.2	1.51504	49.90	98.2	1.54440	51.74
90.3	1.48700	48.07	94.3	1.51577	49.94	98.3	1.54515	51.79
90.4	1.48771	48.12	94.4	1.51649	49.99	98.4	1.54590	51.83
90.5	1.48842	48.17	94.5	1.51722	50.04	98.5	1.54665	51.88
90.6	1.48913	48.21	94.6	1.51795	50.08	98.6	1.54740	51.92
90.7	1.48985	48.26	94.7	1.51868	50.13	98.7	1.54815	51.97
90.8	1.49056	48.31	94.8	1.51941	50.18	98.8	1.54890	52.01
90.9	1.49127	48.35	94.9	1.52014	50.22	98.9	1.54965	52.06
91.0	1.49199	48.40	95.0	1.52087	50.27	99.0	1.55040	52.11
91.1	1.49270	48.45	95.1	1.52159	50.32	99.1	1.55115	52.15
91.2	1.49342	48.50	95.2	1.52232	50.36	99.2	1.55189	52.20
91.3	1.49413	48.54	95.3	1.52304	50.41	99.3	1.55264	52.24
91.4	1.49485	48.59	95.4	1.52376	50.45	99.4	1.55338	52.29
91.5	1.49556	48.64	95.5	1.52449	50.50	99.5	1.55413	52.33
91.6	1.49628	48.68	95.6	1.52521	50.55	99.6	1.55487	52.38
91.7	1.49700	48.73	95.7	1.52593	50.59	99.7	1.55562	52.42
91.8	1.49771	48.78	95.8	1.52665	50.64	99.8	1.55636	52.47
91.9	1.49843	48.82	95.9	1.52738	50.69	99.9	1.55711	52.51
92.0	1.49915	48.87	96.0	1.52810	50.73	100.0	1.55785	52.56
92.1	1.49987	48.92	96.1	1.52884	50.78			
92.2	1.50058	48.96	96.2	1.52958	50.82			
92.3	1.50130	49.01	96.3	1.53032	50.87			
92.4	1.50202	49.06	96.4	1.53106	50.92			
92.5	1.50274	49.11	96.5	1.53180	50.96			
92.6	1.50346	49.15	96.6	1.53254	51.01			
92.7	1.50419	49.20	96.7	1.53328	51.05			
92.8	1.50491	49.25	96.8	1.53402	51.10			
92.9	1.50563	49.29	96.9	1.53476	51.15			
93.0	1.50633	49.34	97.0	1.53550	51.19			
93.1	1.50707	49.39	97.1	1.53624	51.24			
93.2	1.50779	49.43	97.2	1.53698	51.28			
93.3	1.50852	49.48	97.3	1.53772	51.33			
93.4	1.50924	49.53	97.4	1.53846	51.38			
93.5	1.50996	49.57	97.5	1.53920	51.42			
93.6	1.51069	49.62	97.6	1.53994	51.47			
93.7	1.51141	49.67	97.7	1.54068	51.51			
93.8	1.51214	49.71	97.8	1.54142	51.56			
93.9	1.51286	49.76	97.9	1.54216	51.60			

6. *Table of Weight and Volume Relations.*

Degrees Baumé.	Specific gravity 25° C./25° C.	Specific volume (volume of 1 kilogram in liters).*	Weight of 1 U. S. gallon in pounds avoirdupois.†	Volume in U. S. gallons of 100 lbs. avoirdupois.‡	Weight of 1 fluidounce in grains.
70	0.700	1.4286	5.819	17.185	318.2
67	0.710	1.4085	5.902	16.943	322.8
64.5	0.720	1.3889	5.985	16.707	327.3
61.8	0.730	1.3699	6.068	16.479	331.9
59	0.740	1.3514	6.151	16.256	336.4
56.5	0.750	1.3333	6.235	16.039	341
54	0.760	1.3158	6.318	15.828	345.5
51.8	0.770	1.2987	6.401	15.623	350
49.5	0.780	1.2821	6.484	15.422	354.6
47	0.790	1.2658	6.567	15.227	359.1
45	0.800	1.2500	6.650	15.037	363.7
43	0.810	1.2346	6.733	14.851	368.2
41	0.820	1.2195	6.817	14.670	372.8
38.8	0.830	1.2049	6.900	14.494	377.3
36.8	0.840	1.1905	6.983	14.321	381.9
34.8	0.850	1.1765	7.066	14.152	386.4
33	0.860	1.1628	7.149	13.988	391
31	0.870	1.1494	7.232	13.827	395.5
29	0.880	1.1364	7.315	13.670	400.1
27.7	0.890	1.1236	7.398	13.516	404.6
25.5	0.900	1.1111	7.481	13.366	409.1
24	0.910	1.0989	7.565	13.219	413.7
22	0.920	1.0870	7.648	13.075	418.2
20.5	0.930	1.0753	7.731	12.935	422.8
19	0.940	1.0638	7.814	12.797	427.3
17.5	0.950	1.0526	7.897	12.663	431.9
15.5	0.960	1.0417	7.980	12.531	436.4
14.2	0.970	1.0309	8.063	12.401	441
13	0.980	1.0204	8.147	12.275	445.5
11.5	0.990	1.0101	8.230	12.151	450.1
10	1.000	1.0000	8.313	12.029	454.6
3	1.020	0.9804	8.479	11.794	463.7
5.7	1.040	0.9615	8.645	11.567	472.8
8.6	1.060	0.9434	8.812	11.348	481.9
10.5	1.080	0.9259	8.978	11.138	491
13	1.100	0.9091	9.144	10.936	500.1
16	1.120	0.8929	9.310	10.741	509.2
17.6	1.140	0.8772	9.477	10.552	518.3
20	1.160	0.8621	9.643	10.370	527.4
22	1.180	0.8475	9.809	10.194	536.4
24	1.200	0.8333	9.975	10.025	545.5
26.5	1.220	0.8197	10.142	9.860	554.6
28	1.240	0.8065	10.308	9.701	563.7
29.8	1.260	0.7937	10.474	9.547	572.8
31.6	1.280	0.7813	10.640	9.398	581.9
34	1.300	0.7692	10.807	9.253	591.0
35.2	1.320	0.7576	10.973	9.113	600.1
36.8	1.340	0.7463	11.139	8.977	609.2
38	1.360	0.7353	11.305	8.845	618.3
39.6	1.380	0.7246	11.472	8.717	627.4
41	1.400	0.7143	11.638	8.592	636.4
43	1.420	0.7042	11.804	8.471	645.5
44	1.440	0.6944	11.970	8.354	654.6
45.5	1.460	0.6849	12.137	8.239	663.7
47	1.480	0.6757	12.303	8.128	672.8
48	1.500	0.6667	12.469	8.020	681.9
49.5	1.520	0.6579	[illegible]	[illegible]	[illegible]

Table of Weight and Volume Relations.—Continued.

Degrees Baumé.	Specific gravity $\frac{25^\circ \text{C.}}{25^\circ \text{C.}}$	Specific volume (volume of 1 kilogram in liters).*	Weight of 1 U. S. gallon in pounds avoirdupois.†	Volume in U. S. gallons of 100 lbs. avoirdupois.‡	Weight of 1 fluidounce grains.
52	1.560	0.6410	12.968	7.711	709.2
53.4	1.580	0.6329	13.134	7.614	718.3
54.4	1.600	0.6250	13.300	7.519	727.4
55.4	1.620	0.6173	13.467	7.426	736.5
56.6	1.640	0.6098	13.633	7.335	745.6
58	1.660	0.6025	13.799	7.247	754.6
59	1.680	0.5952	13.966	7.160	763.7
60	1.700	0.5882	14.132	7.076	772.8
61	1.720	0.5814	14.298	6.994	781.9
61.7	1.740	0.5747	14.464	6.913	791.0
62.8	1.760	0.5682	14.631	6.835	800.1
63.5	1.780	0.5618	14.797	6.758	809.2
64.2	1.800	0.5556	14.963	6.683	818.3
65.1	1.820	0.5495	15.129	6.610	827.4
66	1.840	0.5435	15.296	6.538	836.5
67.6	1.860	0.5376	15.462	6.467	845.6
68.7	1.880	0.5319	15.628	6.399	854.7
69.5	1.900	0.5263	15.794	6.331	863.8
70.5	1.920	0.5208	15.961	6.265	872.8
71.2	1.940	0.5155	16.127	6.201	881.9
72	1.960	0.5102	16.293	6.137	891.0
73	1.980	0.5051	16.459	6.075	900.1
74	2.000	0.5000	16.626	6.015	909.2

* Or of 1 gram in cubic centimeters; strictly true only at 0° C. in vacuo.

† Multiply these figures by 2 for weight of one U. S. pint in ounces avoirdupois

‡ Divide these figures by 2 for volume in pints of 100 ounces avoirdupois.

IV. Alcohol Tables.

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.

Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.
1.0000	**0.00**	**0.00**						
0.9999	**0.05**	**0.07**	**0.9949**	**2.89**	**3.62**	**0.9899**	**5.94**	**7.40**
8	0.11	0.13	8	2.94	3.69	8	6.00	7.48
7	0.16	0.20	7	3.00	3.76	7	6.07	7.57
6	0.21	0.26	6	3.06	3.83	6	6.14	7.66
5	0.26	0.33	5	3.12	3.90	5	6.21	7.74
4	0.32	0.40	4	3.18	3.98	4	6.28	7.83
3	0.37	0.46	3	3.24	4.05	3	6.36	7.92
2	0.42	0.53	2	3.29	4.12	2	6.43	8.01
1	0.47	0.60	1	3.35	4.20	1	6.50	8.10
0	0.53	0.66	0	3.41	4.27	0	6.57	8.18
0.9989	**0.58**	**0.73**	**0.9939**	**3.47**	**4.34**	**0.9889**	**6.64**	**8.27**
8	0.63	0.79	8	3.53	4.42	8	6.71	8.36
7	0.68	0.86	7	3.59	4.49	7	6.78	8.45
6	0.74	0.93	6	3.65	4.56	6	6.86	8.54
5	0.79	0.99	5	3.71	4.63	5	6.93	8.63
4	0.84	1.06	4	3.76	4.71	4	7.00	8.72
3	0.89	1.13	3	3.82	4.78	3	7.07	8.80
2	0.95	1.19	2	3.88	4.85	2	7.13	8.88
1	1.00	1.26	1	3.94	4.93	1	7.20	8.96
0	1.06	1.34	0	4.00	5.00	0	7.27	9.04
0.9979	**1.12**	**1.42**	**0.9929**	**4.06**	**5.08**	**0.9879**	**7.33**	**9.13**
8	1.19	1.49	8	4.12	5.16	8	7.40	9.21
7	1.25	1.57	7	4.19	5.24	7	7.47	9.29
6	1.31	1.65	6	4.25	5.32	6	7.53	9.37
5	1.37	1.73	5	4.31	5.39	5	7.60	9.45
4	1.44	1.81	4	4.37	5.47	4	7.67	9.54
3	1.50	1.88	3	4.44	5.55	3	7.73	9.62
2	1.56	1.96	2	4.50	5.63	2	7.80	9.70
1	1.62	2.04	1	4.56	5.71	1	7.87	9.78
0	1.69	2.12	0	4.62	5.78	0	7.93	9.86
0.9969	**1.75**	**2.20**	**0.9919**	**4.69**	**5.86**	**0.9869**	**8.00**	**9.95**
8	1.81	2.27	8	4.75	5.94	8	8.07	10.03
7	1.87	2.35	7	4.81	6.02	7	8.14	10.12
6	1.94	2.43	6	4.87	6.10	6	8.21	10.21
5	2.00	2.51	5	4.94	6.17	5	8.29	10.30
4	2.06	2.58	4	5.00	6.24	4	8.36	10.38
3	2.11	2.62	3	5.06	6.32	3	8.43	10.47
2	2.17	2.72	2	5.12	6.40	2	8.50	10.56
1	2.22	2.79	1	5.19	6.48	1	8.57	10.65
0	2.28	2.86	0	5.25	6.55	0	8.64	10.73
0.9959	**2.33**	**2.93**	**0.9909**	**5.31**	**6.63**	**0.9859**	**8.71**	**10.82**
8	2.39	3.00	8	5.37	6.71	8	8.79	10.91
7	2.44	3.07	7	5.44	6.78	7	8.86	11.00
6	2.50	3.14	6	5.50	6.86	6	8.93	11.08
5	2.56	3.21	5	5.56	6.94	5	9.00	11.17
4	2.61	3.28	4	5.62	7.01	4	9.07	11.26
3	2.67	3.35	3	5.69	7.09	3	9.14	11.35

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.
0.9849	**9.43**	**11.70**	**0.9799**	**13.23**	**16.33**	**0.9749**	**17.33**	**21.29**
8	9.50	11.79	8	13.31	16.43	8	17.42	21.39
7	9.57	11.87	7	13.38	16.52	7	17.50	21.49
6	9.64	11.96	6	13.46	16.61	6	17.58	21.59
5	9.71	12.05	5	13.54	16.70	5	17.67	21.69
4	9.79	12.13	4	13.62	16.80	4	17.75	21.79
3	9.86	12.22	3	13.69	16.89	3	17.83	21.89
2	9.93	12.31	2	13.77	16.98	2	17.92	21.99
1	10.00	12.40	1	13.85	17.08	1	18.00	22.09
0	10.08	12.49	0	13.92	17.17	0	18.08	22.18
0.9839	**10.15**	**12.58**	**0.9789**	**14.00**	**17.26**	**0.9739**	**18.15**	**22.27**
8	10.23	12.68	8	14.09	17.37	8	18.23	22.36
7	10.31	12.77	7	14.18	17.48	7	18.31	22.46
6	10.38	12.87	6	14.27	17.59	6	18.38	22.55
5	10.46	12.96	5	14.36	17.70	5	18.46	22.64
4	10.54	13.05	4	14.45	17.81	4	18.54	22.73
3	10.62	13.15	3	14.55	17.92	3	18.62	22.82
2	10.69	13.24	2	14.64	18.03	2	18.69	22.92
1	10.77	13.34	1	14.73	18.14	1	18.77	23.01
0	10.85	13.43	0	14.82	18.25	0	18.85	23.10
0.9829	**10.92**	**13.52**	**0.9779**	**14.90**	**18.36**	**0.9729**	**18.92**	**23.19**
8	11.00	13.62	8	15.00	18.48	8	19.00	23.28
7	11.08	13.71	7	15.08	18.58	7	19.08	23.38
6	11.15	13.81	6	15.17	18.68	6	19.17	23.48
5	11.23	13.90	5	15.25	18.78	5	19.25	23.58
4	11.31	13.99	4	15.33	18.88	4	19.33	23.68
3	11.38	14.09	3	15.42	18.98	3	19.42	23.78
2	11.46	14.18	2	15.50	19.08	2	19.50	23.88
1	11.54	14.27	1	15.58	19.18	1	19.58	23.98
0	11.62	14.37	0	15.67	19.28	0	19.67	24.08
0.9819	**11.69**	**14.46**	**0.9769**	**15.75**	**19.39**	**0.9719**	**19.75**	**24.18**
8	11.77	14.56	8	15.83	19.49	8	19.83	24.28
7	11.85	14.65	7	15.92	19.59	7	19.92	24.38
6	11.92	14.74	6	16.00	19.68	6	20.00	24.48
5	12.00	14.84	5	16.08	19.78	5	20.08	24.58
4	12.08	14.93	4	16.15	19.87	4	20.17	24.68
3	12.15	15.02	3	16.23	19.96	3	20.25	24.78
2	12.23	15.12	2	16.31	20.06	2	20.33	24.88
1	12.31	15.21	1	16.38	20.15	1	20.42	24.98
0	12.38	15.30	0	16.46	20.24	0	20.50	25.07
0.9809	**12.46**	**15.40**	**0.9759**	**16.54**	**20.33**	**0.9709**	**20.58**	**25.17**
8	12.54	15.49	8	16.62	20.43	8	20.67	25.27
7	12.62	15.58	7	16.69	20.52	7	20.75	25.37
6	12.69	15.68	6	16.77	20.61	6	20.83	25.47
5	12.77	15.77	5	16.85	20.71	5	20.92	25.57
4	12.85	15.86	4	16.92	20.80	4	21.00	25.67
3	12.92	15.96	3	17.00	20.89	3	21.08	25.76
2	13.00	16.05	2	17.08	20.99	2	21.15	25.86
1	13.08	16.15	1	17.17	21.08	1	21.23	25.95

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.
0.9699	**21.38**	**26.13**	**0.9649**	**25.21**	**30.65**	**0.9599**	**28.62**	**34.61**
8	21.46	26.22	8	25.29	30.73	8	28.69	34.69
7	21.54	26.31	7	25.36	30.82	7	28.75	34.76
6	21.62	26.40	6	25.43	30.90	6	28.81	34.83
5	21.69	26.49	5	25.50	30.98	5	28.87	34.90
4	21.77	26.58	4	25.57	31.07	4	28.94	34.97
3	21.85	26.67	3	25.64	31.15	3	29.00	35.05
2	21.92	26.77	2	25.71	31.23	2	29.07	35.12
1	22.00	26.86	1	25.79	31.32	1	29.13	35.20
0	22.08	26.95	0	25.86	31.40	0	29.20	35.28
0.9689	**22.15**	**27.04**	**0.9639**	**25.93**	**31.48**	**0.9589**	**29.27**	**35.35**
8	22.23	27.13	8	26.00	31.57	8	29.33	35.43
7	22.31	27.22	7	26.07	31.65	7	29.40	35.51
6	22.38	27.31	6	26.13	31.72	6	29.47	35.58
5	22.46	27.40	5	26.20	31.80	5	29.53	35.66
4	22.54	27.49	4	26.27	31.88	4	29.60	35.74
3	22.62	27.59	3	26.33	31.96	3	29.67	35.81
2	22.69	27.68	2	26.40	32.03	2	29.73	35.89
1	22.77	27.77	1	26.47	32.11	1	29.80	35.97
0	22.85	27.86	0	26.53	32.19	0	29.87	36.04
0.9679	**22.92**	**27.95**	**0.9629**	**26.60**	**32.27**	**0.9579**	**29.93**	**36.12**
8	23.00	28.04	8	26.67	32.34	8	30.00	36.20
7	23.08	28.13	7	26.73	32.42	7	30.06	36.26
6	23.15	28.22	6	26.80	32.50	6	30.11	36.32
5	23.23	28.31	5	26.87	32.58	5	30.17	36.39
4	23.31	28.41	4	26.93	32.65	4	30.22	36.45
3	23.38	28.50	3	27.00	32.73	3	30.28	36.51
2	23.46	28.59	2	27.07	32.81	2	30.33	36.57
1	23.54	28.68	1	27.14	32.90	1	30.39	36.64
0	23.62	28.77	0	27.21	32.98	0	30.44	36.70
0.9669	**23.69**	**28.86**	**0.9619**	**27.29**	**33.06**	**0.9569**	**30.50**	**36.76**
8	23.77	28.95	8	27.36	33.15	8	30.56	36.83
7	23.85	29.04	7	27.43	33.23	7	30.61	36.89
6	23.92	29.13	6	27.50	33.31	6	30.67	36.95
5	24.00	29.22	5	27.57	33.39	5	30.72	37.02
4	24.08	29.31	4	27.64	33.48	4	30.78	37.08
3	24.15	29.40	3	27.71	33.56	3	30.83	37.14
2	24.23	29.49	2	27.79	33.64	2	30.89	37.20
1	24.31	29.58	1	27.86	33.73	1	30.94	37.27
0	24.38	29.67	0	27.93	33.81	0	31.00	37.34
0.9659	**24.46**	**29.76**	**0.9609**	**28.00**	**33.89**	**0.9559**	**31.06**	**37.41**
8	24.54	29.86	8	28.06	33.97	8	31.12	37.48
7	24.62	29.95	7	28.12	34.04	7	31.19	37.55
6	24.69	30.04	6	28.19	34.11	6	31.25	37.62
5	24.77	30.13	5	28.25	34.18	5	31.31	37.69
4	24.85	30.22	4	28.31	34.25	4	31.37	37.76
3	24.92	30.31	3	28.37	34.33	3	31.44	37.83
2	25.00	30.40	2	28.44	34.40	2	31.50	37.90

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.
0.9549	**31.69**	**38.11**	**0.9499**	**34.57**	**41.37**	**0.9449**	**37.17**	**44.24**
8	31.75	38.18	8	34.62	41.42	8	37.22	44.30
7	31.81	38.25	7	34.67	41.48	7	37.28	44.36
6	31.87	38.33	6	34.71	41.53	6	37.33	44.43
5	31.94	38.40	5	34.76	41.58	5	37.39	44.49
4	32.00	38.47	4	34.81	41.63	4	37.44	44.55
3	32.06	38.53	3	34.86	41.69	3	37.50	44.61
2	32.12	38.60	2	34.90	41.74	2	37.56	44.67
1	32.19	38.68	1	34.95	41.79	1	37.61	44.73
0	32.25	38.75	0	35.00	41.84	0	37.67	44.79
0.9539	**32.31**	**38.82**	**0.9489**	**35.05**	**41.90**	**0.9439**	**37.72**	**44.86**
8	32.37	38.89	8	35.10	41.95	8	37.78	44.92
7	32.44	38.96	7	35.15	42.01	7	37.83	44.98
6	32.50	39.04	6	35.20	42.06	6	37.89	45.04
5	32.56	39.11	5	35.25	42.12	5	37.94	45.10
4	32.62	39.18	4	35.30	42.17	4	38.00	45.16
3	32.69	39.25	3	35.35	42.23	3	38.06	45.22
2	32.75	39.32	2	35.40	42.29	2	38.11	45.28
1	32.81	39.40	1	35.45	42.34	1	38.17	45.34
0	32.87	39.47	0	35.50	42.40	0	38.22	45.41
0.9529	**32.94**	**39.54**	**0.9479**	**35.55**	**42.45**	**0.9429**	**38.28**	**45.47**
8	33.00	39.61	8	35.60	42.51	8	38.33	45.53
7	33.06	39.68	7	35.65	42.56	7	38.39	45.59
6	33.12	39.74	6	35.70	42.62	6	38.44	45.65
5	33.18	39.81	5	35.75	42.67	5	38.50	45.71
4	33.24	39.87	4	35.80	42.73	4	38.56	45.77
3	33.29	39.94	3	35.85	42.78	3	38.61	45.83
2	33.35	40.01	2	35.90	42.84	2	38.67	45.89
1	33.41	40.07	1	35.95	42.89	1	38.72	45.95
0	33.47	40.14	0	36.00	42.95	0	38.78	46.02
0.9519	**33.53**	**40.20**	**0.9469**	**36.06**	**43.01**	**0.9419**	**38.83**	**46.08**
8	33.59	40.27	8	36.11	43.07	8	38.89	46.14
7	33.65	40.34	7	36.17	43.13	7	38.94	46.20
6	33.71	40.40	6	36.22	43.19	6	39.00	46.26
5	33.76	40.47	5	36.28	43.26	5	39.05	46.32
4	33.82	40.53	4	36.33	43.32	4	39.10	46.37
3	33.88	40.60	3	36.39	43.38	3	39.15	46.42
2	33.94	40.67	2	36.44	43.44	2	39.20	46.48
1	34.00	40.74	1	36.50	43.50	1	39.25	46.53
0	34.05	40.79	0	36.56	43.56	0	39.30	46.59
0.9509	**34.10**	**40.84**	**0.9459**	**36.61**	**43.63**	**0.9409**	**39.35**	**46.64**
8	34.14	40.90	8	36.67	43.69	8	39.40	46.70
7	34.19	40.95	7	36.72	43.75	7	39.45	46.75
6	34.24	41.00	6	36.78	43.81	6	39.50	46.80
5	34.29	41.05	5	36.83	43.87	5	39.55	46.86
4	34.33	41.11	4	36.89	43.93	4	39.60	46.91
3	34.38	41.16	3	36.94	44.00	3	39.65	46.97
2	34.43	41.21	2	37.00	44.06	2	39.70	47.02

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.
0.9399	**39.85**	**47.18**	**0.9349**	**42.33**	**49.86**	**0.9299**	**44.68**	**52.34**
8	39.90	47.24	8	42.38	49.91	8	44.73	52.39
7	39.95	47.29	7	42.43	49.96	7	44.77	52.44
6	40.00	47.35	6	42.48	50.01	6	44.82	52.48
5	40.05	47.40	5	42.52	50.06	5	44.86	52.53
4	40.10	47.45	4	42.57	50.11	4	44.91	52.58
3	40.15	47.51	3	42.62	50.16	3	44.96	52.63
2	40.20	47.56	2	42.67	50.21	2	45.00	52.68
1	40.25	47.62	1	42.71	50.26	1	45.05	52.72
0	40.30	47.67	0	42.76	50.31	0	45.09	52.77
0.9389	**40.35**	**47.72**	**0.9339**	**42.81**	**50.37**	**0.9280**	**45.55**	**53.24**
8	40.40	47.78	8	42.86	50.42	70	46.00	53.72
7	40.45	47.83	7	42.90	50.47	60	46.46	54.19
6	40.50	47.89	6	42.95	50.52	50	46.91	54.66
5	40.55	47.94	5	43.00	50.57	40	47.36	55.13
4	40.60	47.99	4	43.05	50.62	30	47.82	55.60
3	40.65	48.05	3	43.10	50.67	20	48.27	56.07
2	40.70	48.10	2	43.14	50.72	10	48.73	56.54
1	40.75	48.16	1	43.19	50.77	00	49.16	56.98
0	40.80	48.21	0	43.24	50.82			
0.9379	**40.85**	**48.26**	**0.9329**	**43.29**	**50.87**	**0.9190**	**49.64**	**57.45**
8	40.90	48.32	8	43.33	50.92	80	50.09	57.92
7	40.95	48.37	7	43.39	50.97	70	50.52	58.36
6	41.00	48.43	6	43.43	51.02	60	50.96	58.80
5	41.05	48.48	5	43.48	51.07	50	51.38	59.22
4	41.10	48.54	4	43.52	51.12	40	51.79	59.63
3	41.15	48.59	3	43.57	51.17	30	52.23	60.07
2	41.20	48.64	2	43.62	51.22	20	52.68	60.52
1	41.25	48.70	1	43.67	51.27	10	53.13	60.97
0	41.30	48.75	0	43.71	51.32	00	53.57	61.40
0.9369	**41.35**	**48.80**	**0.9319**	**43.76**	**51.38**	**0.9090**	**54.00**	**61.84**
8	41.40	48.86	8	43.81	51.43	80	54.48	62.31
7	41.45	48.91	7	43.86	51.48	70	54.95	62.79
6	41.50	48.97	6	43.90	51.53	60	55.41	63.24
5	41.55	49.02	5	43.95	51.58	50	55.86	63.69
4	41.60	49.07	4	44.00	51.63	40	56.32	64.14
3	41.65	49.13	3	44.05	51.68	30	56.77	64.58
2	41.70	49.18	2	44.09	51.72	20	57.21	65.01
1	41.75	49.23	1	44.14	51.77	10	57.63	65.41
0	41.80	49.29	0	44.18	51.82	00	58.05	65.81
0.9359	**41.85**	**49.34**	**0.9309**	**44.23**	**51.87**	**0.8990**	**58.50**	**66.25**
8	41.90	49.40	8	44.27	51.91	80	58.95	66.69
7	41.95	49.45	7	44.32	51.96	70	59.39	67.11
6	42.00	49.50	6	44.36	52.01	60	59.83	67.53
5	42.05	49.55	5	44.41	52.06	50	60.26	67.93
4	42.10	49.61	4	44.46	52.10	40	60.67	68.33
3	42.14	49.66	3	44.50	52.15	30	61.08	68.72
2	42.19	49.71	2	44.55	52.20	20	61.50	69.11
1	42.24	49.76	1	44.59	52.25	10	61.92	69.50

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percentage of absolute alcohol by volume.
0.8890	**62.82**	**70.35**	40	77.71	83.60	**0.8190**	**91.36**	**94.26**
80	63.26	70.77	30	78.12	83.94	80	91.71	94.51
70	63.70	71.17	20	78.52	84.27	70	92.07	94.76
60	64.13	71.58	10	78.92	84.60	60	92.44	95.03
50	64.57	71.98	00	79.32	84.93	50	92.81	95.29
40	65.00	72.38				40	93.18	95.55
30	65.42	72.77	**0.8490**	**79.72**	**85.26**	30	93.55	95.82
20	65.83	73.15	80	80.13	85.59	20	93.92	96.08
10	66.26	73.54	70	80.54	85.94	10	94.28	96.32
00	66.70	73.93	60	80.96	86.28	00	94.62	96.55
			50	81.36	86.61			
0.8790	**67.13**	**74.33**	40	81.76	86.93	**0.8090**	**94.97**	**96.78**
80	67.54	74.70	30	82.15	87.24	80	95.32	97.02
70	67.96	75.08	20	82.54	87.55	70	95.68	97.27
60	68.38	75.45	10	82.92	87.85	60	96.03	97.51
50	68.79	75.83	00	83.31	88.16	50	96.37	97.73
40	69.21	76.20				40	96.70	97.94
30	69.63	76.57	**0.8390**	**83.69**	**88.46**	30	97.03	98.16
20	70.04	76.94	80	84.08	88.76	20	97.37	98.37
10	70.44	77.29	70	84.48	89.08	10	97.70	98.59
00	70.84	77.64	60	84.88	89.39	00	98.03	98.80
			50	85.27	89.70			
0.8690	**71.25**	**78.00**	40	85.65	89.99	**0.7990**	**98.34**	**98.98**
80	71.67	78.36	30	86.04	90.29	80	98.66	99.16
70	72.09	78.73	20	86.42	90.58	70	98.97	99.35
60	72.52	79.12	10	86.81	90.88	60	99.29	99.55
50	72.96	79.50	00	87.19	91.17	50	99.61	99.75
40	73.38	79.86				40	99.94	99.96
30	73.79	80.22	**0.8290**	**87.58**	**91.46**			
20	74.23	80.60	80	87.96	91.75	**0.7939**	**99.97**	**99.98**
10	74.68	81.00	70	88.36	92.05		Absolute	Alcohol.
00	75.14	81.40	60	88.76	92.36	**0.7938**	**100.00**	**100.00**
			50	89.16	92.66			
0.8590	**75.59**	**81.80**	40	89.54	92.94			
80	76.04	82.19	30	89.92	93.23			
70	76.46	82.54	20	90.29	93.49			
60	76.88	82.90	10	90.64	93.75			
50	77.29	83.25	00	91.00	94.00			

V. Physical and Chemical Constants of Fixed Oils and Fats.

(From Lewkowitsch and other authorities.)

	Specific gravity at 15°C.	Specific gravity at 100°C.	Melting-point. C.	Solidifying-point. C.
Linseed oil	0.931–0.938	0.880	—16° to —26°	—16°
Hemp-seed oil	0.925–0.931	. . .	. . . .	—27°
Walnut oil	0.925–0.926	0.871	. . . .	—27°
Poppy-seed oil	0.924–0.927	0.873	. . . .	—18°
Sunflower oil	0.924–0.926	0.919	. . . .	—17°
Fir-seed oil	0.925–0.928	. . .	. . . .	—27° to —30°
Maize oil	0.921–0.926	. . .	. . . .	—10° to —15°
Cotton-seed oil	0.922–0.930	0.867	. . . .	12°
Sesame oil	0.923–0.924	0.871	. . . .	— 5°
Rape-seed oil	0.914–0.917	0.863	. . . .	—2° to —10°
Black mustard oil	0.916–0.920	. . .	. . . .	—17.5°
Croton oil	0.942–0.955	. . .	. . . .	—16 °
Castor oil	0.960–0.966	0.910	. . . .	—12° to —18°
Apricot-kernel oil	0.915–0.919	. . .	. . . .	—14°
Almond oil	0.915–0.920	. . .	. . . .	—10° to —20°
Peanut (arachis) oil	0.916–0.920	0.867	. . . .	—3° to —7°
Olive oil	0.914–0.917	0.862	. . . .	2°
Menhaden oil	0.927–0.933	. . .	. . . .	—4°
Cod-liver oil	0.922–0.927	0.874	. . . .	0° to —10°
Seal oil	0.924–0.929	0.873	. . . .	3°
Whale oil	0.920–0.930	0.872	. . . .	—2°
Dolphin oil	0.917–0.918	. . .	. . . .	5° to —3°
Porpoise oil	0.926	0.871	. . . .	—16°
Neat's-foot oil	0.914–0.916	0.861	. . . .	0° to 1.5°
Cotton-seed stearine	0.919–0.923	0.867	40°	31° to 32.5°
Palm oil	0.921–0.925	0.856	27° to 42°	. . . .
Cacao butter	0.950–0.952	0.858	30° to 33°	25° to 26°
Cocoa-nut oil	0.925–0.926	0.873	20° to 26°	16° to 20°
Myrtle wax	0.995	0.875	40° to 44°	39° to 43°
Japan wax	0.970–0.980	0.875	51° to 54.5°	46°
Lard	0.931–0.938	0.861	41° to 46°	29°
Bone fat	0.914–0.916	. . .	21° to 22°	15° to 17°
Tallow	0.943–0.952	0.860	42° to 46°	35° to 37°
Butter fat	0.927–0.936	0.866	29.5° to 33°	19° to 20°
Oleomargarine	0.924–0.930	0.859	. . . .	. . . .
Sperm oil	0.875–0.884	0.833	. . . .	—25°
Bottle-nose oil	0.879–0.880	0.827	. . . .	. . . .
Carnauba wax	0.990–0.999	0.842	84° to 85°	80° to 81°
Wool-fat	0.973	0.901	39° to 42°	30° to 30.2°
Beeswax	0.958–0.969	0.822	62° to 64°	60.5° to 62°
Spermaceti	0.960	0.812	43.5° to 49°	43.4° to 44.2°
Chinese wax	0.970	0.810	80.5° to 81°	80.5° to 81°
Tung (Chinese wood oil)	0.936–0.942	. . .	. . . .	below —17°
Soya-bean oil	0.924–0.927	. . .	. . . .	8° to 15°

V. Physical and Chemical Constants of Fixed Oils and Fats.—*Continued.*

(From Lewkowitsch and other authorities.)

	Saponification value.	Maumené test.	Iodine value.	Hehner value.	Reichert value.
Linseed oil	190–195	104°–111°	175–190	. . .	. . .
Hemp-seed oil	190–193	95°–96°	148	. . .	. . .
Walnut oil	195	96°–101°	144–147	. . .	. . .
Poppy-seed oil	195	86°–88°	134–141	95.38	. . .
Sunflower oil	193–194	72°–75°	120–129	95	. . .
Fir-seed oil	191.3	98°–99°	118.9–120	. . .	. . .
Maize oil	188–193	56°–60.5°	117–125	89–95.7	2.5
Cotton-seed oil	191–195	68°–77°	104–110	96–17	. . .
Sesame oil	189–193	64°–68°	105–109	95.8	0.35
Rape-seed oil	170–178	51°–60°	95–105	95	. . .
Black mustard oil	174–174.6	43°–44°	96°–110	95.05	. . .
Croton oil	210.3–215	. . . . .	101.7–104	89	13.5
Castor oil	178–186	46°–47°	83.4–85.9	. . .	1.4
Apricot-kernel oil	192.2–193.1	42.5°–46°	100–107	. . .	. . .
Almond oil	190.5–195.4	51°–54°	93–97	96.2	. . .
Peanut (arachis) oil	190–197	45°–49°	85–98	95.86	. . .
Olive oil	191–196	41.5°–45.5°	80.6–84.5	95.43	0.3
Menhaden oil	189.3–192	123°–128°	140–170	. . .	1.2
Cod-liver oil	182–187	102°–103°	154–180	95.3	. . .
Seal oil	190–196	92°	127–140	94.2	0.22
Whale oil	188–193	91°–92°	110–136	93.5	2.04
Dolphin oil { Body oil	197.3	. . . . .	99.5	93.07	5.6
Dolphin oil { Jaw oil	200	. . . . .	32.8	66.28	65.92
Porpoise oil { Body oil	216–218.8	50°	119.4	. . .	23.45
Porpoise oil { Jaw oil	253.7	. . . . .	49.6	68.41	65.8
Neat's-foot oil	194.3	47°–48.5°	69.3–70.4	. . .	. . .
Cotton-seed stearine	194.6–195.1	48°	88.7–92.8	96.3	. . .
Palm oil	196.3–202	. . . . .	53–57	95.6	0.5
Cacao butter	192.2–193.5	. . . . .	32–41	94.59	1.6
Cocoa-nut oil	250–253	. . . . .	8.5–9.3	88.6	3.7
Myrtle wax	205.7–211.7	. . . . .	2.9	. . .	. . .
Japan wax	220–222.4	. . . . .	4.2–8.5	90.6	. . .
Lard	195.3–196.6	27°–32°	57–70	96	. . .
Bone fat	190.9	. . . . .	46.3–49.6	. . .	. . .
Tallow	195–198	. . . . .	36–47	95.6	0.25
Butter fat	221.5–227	. . . . .	26–35	87.5	28.78
Oleomargarine	194–203.7	. . . . .	55.3–60	95–96	2.6
Sperm oil	132.5–147	47°–51°	84	. . .	1.3
Bottle-nose oil	126–134	41°–47°	77.4–82	. . .	1.4
Carnauba wax	80-84	. . . . .	13.5	. . .	. . .
Wool-fat	98.2–102.4	. . . . .	25–28	. . .	. . .
Beeswax	91–96	. . . . .	8.3–11	. . .	. . .
Spermaceti	128	. . . . .	. . . . .	. . .	. . .
Chinese wax	63	. . . . .	. . . . .	. . .	. . .
Tung (Chinese wood oil)	193	. . . . .	150–165	. . .	. . .
Soya-bean oil	190.6–192.9	59°–61°	121.3–124	95.5	. . .

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