AN INTRODUCTION
TO THE
CHEMISTRY OF PAINTS

J. NEWTON FRIEND

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LONGMANS, GREEN, AND CO.
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BY

J. NEWTON FRIEND
PH.D. (WÜRZ.) D.SC. (B'HAM.)
AUTHOR OF "THE THEORY OF VALENCY"

WITH DIAGRAMS

LONGMANS, GREEN, AND CO.
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INTRODUCTION

THIS little work is the outcome of a series of lectures delivered to a class of Practical Painters and Decorators at the Darlington Technical College. The majority of the students could not be accused of possessing even a most elementary knowledge of chemistry, and further inquiries have shown that such is the condition of affairs amongst painters generally; although, of course, there are notable exceptions, which serve to "prove the rule," as the saying is. The appreciation with which these lectures were received encouraged me to publish the same in book form, in the hope of appealing to a much larger circle, and of thus creating a wider interest in the subject.

It is all very well to tell the youthful painter that cadmium yellow may not be tinted with white lead, and that it is unwise to mix together Prussian blue and lime; but he is very liable to forget such rules until he has learned their force by bitter experience. If, however, he is made to understand *why* these pigments are incompatibles, his interest is awakened, and the subject presents itself to him in an entirely new light. Now, this can only be done by a judicious inclusion of chemistry into the curriculum of the painter.

But the very name of chemistry is enough to frighten many practical men, for the simple reason that the majority of chemists will persist in laying such stress on symbols and formulæ, atoms and molecules. The consequence is that, before the student can begin to acquire a really practical and useful knowledge of chemistry, he has to wade through and memorize a number of (to him) dull and isolated facts, which might well be left out altogether, or at any rate reserved until the student has reached a more advanced stage. As the practical man has neither time nor inclination to do this, he not infrequently leaves chemistry severely alone, and therefore fails to appreciate its value and importance.

It has been my endeavour, therefore, to show that a very thorough knowledge of the chemistry of paints may be acquired by the average student, without even a mention of such things as symbols, formulæ, atomic weights, and the like; but for the sake of those who may wish to pursue any branch of the subject further, references are given, whenever possible, to more advanced literature and to original papers. Many well recognized tests for pigments and liquid vehicles are included in the various chapters, and will, it is hoped, prove of service to manufacturers and colour mixers. Should this work fall into the hands of the expert chemist, I trust that its pages will not be found altogether devoid of interest even for him.

It is at once my duty and pleasure to acknowledge the very kind assistance rendered to me by my friend and colleague, Mr. William Davison, who has patiently read through this work both in manuscript and in proof, and has made numerous useful suggestions, at the same time correcting many errors. Although I can scarcely hope that the book is, even now, entirely free from error, I believe that any inaccuracies will be of a relatively unimportant nature, for every endeavour has been made to consult the best authorities, and to include the newest and most reliable work.

J. N. F.

THE TECHNICAL COLLEGE,
DARLINGTON.

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AN INTRODUCTION TO THE CHEMISTRY OF PAINTS

I

THE AIR

THAT we are surrounded by air is a matter of common knowledge. Although we can neither smell it nor taste it when it is pure, yet we can feel it when once it has been set in motion. It is then called *wind*, and every cyclist knows how exhausting it is to toil against a heavy head wind. Further, we can actually *see* the air under certain exceptional conditions. During the past few years science has been progressing by leaps and bounds, and it has been found possible to produce such intense cold as is never experienced in nature as we know it, not even in the Arctic regions, about which we have been hearing so much of late. We have learned that, just as steam on being cooled turns into water, so the air, if exposed to a sufficient intensity of cold, can be converted into a liquid; and there are those who prophesy that within the near future liquid air will become as common as petrol, and will be used for driving motor cars and many other machines. Here, then, in liquid air we have our atmosphere in a visible form, and we are able to look at it and examine it just as we can any other ordinary object.

It will be evident to you, however, that if we confine the wind in a room it will cease to blow, and will thus become ordinary air again; and if we boil the liquid air, about which we have been speaking, we shall simply get our ordinary air back again in its usual form. No new substance has been produced in either case. We have therefore been dealing with what are known as **physical changes**. In fact, we may define a **physical change** as *one which a body may undergo without the formation of a new substance.*

Now, we know very well that there are several different kinds of air. In our ordinary conversation we speak about good air and bad air, fresh air and stale air. In order to fully appreciate the meaning of these terms, however, we need to know something about the composition of the air.

A few days ago a piece of bright iron wire gauze was pushed into this gas jar, and after moistening with water the jar was inverted in a basin of water (Fig. 1). You notice that two things have taken place—

i. The gauze has become covered with rust.
ii. The water has risen about one-fifth of the way up the gas jar.

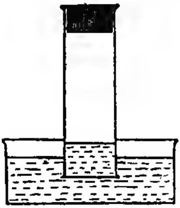

FIG. 1.

Let us now see if the air which is left behind in the jar is the same as that with which we originally started. We will close the mouth of the jar with this glass plate, and stand it, mouth upwards, on the table. If now I plunge a lighted taper into the jar, you notice that the flame is immediately extinguished. I will do it again. The result is just the same. The gas which is left behind in the jar is thus seen to be incapable of supporting ordinary combustion. Part of the air must therefore have disappeared, namely, that part which supports combustion.

From these experiments it is clear that—

i. Air is composed of two gases, one of which will support combustion, whereas the other will not.
ii. These gases are present in the atmosphere in the proportion of 1 to 4, respectively.
iii. The iron has combined with the former gas in the presence of water to produce iron rust.

Of course the chemist has given names to these two gases. The one which supports combustion is called **oxygen**, the other **nitrogen.** It is the former which supports life and constitutes the active principle of the air, for the nitrogen is very inert, serving largely to dilute and tone down the oxygen. With regard to nitrogen, therefore, we shall have little to say, for it is the oxygen which concerns us most as painters.

It is well known that almost all the metals corrode when left in contact with air for any length of time. This is due to the fact that they combine with the oxygen to form new substances, known to the chemist as **oxides.** Thus zinc combines with oxygen to form zinc oxide, more familiar to you, perhaps, under the name of zinc white or Chinese white. Similarly, iron in contact with moist oxygen yields rust, which differs, however, from the oxide of zinc, in that it contains water chemically united with it. It is therefore known as hydrated oxide of iron, and occurs in nature mixed with earthy material under the name of ochre. Such changes as these, which result in the formation of new substances, are known as **chemical changes.** In addition to oxygen and nitrogen, air always contains a certain amount of water vapour. This varies enormously in quantity, not merely from season to season, but from day to day and from hour to hour. In wet weather the air may be completely saturated with it. Even in the height of summer, when no rain perhaps has fallen for weeks, a little water vapour is always present.

As we shall see later, the air is never free from small quantities of carbon di-oxide—a gas which is formed when people and animals breathe, and when coal and wood are burned. Traces of ammonia, nitric acid, sulphur di-oxide, and sulphuretted hydrogen may also be detected, the last particularly in the smoky atmospheres of our large manufacturing towns and cities, like Middlesbrough and Sheffield. As these impurities have a very important action on paints, we shall have occasion to refer to them again later. Although in comparison with oxygen and nitrogen some of the gases are present in such minute quantities that we might regard them as negligible, yet when we bear in mind how vast the atmosphere is, it is clear that the actual amount of these impurities may be very considerable. It has been calculated that the weight of air above every square mile of the earth's surface cannot be less than 25 million tons. If, therefore, the actual amount of any given impurity exists to the extent of only one part by weight in 100 million parts of air, there will still be something like a quarter of a ton distributed over every square mile. As the wind is continually keeping the particles of air in motion, and sweeping fresh supplies over all surfaces exposed to its action, the effect upon our paints may be very considerable in the progress of time.

II

PIGMENTS CONTAINING OXIDE OF IRON

We are now in a position to understand what is meant by the term "oxide pigments." These are pigments obtained by the union of certain metals with oxygen. The majority of them occur in nature, and some few of them in such a condition of purity and softness, that the natural supplies may be used direct for the preparation of the pigment. In other cases they are mixed with so much silica (*i.e.* sandy material) or alumina (*i.e.* clayey substance), that it is more profitable to prepare the pigment by artificial methods, starting either with the pure metal itself, or utilizing some of its compounds which occur in nature in a greater degree of purity than its oxide.

Hydrated Oxide of Iron.—We have already seen that, when exposed to the action of moist air, iron readily combines with oxygen and water to form what we generally call rust, but which is, in scientific language, known as brown hydrated oxide of iron, or ferric hydroxide.[1] It is owing to this susceptibility of the metal to the action of moist oxygen that it is so rarely found native or free in nature; for if any large quantity were formed, as, for example, by the accidental firing of a coal mine in the neighbourhood of an iron ore deposit, the liberated metal would be gradually but steadily oxidized again by the corrosive action of the atmosphere. The hydrated oxide of iron occurs in vast quantities, under

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[1] A ferrous hydroxide is also known (see p. 14), which contains less oxygen in proportion to the iron, and when moist rapidly absorbs oxygen, yielding brown ferric hydroxide.

the name of brown hæmatite, in different parts of the world, and from it we get no inconsiderable amount of iron for commercial purposes. Although it possesses the characteristic ochre colour of iron rust, ordinary hæmatite is seldom if ever used as a pigment owing to the difficulty of grinding. Fortunately, deposits of hydrated oxide of iron occur in many countries, associated with silica, alumina, and other earthy materials, which are much more suitable. These are known as **ochres**, **siennas**, and **umbers**, and on grinding yield very beautiful pigments.

Whilst the colour of the ochres is due almost entirely to the oxide of iron which they contain, that of the siennas and umbers is modified by the presence of varying quantities of an oxide of the metal manganese. Generally speaking, the greater the amount of the manganese the darker is the shade of the pigment.

Ochres and umbers are found in Wales, Derbyshire, Cornwall, and Oxfordshire, as well as in many other countries, such as France, Italy, America, and Australia. Umber was first brought from ancient Ombria, the modern Spoleto, in Italy—whence its name. The finest umbers are imported from Cyprus, and are known as Turkey umbers, from the fact that they were first received through Constantinople, and their real source was not then known.

Sienna received its name from the fact that it was first discovered near the town of Sienna in Italy. Although sienna is now found elsewhere, the Italian varieties fetch the highest prices.

Similar pigments obtained from different sources frequently show marked differences in their chemical composition. This is particularly true of the umbers. A glance at the following analyses[1] of typical ochres, siennas, and umbers will suffice to show you what I mean.

---

[1] These analyses are taken from "Painters' Colours, Oils, and Varnishes," by G. H. Hurst. Published by Chas. Griffin & Co. 1906.

DERBYSHIRE OCHRE.

Water, combined	6·1
Barytes	20·9
Silica	4·5
Calcium sulphate	2·5
Calcium carbonate	21·8
Alumina	10·7
Anhydrous iron oxide [1]	33·5
Magnesia	trace
	100·0

AMERICAN OCHRE.

Water, free	1·3
Water, combined	3·7
Anhydrous iron oxide	11·0
Alumina	4·1
Silica	4·5
Calcium carbonate	trace
Barytes	75·3
	99·9

ITALIAN SIENNA.

Water, free	17·6
Water, combined, and organic matter	9·0
Silica	22·7
Calcium carbonate	1·0
Alumina	2·8
Oxide of manganese	1·2
Anhydrous iron oxide	45·8
	100·1

AMERICAN SIENNA.

Water, free	7·0
Water, combined	6·2
Anhydrous iron oxide	74·8
Alumina	5·2
Oxide of manganese	trace
Lime	trace
Silica	6·8
	100·0

TURKEY UMBER.

Water, free	4·3
Water, combined	8·5
Silica	29·6
Calcium carbonate	5·6
Oxide of manganese	12·3
Alumina	2·7
Anhydrous iron oxide	36·5
	99·5

DEVONSHIRE UMBER.

Water, free	6·6
Water combined	10·3
Silica	24·5
Calcium carbonate	6·1
Oxide of manganese	7·1
Alumina	12·8
Anhydrous iron oxide	30·0
Calcium sulphate	2·1
	99·5

The adulteration of ochres is of rare occurrence. Occasionally those which are poor in colour have a little chrome yellow added to them to develop their tint.

In order to be able to utilize these natural deposits as

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[1] The word "anhydrous" means "water-free." Although the oxide is really present in these pigments in the hydrated form, the percentage of water combined with it is given separately in this as in the accompanying analyses.

pigments, it is obviously necessary to obtain them in a state of fine division. In the case of the siennas the simple process of grinding is usually sufficient, for they contain but little material which cannot be safely admitted into the prepared pigments. The latter are, therefore, sent into the market as "raw sienna." Ochres, on the other hand, require somewhat different treatment. They may or may not be ground, according as they are hard or soft. But they are all submitted to the process of "levigation," as it is called. This process hinges on the fact that when different substances are thrown into water, the rate at which they sink to the bottom depends both upon their nature and their state of division. An experiment will make this clear. Some soil, containing a few small stones, has been put into this tall gas jar, which we will now fill with water, shake thoroughly, and replace on the table. What do you notice? The pebbles have already sunk to the bottom, and are being rapidly covered by the coarser particles of soil. Now all the coarse particles of soil have settled, and a finer deposit is slowly forming on top of them. The liquid above is still very muddy, but the suspended particles of soil will gradually fall to the bottom, the finest, of course, depositing themselves last of all. In a few hours the water will be clear again. Turning your attention to the bottom of the jar once more, you will see that we have thus been able to separate the particles of soil according to their varying degrees of lightness. But they are all lying together, one on top of the other, in successive layers. Now, suppose that instead of having one jar only, we were to have five, and that when the pebbles and coarser particles of soil had subsided in the first, we poured off the top or super-natant liquid into a second jar; we should thus have effected a complete separation of the soil into two distinct portions. When the coarser particles in this second jar had subsided, we could repeat the process, making use of a third jar, and then of a fourth, and finally of a fifth. In this way we could separate the soil into as many different portions as we please. This is all that the process of levigation means. Of course, in the commercial process the gas jars of the lecture-room are replaced by large tanks. The first (Fig. 2), into which the rough ochre is put, either directly as it comes from the ground or after it has been subjected to a preliminary grinding, is known in many places, particularly in Derbyshire and Cornwall, as the "buddle." Here it is thoroughly mixed with water, kept flowing in a gentle stream, which bears away the finer particles in suspension, and deposits them, as we have already seen, in varying degrees of fineness in the settling tanks 2, 3, 4, and 5. The coarse material, left behind in the buddle, is thrown away. It will be clear that the number of settling tanks required will depend upon two factors, namely—

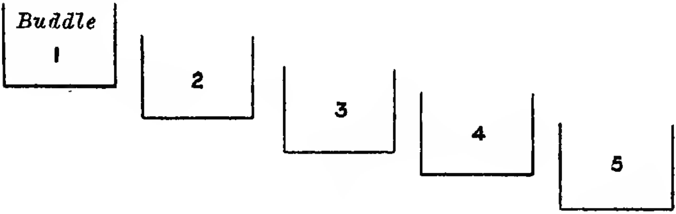

FIG. 2.

i. The quality of the crude material; and
ii. The desired quality of the levigated ochre.

It is universally found that the depth of colour of the ochre varies according to the degree of fineness. Thus the product from the second tank is darker than that from the third, and the fifth tank gives us the palest and finest ochres of all.

The sediment obtained in this way must now be dried, for it contains something like half its weight of water. This is accomplished by the aid of gentle heat. Great care must be exercised in the operation, for, if the heat is too intense, the ochre turns a reddish colour, being wholly or partially converted into rouge. The reason for this we shall see later. After thorough drying, the pigment is ready for the market. Raw umber is sent into the market in lumps, just as obtained from the mine. Powdered raw umber is prepared by levigation in a precisely similar manner to the ochres. All of these pigments are extremely "permanent"; that is to say, their hue remains unaltered for a practically indefinite time. They may also be safely mixed with any other pigments without fear of their affecting them or being injured by them. They are, therefore, said to possess great "inertia." As you are aware, cadmium yellow cannot be safely mixed with white lead, as the latter rapidly discolours in its presence. The reason for this will be evident later, and does not concern us just now. But the point that I wish to emphasize is this: Whilst pure cadmium yellow is very permanent towards atmospheric influences, yet its inertia is not great, since it attacks many other pigments when mixed with them. This distinction between permanence and inertia is very important, and should never be forgotten.

There is a third term which is very frequently misapplied, and that is "durability." This has no reference at all to the colour of the pigment, but to its preservative power. As we shall see later, with regard to its colour zinc white is excessively permanent, but as a pigment it is not very durable, for it has nothing like the power of protecting the surfaces which it covers such as characterizes lead pigments. It is, therefore, used extensively for inside work, where it is not exposed to severe usage. The ochres, siennas, and umbers, on the other hand, may be classed among the most durable of pigments.

It is interesting to note that the drying power of these oxides increases as the percentage of oxide of manganese rises. Thus the umbers are better driers than the siennas; and these, again, are better than the ochres. This is perhaps what we might expect, for oxide of manganese is one of the most powerful driers that the painter has at his disposal.

In **Vandyke-brown** we have another pigment closely related to the above. It received its name in honour of the great painter, Vandyke, and occurs in natural deposits similar to the ochres and umbers. It differs from these, however, in that it contains a high percentage of organic matter. Artificial Vandyke-browns are now on the market, which are made by mixing together lampblack, red oxide, and ochre. As this mixture is fairly cheap, and extremely permanent, it is largely used by the house-painter. It is very poor, however, and should only be used for cheap work. Not only is its colour of a low grade, but it is opaque; whereas the chief beauty of the genuine Vandyke-brown lies in its transparent nature, which enables the artist to apply it to the surface of other pigments without blocking them out from view. The effects which can thus be produced are extremely subtle and artistic. Although the umbers are good drying pigments, Vandyke-brown is the reverse. The reason for this is not known. It may be due, however, to the presence of so much organic matter.

Cappagh Brown is a complex pigment found in Cork, in Ireland, which when heated above the boiling-point of water acquires a rich red colour, reminding one of burnt sienna. It works well both in oil and water, and is very permanent.

Church[1] gives the following analysis of a sample which may be taken as fairly representative:—

Water	30·3	per cent.
Iron oxide	34·4	„
Oxide of manganese	27·2	„
Alumina	2·6	„
Lime	1·1	„
Silica	4·6	„
Traces of other substances	0·4	„
	100·6	

Anhydrous Oxide of Iron.—Into this porcelain crucible I have put some brown hydrated oxide of iron—as a matter of fact it is some rust scraped from a piece of old iron. We will heat this to redness for a time, and watch the result. Although the crucible is red hot, its contents seem to have become nearly black. We will now cool the crucible and empty its contents on to this sheet of asbestos cardboard. You notice that the brown oxide has yielded a reddish brown powder. The explanation of this change is not far to seek. The heat has expelled the combined water from the brown oxide with which we started, and by doing so has effected the change in colour. This red oxide is therefore spoken of as being "anhydrous" ferric oxide.

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[1] See "Chemistry of Paints and Painting," by Church, p. 206. Published by Seeley & Co.

You are all familiar with the changes which take place in the making of ordinary bricks. The brown clay on being baked assumes a reddish hue. We are now in a position to appreciate the chemistry of the process.

Red anhydrous oxide of iron occurs in enormous quantities both in Great Britain and elsewhere, under the name of red hæmatite, and it is easy to see how it could have been formed from deposits of brown hæmatite subjected to the action of the earth's heat. A very high temperature is not necessary to effect this change, provided sufficient time is allowed, for chemists have shown that the water is steadily, if slowly, expelled even at 400° Fahr.

The deposits of red hæmatite are frequently very pure, and if there is not much gritty matter present, so that they can be easily ground, they may be used direct for the preparation of the pigment. The crude material is ground to a powder, purified by levigation, dried, and sent into the market under the names of **Indian Red, Red Oxide, Rouge,** etc.

We are not, however, dependent upon these natural supplies of red hæmatite for our pigment, since we can prepare the latter in an even higher state of purity by artificial processes.

(1) From ochre.

In connection with the drying of ochres I have already mentioned that the heat must not be too intense, or a reddish colour will be produced. The reason for this change will now be apparent.

Very frequently, however, a red colour is desired. The depth of colour will naturally depend upon the extent to which the water has been expelled, and this is determined partly by the temperature, and partly also by the length of time in which the ochres are exposed to it. For Venetian reds about eight hours at a low red heat are required; light reds require some ten hours; Indian reds about twelve hours; whilst the purple reds require the longest time of all, namely, about sixteen hours. If the temperature is higher, the time required will, of course, be less. As soon as it is cold, the pigment is ready for the market. It will obviously contain all the earthy, non-volatile substances present in the ochre, such as silica, alumina, and lime, and its composition will vary considerably according to the particular variety of ochre which has been employed.

When siennas and umbers are calcined in this way, a change in colour occurs, it is true, but the familiar hue of rouge does not make its appearance. The reason for this is not clear. It may be due to the action of the organic matter which the raw material contains, or to the oxide of manganese masking in some way the action of the iron.

The products are sent into the market under the familiar names of **Burnt Sienna** and **Burnt Umber**, and their colours are known to you all.

(2) From iron sulphate.

Every one is familiar with that brass-like appearance which small pieces of coal frequently exhibit, and which is called by some "fool's gold." It is caused by the presence of a compound of iron and sulphur, known as iron pyrites, or iron sulphide. Here is a specimen which I picked out of a coal-box a few weeks ago.

The mineral occurs in vast quantities in Spain, and is exposed in heaps, together with scrap iron, to the action of air and moisture. Oxygen is thereby absorbed and the sulphur converted into sulphuric acid or oil of vitriol. This in turn attacks the iron, forming iron sulphate,[1] which dissolves readily in water, and is crystallized out and sent into the market as "copperas." In this bottle are crystals of copperas, and you notice their beautiful pale green colour, which has given rise to the very appropriate name "green vitriol," by which they are often known. When the crystals are calcined, they lose all their sulphur and part of their oxygen, yielding anhydrous oxide of iron. This is now ready for the market, and is very pure.

Into this porcelain crucible I have put a little powdered copperas, and will heat it to redness for about fifteen minutes. On cooling you notice the familiar appearance of the rouge.

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[1] Inasmuch as two sulphates of iron are known, this one, which contains a relatively larger amount of iron, is termed *ferrous sulphate.* The other compound, which, however, does not concern us here, is known as *ferric sulphate.*

(3) From solutions containing iron.

Here are two test-tubes. This one contains a solution of washing soda in water. The other is filled with a solution of copperas or ferrous sulphate. On pouring the contents of both tubes into this jar, what do you observe? A greenish precipitate of ferrous hydroxide is formed, which rapidly turns brown, owing to the absorption of oxygen from the air, yielding ferric hydroxide, which is our familiar brown hydrated oxide of iron. We might have added the necessary oxygen to the copperas solution before mixing with the soda, by allowing it to stand for some time in contact with the air. In that case the brown precipitate would have been obtained at once on the addition of the soda. A quicker method would be to add an oxidizer to the copperas solution, that is, some substance which can readily give up its own oxygen, such as nitric acid. In that case the oxidation would proceed independently of the atmosphere. Oxidized solutions of iron such as these are being continually prepared as by-products in many manufacturing processes, and were originally thrown away as useless. Now, however, they are mixed with various alkalies, such as washing soda, ammonia, and lime, whereby the hydrated oxide of iron is precipitated. This is transferred to crucibles and heated to redness; water is expelled, and the red, anhydrous ferric oxide results.

Obtained by these methods, the different forms of red oxide of iron are very useful pigments. They may safely be mixed with any other colours, for they neither injure them nor are they themselves affected. This is a very important point. They do not mix as well with oil as does red lead, neither do they act as driers.

It is interesting to note that the Maori[1] use a species of red oxide of iron for decorative purposes, under the name of *kokowai.* It is generally dug out of the ground, roasted, and ground to a powder. A finer quality, however, is obtained from running streams by throwing in bundles of ferns, which gradually become covered with a fine deposit. This is dried,

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[1] Paper read by Archdeacon Walsh, of Waimate, New Zealand, before the Auckland Institute, 1909.

made into balls, and roasted. The liquid vehicle used is shark oil, and the resulting paint is remarkably permanent and durable, lasting practically as long as the wood to which it is applied. The Maori decorate their houses, canoes, palisades, etc., as well as their persons, with this kokowai.

Terre Verte.—Under the name of **Terre Verte** a number of green earthy pigments of varying composition are sent into the market. Very good qualities of the pigment are found in the Mendip Hills in England, as well as in many places in Italy, France, and Cyprus. The crude material is ground as finely as possible, and sometimes levigated. On drying it is ready for use.

As a pigment terre verte is valuable on account of its permanent character. It mixes well with both oil and water, and was largely used by the early painters, as being one of their best greens. It is very inert, and may therefore be mixed with any other pigments without fear of either injuring them or being injured by them. In this way it is superior to the copper greens, which are readily discoloured by sulphuretted hydrogen. When heated, terre verte is converted to a reddish-brown colour, the change being similar to that which takes place on heating ochres, siennas, and umbers.

The following analyses will give you a good idea of the general composition of terre verte.

1. Analysis of terre verte from Cyprus, by Klaproth:[1]

Silica	51·5	per cent.
Oxide of iron	20·5	,,
Oxide of potassium	18·0	,,
Oxide of magnesium	1·5	,,
Water	8·0	,,
	99·5	

2. Analysis of Italian terre verte, by Hurst:

Water	5·1	per cent.
Oxide of iron	26·9	,,
Alumina	3·2	,,
Calcium oxide	2·1	,,
Silica	52·1	,,
Magnesia	10·6	,,
	100·0	

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[1] Quoted by Hurst, "Painters' Colours," etc., p. 189.

During the course of my lecture I have made frequent use of the words *hue*, *tint*, and *shade*. As these are frequently used synonymously by painters, it will be well for us to bear in mind their true significance. By *hue* we mean the colour of a pigment; thus ochre may be said to have a yellow hue, and rouge a red one. *Tints* are obtained by mixing any colour with white, and *shades* by mixing with black. It is thus obviously incorrect to say that, by mixing a little chrome yellow with Prussian blue, we lighten the shade or tint of the latter, for a new hue or colour is thereby produced. If, on the other hand, we mix some carbon black with chrome yellow, and barytes with Prussian blue, then we have produced a darker shade in the former, and a lighter tint in the latter.

III

MISCELLANEOUS OXIDE PIGMENTS

Oxide of Lead.—One of the oldest and most important pigments used by the painter is the so-called "red lead" or "minium." That this body was known to the ancients is evident from the fact that colour pots have been found to contain it, after having lain buried for hundreds of years amid the ruins of ancient Greek and Roman cities. Red lead is found in small quantities in nature, but for the preparation of his pigment the painter is dependent upon the artificially manufactured substance.

It is a matter of common knowledge that, when lead is melted in air, it becomes covered with a scum, popularly known as dross. This is due to the fact that the metal readily combines with oxygen, and the dross is neither more nor less than lead oxide. But lead, in common with most other metals, can combine with oxygen in several different proportions under varying conditions to form separate and well-defined oxides. The chemist has therefore found it necessary to distinguish between them by giving each a separate name corresponding to its composition. Lead dross is known to him as lead mon-oxide, but it contains some metallic lead as well. This is removed by grinding, which flattens out the unoxidized metal, but powders the oxide. By means of sieves the two can be readily separated. In order to convert lead mon-oxide into red lead it is necessary to add to it some more oxygen. This is readily done by heating the powder in a plentiful supply of air. On a commercial scale this process occupies some forty-eight hours. The changes which take place may be represented by the following equations:—

Lead + oxygen = lead monoxide
Lead monoxide + oxygen = red lead

According to theory, 100 lbs. of pure metallic or "blue" lead should yield 110 lbs. of red lead. In practice, about 108 lbs. are actually obtained, which is a remarkably close approximation. The purer the lead, the better is the quality of the red lead. The presence of iron renders the colour darker.

As a pigment, red lead is of great value, since it mixes readily with linseed oil, and has a good body. It is also a powerful drier, which property, as we shall see later, is regarded by many as due in part to the extra amount of oxygen which it contains. Red lead paint, therefore, dries very rapidly, and for this reason is frequently used for packing and luting pipes and joints. It is very permanent and inert, and may be safely mixed with almost any pigments save those containing sulphur; such as, for example, cadmium yellow, lithophone, and ultramarine, which turn it black. This is a fault common to all lead pigments, and the chemistry of the change will be evident to us before long.

Red lead is occasionally adulterated with the red oxides of iron, but such admixture is readily detected. The suspected sample is warmed with some fairly strong nitric acid: whether adulterated or not, the mass turns brown, owing to the formation of a third oxide of lead, richer in oxygen than either red lead or lead mon-oxide. It is known as lead di-oxide. In fact, red lead is generally looked upon as being a compound of lead mon-oxide and lead di-oxide. If the heating is prolonged, however, the whole of the oxide dissolves, yielding a clear solution of lead nitrate. Any insoluble residue indicates the presence of some impurity, such as silica or sand. If the solution is slightly yellow, the presence of iron is to be expected. I will filter and add some dilute sulphuric acid to the liquid which passes through. A heavy white precipitate is at once formed, consisting of lead sulphate. This is frequently used as a white pigment in place of white lead, under the name of "patent white lead," etc., being both less poisonous and more permanent than white lead. Any iron present will still remain in solution, and if, on filtering, we add a few drops of a solution of yellow prussiate of potash, known to the chemist as potassium ferro-cyanide, a deep blue colour is formed. This is Prussian blue, and confirms the presence of iron. If no colour had been formed, the absence of iron would have been demonstrated.

Red lead is often very pure, however. The sample I used just now was purposely adulterated with rouge in order to show you how the test is carried out. The red lead in this bottle yielded the following analysis, which may be regarded as fairly representative:

Water	0·00	per cent.
Insoluble residue	1·07	,,
Red lead	98·93	,,
	100·00	

It is easy to show that red lead contains lead by mixing a little of the pigment with sodium carbonate, and placing it in the hollow scooped out of a piece of charcoal. On heating in the blow-pipe for a few minutes, small metallic beads make their appearance. When rubbed on paper they leave a black mark behind. When hammered they do not split, but flatten out. Clearly they are beads of metallic lead.

The chemical change involved is very simple. Charcoal is known to the chemist under the name of carbon. When heated it readily burns in oxygen, yielding a gaseous oxide, to which the name carbon di-oxide has been given. This is what goes on every day in our fires, for coal is only another form of carbon, though rather an impure one. In our experiment the carbon has united with the oxygen in the red lead, leaving the metal behind. Thus—

$$\text{Carbon} + \text{lead oxide} = \text{carbon di-oxide} + \text{lead}$$

When gently heated, red lead turns a darker colour, but on cooling returns to its original tint. At red heat it loses oxygen and is converted into the mon-oxide. I have referred to the fact that red lead is often termed "minium." It is interesting to note that this name was originally applied to cinnabar, which, on account of its cost, was extensively adulterated with red lead, and the name thus gradually passed to the adulterant. Red lead is a very heavy pigment, weighing some 8·5 times as much as an equal volume of water. The chemist therefore says that its *specific gravity* is 8·5, where by that term he means "the number of times heavier a given volume of a substance is, than an equal volume of water." Inasmuch as the temperature at which the determinations are carried out has a considerable influence on the value obtained for the specific gravity, the standard temperature is taken as 60° F., which is the average room temperature.

Zinc Oxide.[1]—Here is a strip of zinc, which I will hold in the blow-pipe flame with a pair of crucible tongs. Now the metal is very hot, and I will direct upon it a stream of oxygen gas from this cylinder. You see that the zinc readily burns with a bluish flame, evolving clouds of whitish smoke, and a pale yellow, crumbling mass remains behind, which on cooling becomes quite white. This is zinc oxide, known to the early chemists as "philosopher's wool," but more familiar to you perhaps under the name of zinc white or Chinese white. In the commercial preparation of this pigment, ingots of metallic zinc are thrown into fire-clay retorts already at white heat, whereby the metal is rapidly volatilized, and, on issuing from the mouth of the retort, burns with a smoky flame. The fumes are collected in large chambers arranged in series, one after the other, so as to present a large surface on which the solid oxide can collect. The end chamber is connected with the furnace chimney, and a good draught is thus ensured, which draws the fumes by a circuitous course through each successive chamber. The bottom of each chamber is made to slope as shown in the diagram (Fig. 3), so that, on opening a slide, the zinc white falls into barrels underneath.

Owing to the expense entailed by the use of a pure metal such as zinc as raw material, attempts have been made to

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[1] See Holley, "The Lead and Zinc Pigments." Published by Chapman and Hall.

obtain the oxide from the natural ores, namely the carbonate, or *calamine*, and the sulphide, known variously as *zinc blende* and *black Jack*. Whilst these ores can be volatilized readily enough, however, the resulting zinc white contains as impurities the oxides of a number of other metals, notably cadmium. If these were white it would not matter so much. But unfortunately for the process, cadmium oxide is brown, and a very small quantity of it suffices to spoil a large amount of zinc white. Consequently such methods have not hitherto proved generally successful.

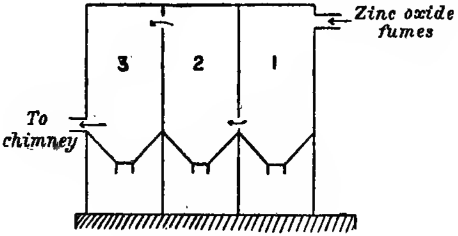

FIG. 3.

As a pigment zinc oxide has, in recent years, greatly increased in popularity with painters. When of good quality it is beautifully white, very fine, and easily worked. It is quite insoluble in oil, water, and turpentine, and possesses several advantages over the older and more commonly used pigment, white lead. These advantages may be enumerated as follows:—

1. Zinc oxide is not poisonous. This is a very important feature, and one which will, I am sure, appeal to you very strongly. It has been urged that painters who wash themselves frequently are very little likely to suffer from plumbism or lead poisoning. But a man cannot always be washing his hands, and the most particular of us are sure at times to neglect the necessary precautions when work is heavy.

2. It is well known that white lead has a peculiar knack of darkening when exposed to the fumes from burning coal or coal gas, etc. A precisely similar change is observed when it

is mixed with cadmium yellow, ultramarine, and many other common pigments containing sulphur. Zinc oxide, on the other hand, is exceedingly permanent, being affected by none of the substances mentioned above. It may therefore be used in painting buildings exposed to practically any atmosphere, and may also be mixed with any other pigments, without either affecting them or being affected by them. Zinc white is not so durable, however, as white lead, and is hence used for inside work, where it is less exposed to rough usage, the latter pigment being employed in outdoor painting.

In ordinary conversation "body" and "covering power" are frequently spoken of as being synonymous, which is a mistake. Correctly speaking, by "body" is meant the power of blocking out from view the surface over which the pigment is brushed. This property is possessed to a marked degree by white lead, and that is undoubtedly why this very poisonous pigment has been used for so long. "Covering power," on the other hand, refers to the property by which a pigment can be made to spread over a large area, and might with advantage be termed "spreading power." Zinc oxide excels particularly in this respect.

It is usually stated that zinc oxide is lacking in body. But since a pound of zinc oxide has a very much greater bulk than an equal weight of white lead, it is obviously difficult to make a fair comparison. For if each were mixed with the same amount of oil, either the white lead would be too thin, or the oxide of zinc would be too thick for proper application with a brush. The fact of the matter is, the two pigments must be treated differently.

With regard to white lead we shall have a good deal more to say later. It is universally agreed, however, that the best way to treat zinc oxide is to mix it with boiled linseed oil, without the addition of any driers, although a little turpentine may be added to bring the mixture to the right consistency.

Unfortunately zinc oxide is rather expensive, and is liable to adulteration by unscrupulous dealers with barytes, whiting, china clay, etc. It is easy to determine, however, whether or on a given sample is pure. On warming gently with dilute sulphuric acid the whole mass should dissolve without effervescence. No other commonly used white pigment does this. The solution now contains zinc sulphate, which, on evaporation, can be obtained as colourless crystals, known as white vitriol. The equation representing this reaction may be written as follows :—

Zinc oxide + sulphuric acid = zinc sulphate

If effervescence occurs on the addition of acid, adulteration with a carbonate is to be suspected. An insoluble residue indicates the presence of silica (sand) or some compound of barium, calcium, or lead, which was either present as the insoluble sulphate, or has been converted into the same by the added sulphuric acid.

Oxide of Chromium.—Under the name of **Chrome Green,**[1] the sesqui-oxide of chromium forms a very valuable pigment, both on account of its beautiful colour and its remarkable permanence and inertia. Guignet appears to have been one of the first to prepare it, and the pigment is therefore frequently known as **Guignet's Green.**

Chrome green is prepared in a variety of ways. One of the most usual is by heating to redness a mixture of boric (or boracic) acid and bichromate of potash. After about four hours the fused mass is thoroughly washed with water, ground and dried.

The chemical changes involved during the process are somewhat complex, but I will try and make their general nature clear.

Potassium bichromate is a compound of potash and chromium tri-oxide, which latter substance contains twice as much oxygen in proportion to the chromium as does chrome green. Although of a bright red colour, chromium tri-oxide cannot be used as a pigment, partly on account of its excessive solubility in water, but chiefly because it is a very powerful oxidizer, attacking most metals and organic substances, being itself reduced to the green sesqui-oxide. When, therefore,

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[1] Not to be confused with the chrome greens mentioned in Chapter IX., which are mixtures of chrome yellow, Prussian blue, and barytes.

potassium bichromate is fused with boric acid, reduction takes place, resulting in the formation of chrome green, which is insoluble in water and in acids alike. It is therefore readily extracted from the fused mass, and washed free from any impurity.

Manganese Di-oxide.—Manganese di-oxide, or **Manganese Black** is occasionally used as a black pigment. It has, however, no advantage over the carbon blacks, and, being relatively expensive, is little used. It has an extensive application as a drier, and in this capacity we shall have occasion to refer to it again later.

Manganese di-oxide occurs in nature as the mineral *pyrolusite.* This is ground to a powder with water, when, on drying, it is ready for the market.

When warmed with hydrochloric acid or spirits of salt, manganese di-oxide causes the evolution of a greenish-yellow gas, known as chlorine. This gas is easily recognized by its powerful and penetrating odour, and by the fact that it readily bleaches a damp, coloured rag. If the pigment is pure, the whole of it will go into solution as manganese chloride. This test serves at once to distinguish it from the carbon blacks, which are unaffected by hydrochloric acid. The explanation of this reaction is not far to seek. Hydrochloric acid is a compound of hydrogen and chlorine—as its name implies. In manganese di-oxide the metal is combined very firmly with half the oxygen it contains, whilst the other half is but comparatively loosely attached. On warming with the acid, therefore, this loosely attached oxygen unites with some of the hydrogen to form water—for water is simply a compound of oxygen and hydrogen—liberating the chlorine.

The lower oxide of manganese thus obtained now dissolves in the remainder of the acid, yielding, as already stated, manganese chloride. The equations representing this change may be written as follows:

1. Manganese di-oxide + hydrochloric acid = manganese mon-oxide + water + chlorine
2. Manganese mon-oxide + hydrochloric acid = manganese chloride + water

China Clay.—China clay is a naturally occurring mineral, consisting chiefly of silica and alumina, and is used very largely in the manufacture of pottery. It occurs in large quantities in this country, particularly in Devonshire and Cornwall. Before these deposits were known and worked our English made pottery had a brownish colour, due to the presence of oxide of iron or ochre. White pottery was, however, imported chiefly from China; hence the name "china" for such articles. When the white clay was found in England it was at once used for the manufacture of our own pottery, and thus received the name of "china clay." Sometimes it is called *kaolin*, which is its Chinese name.

China clay is a decomposition product of granite, and contains silica, alumina, and water, chemically united together with traces of other substances. The following analyses may be regarded as typical :—

Analyses of China Clay.

	Cornwall.	Devon.	French.	China.	America.
Silica	46·78	47·20	48·37	50·50	47·13
Alumina	39·60	38·80	34·95	33·76	36·76
Water	13·16	12·00	12·62	11·22	15·13
Potash	0·12	1·76	2·4	1·90	—
Iron oxide	0·09	—	1·26	1·80	trace
Lime	0·07	0·24	—	—	0·04
Magnesia	—	—	—	0·80	—
	99·82	100·00	99·60	99·98	99·06

Theoretically, perfectly pure kaolin should have the following composition :

Silica	47·1	per cent.
Alumina	39·2	,,
Water	13·7	,,
	100·0	

and comparison with the results quoted above shows the state of purity of the natural product.

Granite is a so-called "eruptive" rock, because ages ago it was forced up in a molten or plastic condition into or through the crust of the earth. It exhibits a crystalline structure, and the individual minerals composing it are large enough to be distinctly recognized by the naked eye. The three most important of these are felspar, quartz, and mica, the first named occurring in largest quantity, and consisting of potash, alumina, and silica. When exposed to the destructive action of the atmosphere, the potash is gradually washed out of the felspar, and china clay remains. The quartz and mica are more resistant, the former consisting of nearly pure silica, whereas the latter has the same constituents as felspar, but in different proportions.

The process of extracting the china clay from the undecomposed quartz and mica is comparatively simple, and is carried out at the mouth of the clay pits in order to save cost of transit. After the deposit of clay has been laid bare by the removal of any surface-soil or "over-burthen," a stream of water is directed into the pit. This washes the clay, sand or quartz, and mica to the lowest part, where the bulk of the quartz settles out, the mica, clay, and finer particles of quartz remaining suspended. The water is now pumped out of the pit and levigated. The sand is deposited in a series of wooden troughs, known as "launders," and the clayey waters are then led through a series of long narrow troughs, known as "micas," in which the mica collects. Finally, the clay itself is allowed to settle in large tanks or pits. The clear water is pumped off and used over again, and the clay, which contains about 50 per cent. of water, is dried on a series of flues and sent into the market.

As a pigment china clay is not much used, although it is remarkably permanent and inert, being insoluble in water, dilute acids, and alkalies alike. Prolonged boiling with strong sulphuric acid effects the solution of the alumina, whereby aluminium sulphate is produced, and a gelatinous residue of silica remains behind.

When mixed with oil, china clay loses much of its body, becoming somewhat transparent. It may be used with good results in water colours and in distemper work, and is frequently employed in the preparation of the aniline lakes. It is cheap, and rarely adulterated.

Smalt.—Smalt is now much less used than formerly, having been superseded by artificial ultramarine. It is chemically a potash glass, which contains cobalt oxide instead of lime. The following analysis, quoted by Blount and Bloxam,[1] shows its general composition, though this is variable.

Silica	70·86	per cent.
Potash and Soda	21·41	,,
Cobalt oxide	6·49	,,
Alumina, etc.	1·24	,,
	100·00	

Smalts containing as much as 16 per cent. of cobalt oxide are also prepared, as is seen from the analysis given by Rivot.[2]

Silica	56·4	per cent.
Alumina	3·5	,,
Iron oxide	4·1	,,
Cobalt oxide	16·0	,,
Calcium oxide	1·6	,,
Potash	13·2	,,
Lead oxide	4·7	,,
	99·5	

The cobalt oxide, known technically as *Zaffre*, is obtained by roasting certain cobalt ores, and is mixed with ground quartz or silica, whose amount varies according to the depth of colour required in the finished pigment. About one-third of its weight of potassium carbonate is now added to the mixture, and the whole heated to whiteness in earthenware crucibles, free from lime, and composed of highly resistant clay. The fused product is thrown into cold water, which breaks it up into small angular pieces. After being ground, levigated, and dried, the pigment is ready for the market.

Smalt is not altered in colour by exposure to light, but its colouring power is weak. This defect, together with its cost,

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[1] See "Chemistry for Engineers and Manufacturers," by Blount and Bloxam. Published by Chas. Griffin & Co., 1900, vol. ii. p. 357.

[2] See Hurst, "Painters' Colours," etc., p. 230.

has caused it to be considerably less used than formerly. Chemically, it is extremely inert, not being readily affected by acids or alkalies, and can thus be distinguished from most other blues. Owing to its inertness, it may safely be mixed with any other pigments without danger of either injuring them or being affected by them.

Cobalt Blue.—This pigment, which consists essentially of the oxides of cobalt and alumina, can be prepared in several different ways. A usual method is to add a solution of sodium carbonate or washing soda to one containing the requisite proportions of alum and a soluble cobalt salt. If cobalt nitrate is used, one part is taken to every twelve parts of alum. The precipitated oxides are heated to redness in a crucible, and, when the required colour has been attained, the crude mass is washed, dried, and ground.

Sometimes sodium phosphate is used for the precipitation of the cobalt, and the cobalt phosphate is mixed with the alumina, obtained by adding soda to alum separately, and then the resulting mixture is treated in the way already explained, namely, heated in a crucible and ground for the market.

As a pigment, cobalt blue is very permanent under the combined influence of light and air. It is also very resistant to the action of acids and alkalies. It works rather better in water than in oil, and is therefore largely used by water-colour artists and for superior decorative purposes. The following analysis, given by Hurst,[1] will suffice to give you a general idea of the percentage composition of the pigment.

Water	3·08	per cent.
Alumina	80·80	,,
Cobalt oxide	15·13	,,
Other bodies	0·99	,,
	100·00	

Cobalt Green.—This pigment is analogous to cobalt blue the alumina of the latter being replaced by zinc oxide. It can be prepared in a variety of ways. One of the simplest

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[1] See Hurst, *opus cit.*, p. 232.

is to dissolve one part of cobalt nitrate and six parts of zinc sulphate in water and precipitate the hydrated oxides of the two metals with a solution of sodium carbonate. After thorough washing, the precipitate is dried and heated to redness. When the required colour has been attained, the crude mass is washed, dried, and ground, and sent into the market under various names, such as **Cobalt Green, Rinman's Green, Zinc Green.**

As a pigment, cobalt green is not much used on account of its cost. It has a bright green colour, slightly tinged with yellow, and is very permanent. Dilute acids do not affect it, though concentrated mineral acids effect its solution. Alkalies are without action upon it. The following analysis given by Wagner[1] will give you a good idea of the composition of the pigment.

Zinc oxide	88·0	per cent.
Cobalt oxide	11·6	„
Iron oxide	0·3	„
	99·9	

As in the preparation of cobalt blue, sodium phosphate is frequently used to precipitate the metals as phosphates, and a somewhat bluer hue is obtained.

Turner's Yellow.—This pigment is an oxy-chloride of lead, and is known by various other names, such as **Patent Yellow, Montpelier Yellow, Cassel Yellow, Verona Yellow, Mineral Yellow,** etc. It may be prepared in the following manner:—

Oxide of lead (litharge) is mixed to a thin paste with water containing common salt (sodium chloride) dissolved in it. After the lapse of about twenty-four hours, the mixture has become white owing to the formation of lead chloride.

$$\begin{matrix}\text{Lead}\\\text{oxide}\end{matrix} + \begin{matrix}\text{sodium}\\\text{chloride}\end{matrix} = \begin{matrix}\text{lead}\\\text{chloride}\end{matrix} + \begin{matrix}\text{sodium}\\\text{hydroxide}\end{matrix}$$

The precipitate is removed, washed and dried, and heated to melting point in a crucible until the proper colour has developed. During this operation the lead chloride combines

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[1] Quoted by Hurst, *opus cit.*, p. 191.

with oxygen in the air to form the oxy-chloride or basic chloride—both names signifying the same thing. The pigment thus obtained possesses good body, and mixes well both with oil and water. It is not very permanent, and, in common with all lead pigments, is very susceptible to the action of sulphuretted hydrogen and of sulphides generally. It is not now used to any great extent, having been superseded by the more permanent chromes.

IV

SULPHUR AND THE SULPHIDE PIGMENTS

Let us now pass on to consider the element sulphur, which is a very important factor in many of our most common pigments.

Sulphur, or brimstone, occurs free in nature in volcanic districts, such as Italy, South America, and Japan. A few years ago Sicily was exporting something like half a million tons of sulphur per annum. In Great Britain it rarely occurs in an uncombined state.

The pale lemon colour and characteristic taste of sulphur are familiar to all, as also, no doubt, is the famous homely remedy of brimstone and treacle. It is almost a pity, from the painter's point of view, that sulphur is so susceptible to the action of heat and moist air, as it might otherwise form a very cheap and useful pigment.

We will put some sulphur into a test-tube and heat gently. You notice that the sulphur melts to a thin, amber coloured liquid. As the heating is continued the liquid thickens and darkens. Now it is boiling, and the vapour has caught fire and burns with a bluish flame, emitting suffocating fumes of a gaseous oxide of sulphur. It is this power of burning which has given to sulphur its name of "brimstone," which word means "burning stone."

When heated with many metals combination takes place, and sulphides are formed. Let us heat some copper turnings in a test-tube with some sulphur. As the two unite the whole mass glows, and on cooling and breaking the tube you see that a black substance is left behind. This is copper sulphide. In a similar manner we can prepare iron sulphide, which is likewise black. Although neither of these substances is of direct use to the painter, there are many sulphides of other metals which can be so employed, and constitute some of our most valuable pigments. Into this test-tube we will put a small piece of iron sulphide, and cover it with dilute sulphuric acid. You see that the whole mass effervesces vigorously. The gas which is being evolved has a most disgusting odour, like that of rotten eggs. In fact, the odour of rotten eggs is due to this very gas, and is caused by the sulphur which the eggs contain, combining with a gas called hydrogen, yielding sulphuretted hydrogen or hydrogen sulphide. On applying a light to the tube you notice that the gas burns with a pale flame. If I hold this cool glass plate in the flame it becomes covered with a white powder, which is sulphur, proving to us that the gas we are burning contains sulphur.

We have already seen that when sulphur is heated with some metals sulphides are formed. Another way of preparing the sulphides is to pass sulphuretted hydrogen through solutions of the metallic salts in water.

Here are some crystals of blue vitriol or copper sulphate, which can easily be prepared by dissolving copper oxide in dilute sulphuric acid and evaporating off excess of water. On dissolving these in water and bubbling sulphuretted hydrogen through the liquid, you notice that a black precipitate is immediately formed. This is copper sulphide. Now we come to something very important. These white crystals are known as sugar of lead or lead acetate, and are made by dissolving lead in acetic acid or vinegar. They are readily soluble in water, and on bubbling some sulphuretted hydrogen through the solution what do you notice? A black precipitate of lead sulphide is formed. Here is some white lead ground to a thin paste with water. On passing the sulphuretted hydrogen through, the whole mass turns black, due, as before, to the formation of lead sulphide. In fact, no matter what compound of lead we take, if we bring it into contact with sulphuretted hydrogen some black lead sulphide is sure to be formed. This is a fact of supreme importance to us as painters.

Coal contains a good deal of sulphur, and on burning coal the sulphur escapes into the air partly as oxide and partly as sulphuretted hydrogen. Consequently the air of our manufacturing towns and cities always contains traces of these gases, the latter of which rapidly attacks any lead painting, turning it black.

Coal gas, as supplied to our houses, generally contains traces of sulphuretted hydrogen, although the bulk of this gas is removed at the gas works. The sensitiveness of lead acetate to the gas serves as a ready chemical test for sulphuretted hydrogen. We have only to pour a few drops of lead acetate solution on to some filter paper and expose it to the suspected gas. If a black colouration ensues we know what to conclude.

Another method is to cause the suspected gas to bubble through a solution of lead acetate in a flask (Fig. 4).

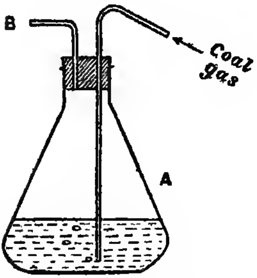

FIG. 4.

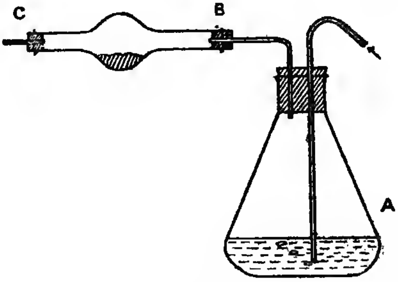

FIG. 5.

This method is scarcely so sensitive as the preceding one, but has the advantage of removing the sulphuretted hydrogen completely, and a purer coal gas therefore escapes at B, which does not blacken lead acetate paper. We will now pass this purified coal gas, which consists very largely of hydrogen, through a tube containing molten sulphur (BC, Fig. 5).

On testing the gas which emerges at C with filter paper moistened with lead acetate solution, darkening occurs at once, showing that sulphuretted hydrogen is formed by the direct combination of hydrogen and sulphur. It is easy to see, therefore, why sulphuretted hydrogen should be present in coal gas.

We are now in a position to understand why the paintings in art galleries and elsewhere so often become dark and lose their definition. As you know, old pictures are frequently almost black. This is a problem which museum authorities have constantly to face, particularly in such cities as Birmingham, Sheffield, and Manchester. A partial solution of the difficulty, of course, lies in the use of the electric light in the museums themselves. But whilst this prevents the further contamination of the air when once inside the building, it cannot effect the purification of that air as it enters. I shall have occasion, however, to refer to this interesting subject again later. Meanwhile, let us pass on to consider those sulphides which possess the various properties necessary to render them serviceable as pigments. These may be prepared by either of the two methods already outlined. The one method, namely by direct combination of the metal with sulphur, is known as the "Dry Method." The "Precipitation Method" involves the use of sulphuretted hydrogen or of soluble sulphides. We shall deal with each of these as the occasion serves.

1. **Mercury Sulphide.**—In the very front rank of our sulphide pigments we must place mercury sulphide, better known to you, perhaps, under the name of **Vermilion.** It has been used from the earliest times as a colour, and mention is made of it as being used by the Egyptians as long ago as 400 B.C. in painting pictures of their gods.

Vermilion occurs in nature as the mineral *cinnabar*, being found in Spain, Austria, China, and Japan, as well as in many parts of America. The ancients were dependent upon these natural supplies for their pigment, but most of that employed technically at the present time is a manufactured product. Metallic mercury is first of all obtained by roasting the crude cinnabar. This causes the sulphur to unite with the oxygen of the air to form a gaseous oxide, which escapes into the atmosphere, whilst the vapours of the liberated mercury are condensed in earthenware vessels.

The old name for mercury was quicksilver, and the Germans still call it "Quecksilber," nor is the reason far to seek. When a little mercury is placed in the palm of the hand, the slight tremor caused by the blood coursing through the veins causes ripples to appear on its surface. Hence it was called the living or the quick silver, to distinguish it from genuine solid or dead silver, which possesses a similar lustre.

Having procured the mercury in a fairly pure form, the next thing is to make it combine with sulphur. To this end the two substances are well mixed and gently heated in an iron pot, and combination gradually ensues. The resulting compound, however, is black, and contains some free sulphur and mercury. It is known to the workmen as "ethiops," and is perfectly useless as a pigment. The next operation, therefore, consists in "colouring" the ethiops, which is effected by throwing small quantities of the ethiops into earthenware pots fitted with lids and heated to redness. Much of the sulphur burns off, and more ethiops is added at intervals of about thirty-six hours. The pots are now allowed to cool, and on opening vermilion is seen to have collected on the under-side of the cover, and around the upper and cooler part of the walls of the pot. This is scraped out, ground, washed, and dried. The pigment is then ready for market.

The process just described is known as the Dutch method, and with slight variations is the one usually adopted in Europe.

The Chinese have always been regarded as the best makers of vermilion, but their process is essentially the same. Perhaps they take more pains with their work, and thus produce a finer substance, for they are a people gifted with a remarkable amount of patience.

Why, when it is first formed, mercury sulphide should be black, we do not know. Here is a solution of mercury in hydrochloric acid. On passing in sulphuretted hydrogen we get a precipitate of mercury sulphide, but again it is black. If this is dried, however, and heated in a similar manner to the ethiops, it will turn into vapour and collect on the lid and cooler sides of the pot as vermilion, in just the same way. Although in colour the black mercury sulphide and vermilion are so widely different, yet in their chemical properties they are identical. We can only conclude, therefore, that the little particles of which the substance is built up are arranged differently in the two cases. In vermilion we are dealing with a crystalline substance, whereas the black sulphide is an amorphous or non-crystalline form. Other examples of the same thing are by no means rare. Sulphur itself can exist in no fewer than four different forms, two of which are crystalline, and two non-crystalline. As we shall see later, the diamond, graphite, and charcoal are only different forms of the element carbon, though widely removed from one another in their physical properties.

Vermilion is one of the heaviest pigments known, its specific gravity being 8·2. It is therefore apt to settle out of paints, which is troublesome. It is very opaque, and therefore possesses good body. Owing to the fact that water, alkalies, and dilute acids are without action upon it, vermilion is a very inert pigment, and may be mixed with most other colours without fear of injuring them, or being affected by them. It can scarcely be called a permanent pigment, however, for it is apt to discolour. Whether this is due to reversion to the black, non-crystalline form, or to the formation of a black sulphide containing less sulphur in proportion to the mercury than does vermilion, is very uncertain. It is when used as an oil colour, or under varnish, that vermilion is in its most permanent form. On the other hand, when used as a water colour, and exposed to the combined action of light and air and moisture, vermilion is unsatisfactory. A really permanent substitute for vermilion is not an easy thing to make, however, although it must be admitted that many of the permanent or fast reds now on the market offer a very stout resistance to the destructive action of the atmosphere.

When gently warmed in a tube vermilion becomes black, but the scarlet hue returns on cooling. If, however, the heating is intense and prolonged, the pigment is decomposed, mercury vapour being evolved, and the sulphur burning with its characteristic pale blue flame. If the pigment is pure, only a trace of ash will remain. The sample on the table contains:

Mercury sulphide	99·56	per cent.
Ash	0·44	„
	100·00	

and may be regarded as fairly representative.

Owing to its cost, vermilion lends itself to adulteration; red lead and the red oxides of iron being usually employed for that purpose. As these are not volatile, on heating the pigment in a crucible they are left behind with their ash, and their presence is thus readily detected.

Vermilion was originally known as *minium*, but owing to its frequent and excessive adulteration with red lead, the term is now used to denote the latter substance alone.

When mixed with dried sodium carbonate and gently heated in a small tube, mercury vapour is expelled, and collects as a mirror on the cooler parts of the tube. This is a characteristic reaction of all mercury compounds. A mixture of strong hydrochloric containing a little nitric acid dissolves vermilion with ease. The solution contains mercury chloride, also known as "corrosive sublimate," which is excessively poisonous.

2. **Zinc Sulphide.**—I have dissolved some crystals of white vitriol, or zinc sulphate, in water, and added a few drops of sulphuric acid. On bubbling sulphuretted hydrogen through the solution you observe that nothing takes place. This is because zinc sulphide is readily soluble in acids. If, however, I first of all make the solution alkaline with caustic soda, and then pass in the sulphuretted hydrogen, we get a white precipitate of zinc sulphide.

This substance is rarely, if ever, used by itself as a pigment, for, although it possesses good body, its colour is not pure. By the addition of other white pigments, such as zinc oxide and barytes (or barium sulphate), a product possessing good colour as well as good body is obtained. Quite a number of such mixtures are on the market, under the names of Griffith's Patent Zinc White, Orr's White, or Lithophone, etc.

The following analyses recently given by Remington and

Smith[1] represent lithophones of average quality obtainable on the English market at the present time.

Sample.	Barium sulphate.	Zinc sulphide.	Zinc oxide.	Barium carbonate.
1	70·12	29·02	0·73	—
2	70·93	26·60	1·66	—
3	66·40	29·36	2·70	0·98
4	70·60	26·28	1·40	0·17
5	70·65	26·52	2·26	0·32
6	66·74	26·24	3·36	0·13
7	66·70	29·64	1·55	0·36
8	75·32	21·54	0·35	0·13
9	58·16	37·42	2·14	0·22
10	63·28	33·92	2·18	0·31
11	80·80	15·68	0·28	0·22
12	71·30	25·06	1·30	0·25

It is used solely as an oil colour, and has only been known for about twenty years. In my last lecture I mentioned that one of the great advantages of using zinc oxide or zinc white as a pigment lay in the fact that it could be mixed with paints containing sulphur, without undergoing any change, whereas lead pigments are gradually darkened owing to formation of black lead sulphide. The reason for this will now be clear. Since zinc sulphide is white it does not matter if, on mixing with sulphide paints, a little zinc oxide is converted into the sulphide, for no change in tint is perceptible. It will be clear, however, that, whilst zinc oxide may safely be mixed with any pigments, those containing zinc sulphide should not be mixed with lead or copper pigments.

3. Cadmium Sulphide.—Cadmium is a metal which in many ways resembles zinc. It dissolves readily in sulphuric acid to form cadmium sulphate, and if we pass a stream of sulphuretted hydrogen through a solution of this salt in water, a beautiful yellow precipitate of cadmium sulphide is at once obtained. This needs only to be washed and dried, when it

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[1] See J. Stewart Remington and Claude Smith, *Oil and Colour Trades Journal*, June, 1909, p. 2035; Hurst, *opus cit.*, p. 75. Also the detailed papers of Kochs and Seyfert, "Zeitschrift angewandte Chemie," 1902, p. 802; and Drawe, *ibid.*, p. 174.

is ready for the market. It is usually sold under the name of **Cadmium Yellow.** The pure substance is one of the most permanent of pigments. When contaminated with sulphur, however, the latter is gradually oxidized by air and moisture to sulphuric acid, which dissolves the pigment, forming colourless cadmium sulphate. In other words, the pigment is bleached. When gently heated it becomes darker, but although the colour is restored on cooling, the original brilliancy is not regained. Hence in drying the pigment, a low temperature must be employed. It must not be mixed with white lead, or, indeed, with any lead or copper pigments, otherwise a black colour will gradually develop.

When warmed with concentrated hydrochloric acid, cadmium sulphide dissolves completely, with evolution of sulphuretted hydrogen. On largely diluting, however, and passing this gas through the liquid again, the pigment is re-precipitated.

Adulteration of cadmium sulphide is not often practised. If it is, arsenic sulphide is the usual adulterant, and, on warming with a dilute aqueous solution of caustic soda, it will dissolve, leaving the insoluble cadmium sulphide behind. If we filter, therefore, the clear filtrate will contain the arsenic, and on addition of acid, the caustic soda will be neutralized, and yellow arsenic sulphide thrown down. The presence of arsenic may also be recognized by any of the other tests usually applied for it (see *Arsenic Sulphide* below).

Chromes are also used to adulterate cadmium yellow, and mixtures of white lead and this pigment are sold as "brilliant yellow." Such combinations are very unstable, however, as the lead pigments are apt to discolour, owing to the formation of black lead sulphide. From four to six shades of cadmium yellow are produced, ranging from lemon to deep orange. Chemically they are identical, differing only in their physical condition, just as is the case with black mercury sulphide and vermilion, though the variation is not so marked. Unfortunately, owing to the high price of cadmium, these pigments cannot be prepared cheaply, and are therefore largely confined to the artist's palette.

4. **Arsenic Sulphide.**—Arsenic differs from cadmium in that

it can combine with sulphur in two different proportions. The di-sulphide occurs in nature as *Realgar* or *Ruby sulphur*, which latter name suggests its colour. It is artificially prepared by heating in earthenware crucibles a mixture of sulphur and white arsenic (oxide of arsenic) in the requisite proportions, and is sent into the market under the name of **Arsenic Orange.**

The tri-sulphide of arsenic is more common as a pigment, however, being known as **King's Yellow.** It is found native in China and elsewhere under the name of **Orpiment,** and constituted the *auri pigmentum* of the Romans—whence its name. Occasionally the mineral is ground up and used direct as a pigment. More usually, however, it is prepared artificially by dissolving white arsenic in hydrochloric acid, and precipitating the sulphide with sulphuretted hydrogen, just as in the case of cadmium. When dried and washed, the pigment is ready for the market. It may also be prepared in the dry way by heating together sulphur and arsenic in the requisite proportions.

Owing to its very poisonous properties orpiment is not now in great demand, its place having been taken by the chromes.

Arsenic sulphide readily dissolves in strong hydrochloric acid, to which a few drops of nitric acid, or a crystal of potassium chlorate, has been added. It is soluble also in caustic soda, which serves to distinguish it from cadmium sulphide.

An excellent test for arsenic is that known as Marsh's test. A strip of pure zinc is put into a test-tube and covered with dilute sulphuric or hydrochloric acid (Fig. 6). The zinc is at once attacked, and bubbles of hydrogen gas escape. The reaction may be represented by the equation—

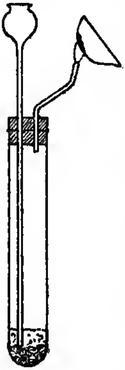

FIG. 6.

Zinc + sulphuric acid = zinc sulphate + hydrogen

When all the air is judged to have been expelled from the tube,[1] a light is applied to the jet, and the emergent hydrogen

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[1] This is a very necessary precaution, as otherwise a violent explosion might result.

burns with an almost colourless flame. As the glass tube gets warm, however, the flame becomes decidedly yellow. This is due to the sodium in the glass, and the same effect can be produced by throwing some common salt (which is a compound of sodium and chlorine, known as sodium chloride) into a fire. If a cold porcelain dish is held in the flame, a little pure water collects on its surface, but evaporates away as the basin gets warm. I will now wash a little arsenic sulphide down the thistle funnel with a small quantity of water. You notice that the flame has acquired a lilac tinge. This is because the arsenic in the pigment is uniting with the hydrogen as it is liberated at the surface of the zinc, forming a gas known as arseniuretted hydrogen, which is now burning along with the hydrogen here. If I hold the cold porcelain basin in the flame once more you see that a black stain is produced. This is a deposit of the element arsenic, and on pouring a solution of bleaching powder in water over the stain, it immediately disappears.

This is a characteristic and indeed a very sensitive test for arsenic. Since zinc is frequently contaminated with arsenic, the hydrogen flame must always be tested first with cold porcelain before the addition of the pigment to be analyzed.

When dealing with vermilion, I showed you that, if the pigment were mixed with some dried sodium carbonate and gently heated in a tube, a mirror of mercury is formed all round the cooler parts of the tube. An exactly similar test may be applied to arsenic sulphide. In this case the mirror consists of pure arsenic, of course, and not mercury.

5. **Antimony Sulphide.**—This pigment comes into the market under the name of antimony vermilion. It is prepared from white antimony in the same way as king's yellow from white arsenic, and the chemical properties of the two bodies are very similar. Both dissolve in solutions of caustic soda, and are re-precipitated by acids. Both respond to Marsh's test, but the stain of metallic antimony produced on the porcelain by the burning antimoniuretted hydrogen is insoluble in bleaching powder solution—a property which enables us readily to distinguish between the two.

V

SULPHATE PIGMENTS

You are all familiar with the smell of burning sulphur. As I explained in my last lecture, it is due to the combination of the sulphur with the oxygen of the air, whereby a gas known as sulphur di-oxide is produced. When dissolved in water this gas yields sulphur*ous* acid, which only differs from sulphur*ic* acid, or oil of vitriol, in that it possesses rather less oxygen in proportion to the sulphur. When a dilute solution of sulphurous acid is exposed to the air, it very gradually takes up the necessary oxygen, and becomes converted into dilute sulphuric acid.

But a second oxide of sulphur is known, namely, sulphur tri-oxide, which contains half as much oxygen again as the di-oxide, and which, when dissolved in water, yields sulphuric acid direct. Here is a sample sealed up in this flask, and you notice its fine silk-like crystals, which are perfectly colourless. When heated strongly it decomposes into sulphur di-oxide and oxygen. It is not formed in any appreciable quantity when sulphur is burned in air, but if a mixture of sulphur di-oxide and oxygen is heated in contact with platinum or with rouge, either being in a very fine state of division, sulphur tri-oxide is readily obtained. As already stated, when this oxide is dissolved in water, sulphuric acid is obtained. In the highly concentrated condition, this acid is somewhat oily in appearance, and is hence frequently known as oil of vitriol, although it is a true oil in no sense of the word.

The majority of metals and their oxides, on being warmed with either concentrated or dilute sulphuric acid, yield compounds known as "sulphates." Thus, to quote a familiar example, zinc dissolves in the dilute acid, as we saw during the last lecture, evolving hydrogen gas, while zinc sulphate is left behind in solution. If we carefully boil off most of the water, and then cool the solution, colourless crystals of zinc sulphate, or white vitriol, separate out. Similarly, iron yields green crystals of ferrous sulphate, known also as green vitriol and as copperas. We cannot use these substances as pigments, however, because they are soluble in water. But there are other sulphates, which, as we shall presently see, are extremely valuable to the painter. As sulphates differ from sulphides only in the fact that they contain oxygen as well as sulphur, it will be evident to you that if we can only add oxygen to a sulphide, it may be possible to obtain a sulphate. I wonder if you can recall any substance in which this is actually done on a large scale. Some time ago, when dealing with the preparation of rouge, I mentioned that the naturally occurring sulphide of iron is exposed in heaps to the combined action of air and moisture, whereby iron sulphate is produced. We might express the reaction in the following way:—

Iron sulphide + oxygen = iron sulphate

A somewhat analogous reaction occurs with certain impure sulphide pigments. Thus cadmium yellow, when contaminated with free sulphur, is gradually converted into the colourless sulphate on exposure to moist air.

The number of sulphate pigments must of necessity be limited, since the majority of metallic sulphates are soluble in water. Sulphates of lead, barium, strontium, and calcium are the commonest insoluble salts, and are consequently the only ones used by the house-painter.

1. **Lead Sulphate.**—Under this heading must be put such pigments as **non-poisonous white lead, patent white lead, sublimed white lead,** etc., for although these do not consist entirely of lead sulphate, yet this substance forms the basis of them all.

Lead sulphate is found in nature as the mineral *anglesite.* Combined with lead oxide, it occurs in the leadhills of Scotland under the name of *lanarkite.* These minerals, however, are rarely if ever used for the preparation of the pigment.

If to a solution of lead acetate we add some dilute sulphuric acid, a white precipitate of lead sulphate is produced, which, when washed and dried, may be used directly as a pigment. This is how much of the lead sulphate which finds its way into the market at the present time is obtained. As a rule, however, the manufacturer prepares his own lead acetate as well, by dissolving the metal in acetic acid—the acid which causes the sour taste in vinegar. This is done in large tubs, heated by steam. The lead is granulated—that is, melted and poured whilst molten into water. Here is some granulated lead, and you see that it is all blown out and full of holes, so that it exposes a very large surface to the air, or to any liquid in which it is immersed. The tubs are charged with this granulated lead, and acetic acid diluted with its own volume of water is added. When a strong solution of lead acetate has thus been obtained, the liquor is run off into a large wooden tank, and treated with sulphuric acid. A heavy white precipitate of lead sulphate is thrown down as you saw just now, and the acetic acid is liberated simultaneously, and goes into solution—

Lead acetate + sulphuric acid = lead sulphate + acetic acid

After the precipitate has settled, the clear liquid containing the acetic acid is pumped off and used over again to effect the solution of a still further quantity of lead in the tubs. From a theoretical point of view, a small quantity of acetic acid should be capable of being used to prepare an indefinite quantity of lead sulphate. In practice, of course, some acid is always lost, and has to be restored by small additions from time to time.

The lead sulphate thus prepared is well washed and dried, and may be used direct as a pigment. It is a heavy white powder, weighing some six times as much as pure water, bulk for bulk, its specific gravity being approximately 6·3. It is practically insoluble in water, and still more so in dilute acids. In concentrated sulphuric acid it dissolves to a slight extent. Since in the ordinary method of preparation of sulphuric acid, as employed in England, large rooms of lead are used in which it is produced, the concentrated commercial acid always contains a little lead sulphate dissolved in it. Here is some commercial acid, and, on pouring it into excess of water, you observe the milky appearance caused by the lead sulphate being thrown out of solution.

As a pigment, lead sulphate is considerably less poisonous than white lead, owing to its insolubility, but unfortunately its body and covering power are likewise inferior. As you see, it is a good white, and is used to tone down the chromes. Although it is less sensitive than white lead to the action of sulphuretted hydrogen, it is not safe to mix it with sulphide pigments such as cadmium yellow, owing to the tendency for black lead sulphide to form.

You have probably been wondering why lead sulphate is not prepared by the direct action of sulphuric acid on lead. The reason is simple. If a piece of lead is put into sulphuric acid, a portion of it is turned into insoluble lead sulphate, which coats the surface of the metal, and protects it from further attack. Such a method would be excessively slow, and therefore cannot be adopted on a commercial scale.

And now I have something exceedingly interesting to tell you. Last week I mentioned that old pictures have frequently lost their clearness and definition, and sometimes have even become quite black, owing to the conversion of the white lead into black sulphide. Now it will be clear to you that if, by any means, we can add oxygen on to that lead sulphide, white lead sulphate will be produced and the original colour of the picture restored. Chemicals which will do this are known as "restorers," and many an old picture has in recent years been made to look like new again by their aid.

The restorers must, of course, be powerful oxidizers, and at the same time be themselves colourless. The most convenient and safe restorer known is hydrogen peroxide, which is used in the form of a dilute solution. Ordinary water is a compound of hydrogen and oxygen, and from a chemical point of view, is really hydrogen mon-oxide, although we rarely use that name for it. But hydrogen per-oxide contains just twice as much oxygen as water does, in proportion to its hydrogen.

The extra oxygen is, however, very loosely attached, and on warming is readily set free, and pure water is left. If therefore a dilute solution of hydrogen per-oxide is brushed over old pictures, the oxygen oxidizes the lead sulphide to lead sulphate, and the picture is thus "restored." Here is a piece of filter paper moistened with lead acetate solution. If I bring it near to a jet from which sulphuretted hydrogen is escaping, you see it turns black immediately. We will now place it in a basin and cover it with a dilute solution of hydrogen per-oxide. As you see, the black colour is gradually disappearing. The paper is now coated with white lead sulphate.

$$\begin{array}{c}\text{Lead}\\\text{sulphide}\end{array} + \begin{array}{c}\text{hydrogen}\\\text{per-oxide}\end{array} = \begin{array}{c}\text{lead}\\\text{sulphate}\end{array} + \text{water}$$

Experiment shows that white lead is less likely to be affected by sulphuretted hydrogen when exposed to strong light; and further, that tarnished pictures may be very gradually restored by the action of prolonged and intense illumination. The effect is obviously one of oxidation induced by the light, and a similar explanation probably applies.

2. Barium Sulphate.—Under the name of **Barytes** or **Permanent White**,[1] barium sulphate is extensively employed as a pigment. It is remarkably insoluble in water, acids, and alkalies, and is therefore an exceedingly permanent pigment, and free from all poisonous effects. For this reason it is used either in place of, or as an adulterant of, white lead. It is readily prepared by adding dilute sulphuric acid to a solution of any soluble barium salt. For example, in this test-tube is a solution of barium chloride, and on adding a few drops of sulphuric acid, a white precipitate is immediately formed. Excess of acid does not cause it to dissolve, and on prolonged boiling you see that there is no change. Exactly the same precipitate is obtained if to the barium chloride we add a soluble sulphate such as iron sulphate or zinc sulphate, with which substances you are already familiar. It is only necessary to wash and dry the precipitate, after which it is ready for use

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[1] This term is also used for zinc oxide.

as a pigment. Prepared in this way the commercial article is known as **Blanc Fixe** or **Artificial Barytes.**

Barium sulphate occurs in nature as the mineral *barytes* also known as *heavy spar*, a name which indicates its great density. It weighs something like four and a half times its own volume of water. It is found in large quantities in Derbyshire, and other deposits are worked in Cornwall, Devonshire, Cumberland, as also in Wales and Ireland. It is not infrequently tinged with a faint yellow colour, due to the presence of iron oxide. Hurst[1] gives the following analysis of a sample obtained from Derbyshire—

Barium sulphate	98·80
Iron oxide	0·21
Calcium sulphate	0·77
Magnesia	trace
	99·78

In order to utilize these natural deposits for the preparation of pigments, the crude ore is crushed and powdered in the usual way. Too much care can scarcely be expended on this part of the operation, as the quality of the resulting pigment depends to a large extent upon the way in which this is done. The powdered ore is washed into settling tanks, made of stone. The coarser particles will obviously settle first, and are usually returned to the grinding mills, the finer portion being transferred to stone cisterns, where it is treated with hydrochloric acid to dissolve out the iron. About one ton of acid is used for every 20 tons of crude ore. After thorough washing the ore may be dried direct, or first submitted to levigation, whereby different grades of fineness can be obtained. The drying operation is simple, for heat has no chemical action on the pigment. It is usually accomplished in two stages. The mud or paste from the settling tanks is thrown on to the tops of drying flues, which, to all intents and purposes, are a series of flagstones, suitably heated underneath. When sufficient water has been driven off to render the mass sufficiently dry to adhere together, it is cut into bricks and heated in drying

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[1] Hurst, "Painters' Colours," etc., p. 76.

stoves for several days. When perfectly dry, the bricks are ground to a powder, and sent into the market.

As a pigment, barium sulphate is inferior in body to white lead. It mixes very well with oil, however, and is largely used for adulterating white lead, even to the extent of from 20 to 25 per cent.

There is one very pretty test for barytes—indeed, for any compound of barium. Here is (Fig. 7) a platinum wire sealed into this glass rod, which serves as a handle. The free end of the wire is bent round in the form of a loop. On holding it in the gas flame it rapidly becomes red hot, but on cooling, it returns to its original condition. A piece of iron or copper wire would have corroded or perhaps melted in the same circumstances. Now I will dip the loop into strong hydrochloric acid, and immediately touch the barium sulphate with it, so that a small portion adheres to the loop. On heating in the gas flame you see that a pale yellowish green tint is imparted to the flame. This is a very characteristic reaction, and by means of it the presence of barium salts (not necessarily the sulphate, of course) in many common pigments may be readily detected.

FIG. 7.

3. Calcium Sulphate.—Calcium sulphate occurs naturally as **Gypsum** in many parts of England, and has received fairly wide application as a pigment under various names, such as **Terra Alba, Mineral White**, etc. The mineral is ground and treated in a similar manner to barytes, and yields a very durable and useful pigment. Gypsum resembles the ochres in that it contains some water chemically combined with it. In the anhydrous condition calcium sulphate occurs in the mineral *anhydrite.* When gently heated gypsum parts with a portion of its water, and *Plaster of Paris* is formed. This, when made into a paste with water, gradually sets and is therefore extremely valuable for cementing purposes. Like barytes, calcium sulphate can also be prepared artificially by adding dilute sulphuric acid or a solution of a soluble sulphate to any calcium salt dissolved in water. As a pigment calcium sulphate is valuable on account of its permanence. At ordinary temperatures it is only very slightly soluble in water, one part of the anhydrous sulphate dissolving in 400 parts of water. It renders the water hard, however, so that a lather with soap is difficult to secure. As regards body it is inferior to white lead, but quite equal to barytes. It mixes well with water and is thus superior to barytes, which in such circumstances seems to lose some of its body. It is used in paper-making and in paper-staining as well as in a score of other trades where a cheap white pigment is required.

It imparts a red colour to the gas flame when introduced in the tip of a platinum wire moistened with hydrochloric acid. A mixture of calcium sulphate and hydrated aluminium oxide or aluminium hydroxide is sold under the name of **Satin White.** It is prepared by adding a hot solution of aluminium sulphate to slaked lime in the form of a cream in hot water. The precipitate is allowed to settle, is washed and dried, and is then ready for the market. The chemistry of the process is very simple. Quicklime is calcium oxide. When slaked with water great heat is evolved and a hydrated oxide is produced, known ordinarily as slaked lime, or calcium hydroxide. When this is mixed with aluminium sulphate, the following change takes place—

$$\begin{array}{c}\text{Calcium}\\\text{hydroxide}\end{array} + \begin{array}{c}\text{aluminium}\\\text{sulphate}\end{array} = \begin{array}{c}\text{calcium}\\\text{sulphate}\end{array} + \begin{array}{c}\text{aluminium}\\\text{hydroxide}\end{array}$$

As a pigment satin white is slightly more opaque than calcium sulphate, is whiter in colour and possesses superior body.

4. **Strontium Sulphate.**—Strontium sulphate occurs in nature as the mineral *celestine*, and is used as a pigment on a limited scale under the name of **Strontian White.** It is prepared from the crude ore in a similar manner to barytes, and if the ore were only more plentiful it would receive an extensive application in the arts. It is considerably less soluble in water than calcium sulphate, and imparts a bright crimson colour to the gas flame when introduced at the top of a platinum wire, moistened with hydrochloric acid.

VI

CARBON AND THE CARBON BLACKS

We now pass on to consider one of the most important of all the elements, namely, carbon. It occurs free in nature in the crystalline form under the name of diamond. This is undoubtedly the purest form of carbon, and, on combustion, the colourless jewel leaves only a very minute trace of ash. Graphite is also a crystalline form of carbon, but is very much softer than the diamond. Its name, which is derived from the Greek word meaning "to write," indicates its characteristic property of marking paper when rubbed across it. Lead also does this, but the mark left by the graphite is blacker, hence the latter substance is commonly known as "black lead," and is used in making pencils.[1]

Carbon can also exist without exhibiting any crystalline form. It is then known as *amorphous*[2] carbon, and it is this variety which concerns us most as painters.

Carbon is the main constituent of organic matter, and can be obtained by heating any organic substance, such as wood, leaves, sugar, and starch, out of contact with air.

This test-tube contains a piece of wood, and we will now heat it strongly. First of all you notice that moisture is set free. Now a gas is escaping, which burns like coal gas, and with a smoky flame. The wood also is becoming blacker, and tarry matter collects on the cooler parts of the tube. The

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[1] A third name for graphite is *plumbago*, from the Latin *plumbum*, meaning "lead."

[2] "Amorphous" is derived from two Greek words meaning "without form."

experiment is now over, and on breaking the tube you see that a lump of cinder or charcoal is left behind. This is really carbon contaminated with the small quantity of mineral matter originally present in the wood.

This is the way in which some of the charcoal of commerce is actually prepared, though, instead of a simple test-tube, large retorts are used, and the gas and tar are collected and sold as valuable by-products. Some of the charcoal obtained by this or other similar processes, is ground thoroughly and washed, and passes into the market as **Charcoal Black** or **Carbon Black.**

Frankfort or **Drop Black** is made in a similar manner by charring vine twigs, bone shavings, ivory cuttings, etc., and the product after grinding is mixed with a little glue and water and made up into pear-shaped drops for sale. Hence the name "drop" black. The composition of such blacks will obviously vary according to the amounts of mineral matter contained in the original substances before charring. The sample on the table here before you may be regarded as fairly representative, perhaps; on analysis it yielded—

Water	4·2	per cent.
Carbon	31·1	,,
Ash	64·7	,,
	100·0	

The names of **Frankfort** or **German Black** have been given to this pigment in recognition of the fact that it was first prepared in Frankfort-on-the-Main, in Germany. **Ivory Black** is almost the same thing as drop black, although, strictly speaking, it should be prepared only from waste cuttings of ivory. Owing to the cost of ivory, however, the pigment is frequently adulterated, bones, etc., being used in its preparation. It contains a relatively small amount of carbon, as will be seen from the analysis of the sample before you—

Water	2·45	per cent.
Carbon	17·05	,,
Ash	80·50	,,
	100·00	

This sample has been supplied to me as ivory black, but I cannot guarantee its genuineness, although I have no reason whatever to doubt the good faith of the sender.

Animal Black is made from all sorts of animal matter, such as hoofs, hair, skin, leather, horns, and the like. As might be expected, its composition is very variable, as you will see by glancing at this list of analyses, given by Hurst[1]—

	1	2	3	4	5
Water . . .	28·75	36·70	45·50	27·75	6·19
Carbon . .	42·03	28·50	29·80	71·51	15·84
Ash . . .	29·22	34·80	24·70	0·74	77·97
	100·00	100·00	100·00	100·00	100·00

Every one is familiar with the fact that when the wicks of an ordinary paraffin lamp are turned up too high, the flame smokes terribly. This is due to the fact that the air supply is too small to completely burn off the paraffin which is drawn up by the wick, and the carbon therefore escapes as soot or **lamp-black.**

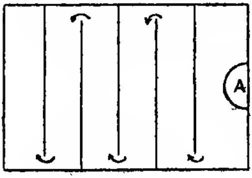

Fig. 8.

In the commercial manufacture of lamp-black, good oils such as paraffin are not used on account of their expense, but heavy oils are taken, such as will not burn in a lamp, but have a relatively low marketable value. These are put into a pan (A, Fig. 8) not unlike the familiar household "copper" used for washing purposes. The oil is first heated by a fire, and then ignited. Owing to the limited amount of air which can gain access to the burning oil, much of the carbon is evolved as soot and is collected in large chambers. These are built of brick, and are divided into compartments by means of partitions, which do not, however, stretch right across the chamber, but are arranged as shown in Fig. 8, which gives an idea as to what a chamber would look like if its roof were removed, and we could look down upon it from above.

As workmen must go between the partitions to scrape

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[1] See Hurst, "Painters' Colours," etc., p. 261.

down the lamp-black, the latter are generally placed some four feet apart. It will be clear that as the fumes from the burning oil spread through the chamber, the soot will gradually settle on the floors and walls of the compartments. That which collects first will be of a coarser quality, the finer material collecting further and further away towards the end of the chamber remote from the burning oil.

The black collected in the first compartment is often mixed with some unburnt oil, which has distilled off from the pan. This is collected separately.

The actual amount of lamp-black obtained from a given weight of oil will obviously depend to a large extent upon the nature of the oil employed. As a rule, however, thirty per cent. is regarded as a very good yield.

As a pigment, lamp-black is beautifully permanent, and may be mixed with any other pigments without either affecting them or being affected by them. It consists almost entirely of pure carbon, as will be seen from the following analysis—

Water	5·65	per cent.
Carbon	90·25	,,
Ash	4·10	,,
	100·00	

As its name implies, **Bone Black** is obtained by the carbonization of animal bones, whereby the volatile products are expelled, and carbon and mineral matter are left behind. The crushed bones are packed into clay crucibles with loosely fitting lids and heated in a furnace. The residue is now ground to a fine powder, and sent into the market. Hurst[1] gives the following analyses of different samples:—

	1	2	3
Water	24·12	6·19	7·11
Carbon	31·70	15·84	15·14
Ash	44·18	77·97	77·75
	100·00	100·00	100·00

The properties of bone black are similar to those of the other carbon blacks, and need not, therefore, be repeated.

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[1] Hurst, *opus cit.*, p. 260.

There is one property possessed by all the carbon blacks to a greater or less degree, to which I have not as yet made reference: it is their power of absorbing colouring matter. A few days ago some ordinary brown vinegar was put into this flask, together with a little bone black. I will now filter this black-looking liquid, whereby the small particles of bone black will remain behind on the filter paper, and the clear liquid will pass through as the filtrate. You see that the filtrate is quite colourless, but if you smell it, you will detect the familiar odour of vinegar. The charcoal has simply removed the organic colouring matter. This property is made use of on a very large scale for the purification of sugar, and in the laboratory the organic chemist uses it in the preparation of his pure chemicals. But how does this affect us as painters? In the following way. You are all familiar with the trouble caused by the so-called "bleeding of the lakes." In a later lecture I hope to explain to you how the lakes are prepared; I may so far anticipate, however, as to say that they contain organic colouring matter, which has the awkward knack of bleeding through an indefinite number of coats of paint applied on top of it. This is particularly troublesome if the upper surface of paint is to be white. I know of a case in which a painter coated some woodwork in a shop which had previously been painted with a carmine lake with eight coats of white, and still the red colour bled through. What is the remedy? Many painters put a coat of knotting varnish over the lake, and then paint on top of that. Knotting varnish is simply ordinary shellac dissolved in methylated spirit. The spirit evaporates and leaves a thin coating of shellac behind, through which the colouring matter of the lake cannot pass. Unfortunately, however, this almost always cracks[1] on drying, and the lake bleeds through the cracks. A very sure remedy is to make use of the property of the carbon blacks already referred to. Give the wood a good coating of a carbon black, and then you can safely paint on top of that. The obvious disadvantage is that, if a white colour is required, an unusual

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[1] Thin knotting varnish, made by adding half a gallon of methylated spirit to one gallon of ordinary knotting is less liable to crack.

number of coatings will have to be applied to completely block out the black. But the bleeding is stopped, and that is the main point.

Indian Ink consists principally of smoke black, bound with a size obtained from fish and leather. Small amounts of camphor and musk are also present, and possibly a little sepia, but the process of manufacture is kept secret. Indian ink varies considerably in body and colour. It is imported from China in small tablets, in which form it is sold in this country, though a liquid ink is also made for the convenience of artists.

Analysis of the Blacks.—Since the various carbon blacks are prepared from such widely different substances, it will be clear to you that a complete analysis of them must be a long and difficult process. Fortunately, however, this is seldom required. Usually it is sufficient to determine the water which they contain loosely held in their pores, and the carbon or carbonaceous material, and finally their ash. The usual way of doing this is to weigh out a small quantity of the black and heat it gently in an air oven similar to this one here (Fig. 9). The temperature can be nicely adjusted by raising or lowering the flame, about 200° Fahr. being a very suitable one for the purpose.

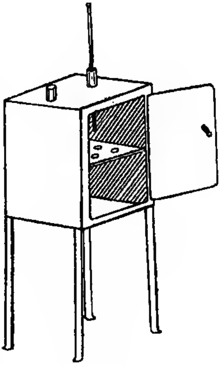

FIG. 9.

When the pigment ceases to lose in weight on further warming, we may safely assume that all the water has been expelled. The dried pigment is now placed in a porcelain crucible and heated to redness until all the carbon has burned away, and only a whitish ash remains. The loss in weight may be taken as carbon. We have thus, you see, obtained an analysis, sufficient for most purposes. A complete analysis of the ash is a task for the expert.

VII

THE CARBONATE PIGMENTS

When carbon burns in air, it unites with oxygen to yield a gaseous oxide known as carbon di-oxide. This is a process which is continually going on in nature. For example, during volcanic eruptions vast quantities of carbon di-oxide are belched forth into the air. As we have already seen, wood contains a great deal of carbon, and in coal the percentage of carbon is higher still. Consequently our furnaces and household fires are daily emitting enormous quantities of carbon di-oxide. Further, it is a matter of common knowledge that, unless a room is well ventilated, its air soon becomes stuffy and close when a few persons have been breathing it. That is due to the fact that all people and animals breathe the air into their lungs, whereby the oxygen comes into direct contact with the blood, and being dissolved by it, is carried round the body, unites with some of the carbon in the organic matter of the tissues, and ultimately leaves the lungs as carbon di-oxide. When you remember what an appalling number of human beings and animals there are on the face of the globe, it will be evident, I think, that an absolutely inconceivable amount of the gas is being projected into the air from this source alone. We might naturally expect, therefore, that the oxygen of the air would soon be used up, and the human race die of suffocation. But careful analysis shows that the air, on an average, contains only about three or four volumes of carbon di-oxide in every 10,000 volumes of air. How is this to be explained? The ancients imagined that we should gradually burn up the earth with our fires. But now we know that such can never be the case.

A few days ago I put some pond weed into this gas jar (Fig. 10) and covered it with water which had been saturated with carbon di-oxide. I then lowered the glass cup into the water in such a way as to expel all the air from it, and to allow of the collection of any gas given off by the plant.

You see that a small quantity of gas has collected. Let us try and find out what it is. I will press the cup down under the water a little more, and on turning the tap the gas will be forced up through the tube and escape into the air. Whilst it is escaping I hold a glowing splinter in its path. The splinter bursts into flame. Obviously the gas supports combustion more vigorously than air does. It is oxygen, and has come from the carbon di-oxide. Under the influence of sunlight the green parts of plants breathe in carbon di-oxide, abstract the carbon, using it to build up their own tissues, and breathe out the oxygen. In this way, therefore, the air is being constantly purified. We might express the reaction as an equation—

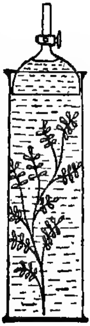

FIG. 10.

$$\text{Carbon di-oxide} = \text{carbon} + \text{oxygen}$$

It is important to remember, however, that sunlight is necessary for this change, for in the dark, plants breathe as we do. Consequently they should not be kept in the bedroom at night unless there is plenty of ventilation.

When carbon di-oxide is dissolved in water a very weak acid known as carbonic acid is formed. This is capable of acting on metals and their oxides, yielding carbonates of various kinds. As we might expect from the prevalence of carbon di-oxide in nature, many metals occur naturally as carbonates. Sometimes these deposits are used directly as pigments. In other cases the carbonates are prepared by purely artificial processes.

Lead Carbonate.—Undoubtedly the most important carbonate pigment is that of lead, known to the painter as white lead. It occurs in nature as the mineral *cerussite.* This is not now used as a pigment, although the Romans and Greeks were accustomed to employ it as such in the ages gone by. The number of processes which have been patented from time to time for the preparation of white lead is legion, and I shall not attempt to weary you with a description of them to-night.[1] I would like very briefly, however, to outline the famous Dutch process, because of its historical interest and wide application even to-day. Although chemists and manufacturers have tried hard for many years to produce white lead by other quicker and surer processes, their efforts have not been altogether successful, for the white lead produced is never of such good quality as that obtainable from the old-fashioned Dutch method. The process hinges on the fact that lead acetate is readily decomposed by carbon di-oxide under the combined influence of warmth and moisture, yielding lead carbonate.

FIG. 11.

Into earthenware crucibles, some 8 inches in height and 4 inches in diameter, is poured a quantity of weak acetic acid or vinegar. A roll of lead rests on the shelf inside, as represented in this diagram (Fig. 11), which shows the vessel partly in section and partly in perspective for the sake of clearness.

Eleven or twelve thousand of such pots are then built up into a stack in the following way. A shed is built with a sloping roof, and its floor covered with a layer of ashes. Upon this a quantity of spent tan is laid, as a bed for the crucibles. The diagram will make this clear (Fig. 12). On top of the crucibles a number of lead gratings (Fig. 13) are made to rest, and these are covered with boards, which serve as the floor for another series of pots. When the stack is full it is left for a period of three months or so, during which time a series of chemical changes take place. The tan ferments and gives out

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[1] See Holley, "The Lead and Zinc Pigments," or any treatise on colour manufacture. An interesting account of a method of preparing white lead electrolytically is given in a paper read by J. A. Yunk at the fifteenth General Meeting of the American Electrochemical Society at Niagara Falls, May, 1909; abstracted in *Chemical News*, August 13, 1909.

a considerable quantity of heat and carbon di-oxide. The acetic acid is thus largely vaporized and attacks the lead coils and gratings with the formation of lead acetate.

Lead + acetic acid = lead acetate

This is attacked by the carbon di-oxide and water vapour, yielding lead carbonate, whilst acetic acid is liberated and is free to attack more lead.

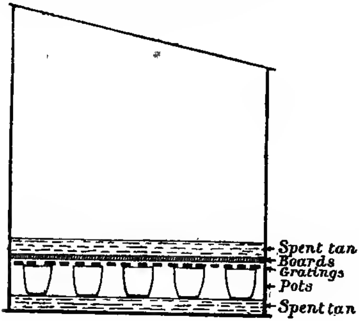

FIG. 12.

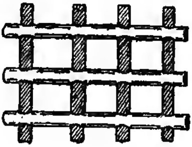

FIG. 13.

After about three months the stack is pulled to pieces, and the lead carbonate scraped off and crushed. This serves to flatten out any unattacked lead, which is sent back to the melting-pot. The carbonate is well washed to remove any traces of lead acetate, and after grinding and drying is ready for the market.

Although white lead is generally regarded as lead carbonate, strictly speaking it is not so, but a basic carbonate of lead. That is to say it contains, in addition to the real lead carbonate, an equal quantity of hydrated lead oxide. The composition, however, is not quite uniform, as will be at once evident from these analyses, quoted by Hurst.[1]

Lead carbonate . . .	63·35	72·15	91·21	87·42	68·36
Lead hydroxide . .	36·14	27·68	8·21	12·33	31·64
Moisture	0·25	—	0·42	0·48	—
	99·74	99·83	99·84	100·23	100·00

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[1] Hurst, "Painters' Colours," etc., p. 44.

As a pigment white lead is extremely valuable to the painter, for it possesses good colour, body, covering power, and durability. It mixes with oil very readily, and the paint thus obtained flows with ease from the brush. White lead, however, is open to the two serious objections which can be raised against all lead pigments, namely, the tendency to blacken in the presence of sulphuretted hydrogen or of the sulphide pigments, and its extremely poisonous nature. Adulteration with barytes is very common, but can readily be detected by the flame test, as I have already shown you. When heated on charcoal a bead of metallic lead is obtained, just as in the case of red lead.

White lead when worked in oil is found in course of time to lose a little of its opacity. This may readily be shown by the following experiment. Over some dry oil-colour rubs, white lead is brushed in just sufficient quantity to obscure them. After a time the forms and colours of the rubs begin to show through very faintly. The explanation will be clear to you when we come on to consider the chemical nature of the oils, etc., used as painters' vehicles. I may so far anticipate, however, as to say that it is due to the white lead gradually combining with the oil to form a translucent, that is to say, a partially transparent lead soap. This reaction is known as saponification, which word means "soap-making."

The presence of lead hydroxide greatly increases the value of the pigment, for it induces saponification more rapidly than the carbonate, and thus yields a rapidly drying paint, and increases very materially the covering power. At the same time, however, the opacity or body of the paint is decreased for the reason given above. It will be clear, therefore, that with a certain proportion of lead hydroxide, the white lead will have a maximum efficiency; in other words, the best combination of body, covering, and drying powers will be arrived at. As a rule, about 25 per cent. of the hydroxide may be regarded as most efficient.

The French Government has recently passed a law to the effect that, after the expiration of five years, the use of white lead shall be illegal for every description of painting work.

This law is designed to remove the cause of lead poisoning which has effected such a high death-rate amongst those classes directly connected with the production and use of white lead. No doubt other countries will soon follow the lead of the French Government, and the time is certainly ripe for such a change. As I have already pointed out to you, zinc oxide is a very efficient and, in some respects, a superior substitute for white lead. Painters, therefore, need not fear the enactment of a similar law in this country, but should welcome its arrival as safeguarding their best interests and health.

Calcium Carbonate.—Calcium carbonate occurs in nature in a variety of forms under the names of chalk, marble, limestone, Iceland spar, etc. The first named occurs in vast quantities in Sussex and Kent, and the chalk cliffs of Dover and the south coast have been famous for centuries. The mineral is largely quarried for the manufacture of whiting, which is used for a number of purposes. As a pigment it is also known as **whiting**, though the names of **English White, Spanish White**, and **Paris White** will be equally familiar to you. The crude material is ground in water to as fine a condition as possible, and dried in a similar manner to barytes. Care must be exercised to avoid overheating, however, for a reason which we shall presently understand. It is then ground again in the dry, and sent into the market.

From a chemical point of view calcium carbonate is most interesting, because it enters into so many of the concerns of our daily life. You are all familiar with quicklime; here is a lump. It is simply the oxide of the metal calcium, and is obtained by heating limestone or calcium carbonate in specially constructed kilns to a high temperature. The limestone loses carbon di-oxide, which escapes into the air, and quicklime remains behind. We might represent this change by the following equation:—

$$\text{Calcium carbonate} = \text{calcium oxide} + \text{carbon di-oxide}$$

If, now, we pour a little water on to this quicklime the whole mass soon becomes very hot, and some of the water escapes as steam, the remainder combining with the lime to form the hydrated oxide or calcium di-oxide. This operation is known as "slaking" the lime.

Calcium oxide + water = calcium hydroxide, or slaked lime

If we stir up this slaked lime with water a milky liquid is obtained, called "milk of lime." On standing for a few hours the solid particles settle, and the clear supernatant liquid, containing a little of the lime dissolved in it, is generally termed "lime-water."

Suppose, now, we cause a stream of bubbles of carbon di-oxide to pass through the lime-water, a milky precipitate is formed. This is because the calcium hydroxide dissolved in the water has united with the gas to form calcium carbonate or chalk, which is insoluble in pure water.

Calcium hydroxide + carbon di-oxide = calcium carbonate

Now notice what happens if we continue to pass carbon di-oxide through the liquid. The white precipitate gradually disappears, and the liquid becomes clear again, for though chalk is insoluble in pure water it dissolves in water containing carbon di-oxide. Now, what do you suppose will happen if we boil this liquid? We will try. First of all, bubbles of gas escape, and gradually the liquid becomes milky. This is precisely what we might expect, isn't it? For when the carbon di-oxide is boiled away only pure water remains, in which the chalk cannot dissolve; so the latter has no choice but to fall out as a milky precipitate. This is the chief cause of the so-called "furring" of kettles and boilers. All natural waters contain carbon di-oxide dissolved in them, and if they happen to flow through chalky or limestone soil, considerable quantities of calcium carbonate will dissolve. This renders the water "hard," that is to say, soap will not readily form a lather with it. Boiling, however, effects the precipitation of the chalk and softens the water.

As a pigment calcium carbonate is useful on account of its cheapness and permanence. It dissolves with effervescence in dilute hydrochloric acid, yielding a colourless solution of calcium chloride.

$$\begin{matrix}\text{Calcium}\\ \text{carbonate}\end{matrix} + \begin{matrix}\text{hydrochloric}\\ \text{acid}\end{matrix} = \begin{matrix}\text{calcium}\\ \text{chloride}\end{matrix} + \begin{matrix}\text{carbon}\\ \text{di-oxide}\end{matrix}$$

This test serves to distinguish it from zinc oxide, which, you will remember, dissolves in acid without any effervescence. Natural whiting always contains a little silica or sandy material, as the following analysis of a sample supplied to me will show :—

Calcium carbonate	97·60 per cent.
Silica	2·11 ,,
Water	0·29 ,,

The amount of silica in a sample is easily estimated, for, being insoluble in acid, it is the residue left on treating a sample of the whiting with acid.

Calcium carbonate does not dissolve in sulphuric acid, for, although it is decomposed with evolution of carbon di-oxide gas, insoluble calcium sulphate is left, which we have already studied under the name of gypsum. This enables us to distinguish between calcium carbonate and magnesite, which latter substance dissolves in sulphuric acid, yielding a clear solution of magnesium sulphate or Epsom salt.

Whiting is seldom, if ever, used as an oil colour, partly owing to its tendency to acquire a dirty grey shade, and also to the fact that its lightness and porosity cause it to absorb so much oil that it becomes almost transparent. It is mostly used in distempers and water paints, about which I shall have something to say later on. Mixed with linseed oil it yields putty.

I have already mentioned that great care must be exercised in drying the ground pigment, as otherwise carbon di-oxide may be evolved and quicklime left. On account of this it cannot be safely mixed with Prussian blue and chrome yellow, which are rapidly acted upon by alkalies, such as quicklime, for reasons which will appear later. Vegetable colours are also destroyed by whiting. Indigo, ochres, umbers, siennas, Venetian red, vermilion, lime blue, and the ultramarines are suitable for mixing with whiting, and will in combination produce an extensive variety of hues.

Gilders' whiting is a finer preparation than that usually sold. Chemically it is, of course, identical with ordinary whiting.

Magnesium Carbonate.—Under the name of **Magnesite** magnesium carbonate sometimes finds its way into the market for use as a pigment, although it has not a general application. It is prepared from the natural ore, which is finely ground and levigated. Its colour is good and permanent, and it possesses very fair body and covering power. Owing to its tendency to alkalinity it is subject to the same limitations in the matter of colouring, as whiting.

Copper Carbonate.—This is considered in connection with those pigments containing copper (Chapter X.).

VIII

THE CHROMATE PIGMENTS

THE metal chromium occurs widely distributed in nature in combination with various other elements. As *chrome iron ore* it is found in Norway, Siberia, North America, Australia, etc., combined with oxygen and iron oxide. In the mineral *crocoisite* it occurs essentially as lead chromate, better known to you, perhaps, as chrome yellow.

Chromium combines with oxygen in two proportions. The lower oxide is green, and, as we saw some time ago,[1] is valued by the painter for its beautiful colour and unusual permanence and inertia. The higher oxide, known to the chemist as chromium tri-oxide, contains just twice as much oxygen relatively to the metal as does the green or sesqui-oxide. Although possessed of a beautiful red colour it cannot be used as a pigment on account of its ready solubility in water and the ease with which it attacks all organic matter, yielding up its oxygen and being converted into the green oxide. It combines with metallic oxides and hydroxides, however, to form very stable compounds known either as "chromates" or as "bi-chromates," according to the amount of the tri-oxide present. Some of these are soluble in water, as, for example, potassium chromate, and are therefore useless as pigments. Others are insoluble in water, although very sensitive to the action of dilute mineral acids. Many of these are invaluable to the painter, as they yield him some of his brightest pigments.

As a rule, in the preparation of chromates it is quite unnecessary to isolate the chromium tri-oxide, for this is both

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[1] See Chapter III.

expensive and tedious. Either the bi-chromate or normal chromate of potash is used, the only difference between the two salts being that the former contains twice as much chromium relatively to the potash as does the latter. If, therefore, to a solution of potassium bi-chromate we add the requisite quantity of potassium hydroxide, the liquid turns from orange to yellow, and on evaporation yellow crystals of potassium chromate make their appearance.

$$\begin{matrix}\text{Potassium} & + & \text{potassium} & = & 2 & \text{potassium}\\ \text{bi-chromate} & & \text{hydroxide} & & & \text{chromate}\end{matrix}$$

On the other hand, if we begin with a solution of potassium chromate and add the correct amount of sulphuric acid to it, half of the potash unites with the latter to form potassium sulphate, and the solution turns a ruby colour owing to the formation of the bi-chromate. On partial evaporation crystals of the two salts separate out.

$$\begin{matrix}2 & \text{Potassium} & + & \text{sulphuric} & = & \text{potassium} & + & \text{potassium}\\ & \text{chromate} & & \text{acid} & & \text{sulphate} & & \text{bi-chromate}\end{matrix}$$

Potassium bi-chromate is prepared commercially by roasting a mixture of finely powdered chrome iron stone with potash and lime, whereby the chromates of potassium and calcium are obtained. Addition of potassium sulphate converts the latter salt into insoluble calcium sulphate or gypsum, and the whole of the chromium passes into solution as potassium chromate.

$$\begin{matrix}\text{Calcium} & + & \text{potassium} & = & \text{calcium} & + & \text{potassium}\\ \text{chromate} & & \text{sulphate} & & \text{sulphate} & & \text{chromate}\end{matrix}$$

Addition of sulphuric acid converts this, as we have already seen, into the bi-chromate, which is crystallized out.

If now a solution of lead acetate is added to one of potassium bi-chromate, an immediate precipitation of lead chromate (not lead bi-chromate) occurs. In other cases it is advisable to use either the normal chromate or an alkaline solution of the metal, for reasons which will appear later.

Lead Chromate.—One of the most valuable and easily prepared of the chromes is the lead salt known as **Chrome**

Yellow. Its tint and shade admit of considerable modification by slightly altering the conditions of its manufacture, whereby small differences in composition are introduced. As we have already learned, the pure salt is prepared by addition of potassium bi-chromate to lead acetate solution, the reaction taking place according to the following equation :—

$$\begin{array}{c}\text{Lead}\\ \text{acetate}\end{array} + \begin{array}{c}\text{potassium}\\ \text{bi-chromate}\end{array} = \begin{array}{c}\text{lead}\\ \text{chromate}\end{array} + \begin{array}{c}\text{potassium}\\ \text{acetate}\end{array} + \begin{array}{c}\text{acetic}\\ \text{acid}\end{array}$$

If yellow potassium chromate were used instead of the bi-chromate, no free acetic acid would be produced. Thus—

$$\begin{array}{c}\text{Lead}\\ \text{acetate}\end{array} + \begin{array}{c}\text{potassium}\\ \text{chromate}\end{array} = \begin{array}{c}\text{lead}\\ \text{chromate}\end{array} + \begin{array}{c}\text{potassium}\\ \text{acetate}\end{array}$$

As, however, lead chromate is not affected by acetic acid, the presence of this latter substance is immaterial. After washing and drying the pigment is ready for the market.

When warmed with a dilute solution of caustic soda, chrome yellow becomes orange or red in colour. This is due to the formation of a basic lead chromate, which contains half as much chromium in proportion to the lead as does the normal chromate, the caustic soda having removed the other half. Thus—

$$2\begin{array}{c}\text{Lead}\\ \text{chromate}\end{array} + \begin{array}{c}\text{caustic}\\ \text{soda}\end{array} = \begin{array}{c}\text{basic lead}\\ \text{chromate}\end{array} + \begin{array}{c}\text{sodium}\\ \text{chromate}\end{array}$$

The extent to which this reaction takes place will obviously determine the hue of the resulting mixture, and by suitably adjusting the proportions any desired combination of red and yellow can be obtained.

The reaction takes place slowly when chrome yellow is mixed with basic pigments, such as whiting, magnesite, etc. The pigment should therefore be tinted by admixture with a neutral substance, such as lead or barium sulphate. The combined action of air and moisture gradually effects the same change, and it is a matter of common knowledge that cornices, etc., which have been painted with lead chromate invariably assume an orange hue in the course of time. The explanation will now be evident. In various conditions of purity the basic chromate of lead finds its way into the market under the names of **Derby Red, Chinese Red, Chrome Red, Orange Chrome,** etc. Although fairly stable in ordinary circumstances, these pigments are open to the objection which characterizes all lead pigments, namely, their discoloration in the presence of sulphuretted hydrogen and the sulphide pigments. Both chrome yellow and chrome red are decomposed by sulphuric acid, white lead sulphate being formed.

It is seldom, however, that the lead chromes find their way into the market in a state of purity, since barytes, white lead, lead sulphate, etc., are added in order to effect changes in tint. Their use, however, is perfectly legitimate, provided the purchaser knows what he is buying.

Zinc Chromate.—Zinc chromate cannot be advantageously prepared by the addition of potassium bi-chromate to a solution of a zinc salt in water, because free acid is liberated during the reaction, which tends to dissolve the pigment as fast as it is formed. This will be clear from the following equation:—

$$\begin{array}{c}\text{Zinc}\\\text{sulphate}\end{array} + \begin{array}{c}\text{potassium}\\\text{bi-chromate}\end{array} = \begin{array}{c}\text{zinc}\\\text{chromate}\end{array} + \begin{array}{c}\text{potassium}\\\text{sulphate}\end{array} + \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}$$

In the case of lead chromate just considered, as the acetate was used, free acetic acid was generated during the reaction. But this did not matter, since lead chromate is not affected by dilute acetic acid.

If, in the above reaction with zinc, an alkali, such as potash or soda, is added to the solution to neutralize the sulphuric acid as fast as it is formed, the zinc chromate will be precipitated without any difficulty. The easiest way of doing this is to add the potash to the bi-chromate solution first; in other words, to convert the potassium bi-chromate into the normal chromate, and then add the zinc salt. Thus—

$$\begin{array}{c}\text{Zinc}\\\text{sulphate}\end{array} + \begin{array}{c}\text{potassium}\\\text{chromate}\end{array} = \begin{array}{c}\text{zinc}\\\text{chromate}\end{array} + \begin{array}{c}\text{potassium}\\\text{sulphate}\end{array}$$

Zinc Chrome or **Citron Yellow** is a yellow pigment, insoluble in water, but readily soluble in dilute acids. It possesses the advantage over lead chromes of not being discoloured by sulphuretted hydrogen or by contact with sulphide pigments. Its powers of body are not equal to those of the lead chromes, however. With caustic soda decomposition takes place, resulting in the formation of white hydrated oxide of zinc, and sodium chromate. In the preparation of the pigment, therefore, it is as necessary to avoid addition of excess of alkali as of acid. In contact with organic substances, zinc chromate is liable to turn green, owing to the chromium parting with half of the oxygen with which it is combined, being converted into the very permanent green oxide.

Zinc chromate is not met with in commerce to any great extent as a separate pigment, for a large proportion of it is mixed with Prussian blue to produce the various zinc greens, about which we shall have more to say later.

Lead chromate is frequently used to adulterate zinc chromate, but its presence can readily be detected by the addition of dilute acetic acid. This effects the solution of the zinc chromate, and an insoluble yellow residue at once betrays the presence of the lead salt, which may be confirmed by the addition of ammonium sulphide, which produces black lead sulphide. A white residue may indicate barytes or lead sulphate. The presence of the former of these is confirmed by the flame test, and ammonium sulphide will reveal the latter. Should effervescence occur on addition of the acetic acid, a carbonate is present, probably either calcium carbonate (whiting) or lead carbonate (white lead), or possibly both.

Barium Chromate.—This pigment finds its way into the market under various names, such as **Lemon Chrome, Barium Chrome**, and **Yellow Ultramarine.** It is readily prepared by the addition of potassium chromate to a solution of barium chloride. Bi-chromate of potash cannot be used for the same reason as in the case of zinc chromate. After washing, a pale, sulphur-yellow powder is obtained, which, though exceedingly permanent, is deficient in brightness and body, and is therefore seldom used as a pigment.

The chromates of copper, mercury, and silver have been suggested from time to time as suitable pigments, but owing to their cost and lack of permanence they have never come much into favour, at any rate amongst the house painters. A basic chromate of iron is used to a limited extent as a water colour, under the name of **Siderin Yellow**, and is formed by heating a solution of iron per-chloride and potassium bichromate. The colour can easily be imitated, however, by mixing together chrome yellow and ochre, etc. It is extremely permanent, but not very brilliant.

IX

PRUSSIAN BLUE AND ULTRAMARINE

Prussian Blue.—Of all the complex pigments used by the painter to-day, none is better understood from a chemical point of view than Prussian blue. It was discovered accidentally in 1710 by Diesbach, a Berlin colour manufacturer.

Prussian blue is a compound of iron, carbon, and nitrogen, and may be obtained by mixing solutions of ferrous sulphate, nitric acid, and potassium ferro-cyanide.

If perfectly air-free solutions of green vitriol and potassium ferro-cyanide are mixed, a white precipitate of ferrous ferro-cyanide is obtained, which rapidly turns blue on exposure to air. This is due to the fact that it is absorbing oxygen, and being converted into Prussian blue. The equation representing these changes may be expressed as follows:—

$$1.\ \begin{array}{c}\text{Ferrous}\\ \text{sulphate}\end{array} + \begin{array}{c}\text{potassium}\\ \text{ferro-cyanide}\end{array} = \begin{array}{c}\text{ferrous}\\ \text{ferro-cyanide}\end{array} + \begin{array}{c}\text{potassium}\\ \text{sulphate}\end{array}$$

$$2.\ \begin{array}{c}\text{Ferrous}\\ \text{ferro-cyanide}\end{array} + \text{oxygen} = \text{Prussian blue}$$

Now, nitric acid contains a great deal of oxygen, and if we first mix this with the ferrous sulphate, then, on the addition of the ferro-cyanide, the blue pigment is precipitated at once without the intervention of atmospheric oxygen. It only remains now to thoroughly wash and dry the pigment, and it is ready for the market.

Prussian blue is characterized by the intensity of its colour, 1 lb. of which will give a perceptible tinge to over 600 lbs. of white lead. In fact, the formation of this colour constitutes one of the most delicate reactions known for the detection of minute traces of iron. Here is a gas jar filled with water, to which a few drops of a solution of potassium ferro-cyanide have been added. I will now add a single drop of ferrous sulphate solution, containing nitric acid, to the jar, and you notice that the whole mass of liquid assumes a decided blue colour, showing the remarkable delicacy of the test.[1]

In the commercial production of the pigment it is more usual to employ bleaching powder as the oxidizing agent, than nitric acid, owing to its comparative cheapness. It is added in small quantities at a time, and is very efficient. Obtained in this way the pigment is very pure, and finds its way into the market as **Chinese Blue.**

The commoner makes of Prussian blue are sold under that name, and also as **Berlin Blue, Paste Blue,** etc. They are prepared in much the same manner as Chinese blue, but the several operations are carried out less carefully, and other ingredients are frequently present. One of the most important of these is alum, which not only gives a lighter tint to the blue, but renders it much easier to grind after drying. In the preparation of **Antwerp Blue,** zinc sulphate, as well as alum, is used; but the properties of the finished product are practically the same as those of the ordinary Prussian blue, save that its tint is somewhat lighter.

Brunswick Blue is simply Prussian blue admixed with varying quantities of barytes and silica. Instead of barytes, gypsum or china clay may be used. Hurst found a sample of the blue to contain—

Water	0·28	per cent.
Alumina	2·45	,,
Iron oxide	3·31	,,
Barytes and silica	89·86	,,
Carbon, nitrogen, and sulphur	4·10	,,
	100·00	

The main drawback to Brunswick blue is the tendency for

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[1] When properly carried out this is a very striking experiment. I have found that, given favourable conditions, the presence of 0·000014 grams of iron in 50 c.c. of water can readily be detected by this method.

the heavy barytes to settle to the bottom when the pigment is mixed with oil, the blue remaining suspended in the liquid. Of course this can be remedied easily enough by stirring immediately before use.

Coming now to the properties of Prussian blues as a whole. Here is a sample of the dry Chinese blue, and you cannot fail to notice its depth of colour and bronze-like appearance. It is very difficult to grind, and this is unfortunate since thorough grinding is essential to the development of its full colouring powers. Herein, therefore, lies one of the great advantages of Brunswick blue, which is more readily obtained in a fine condition.

Unless special precautions are taken, Prussian blue is liable to set up to the consistency of leather when ground in a drying oil, a property known in the trade as "leathering" or "livering." Paint grinders, therefore, use special blends of oil with which the pigment does not show this peculiarity.

Prussian blue is insoluble in dilute mineral acids, such as sulphuric and hydrochloric. Strong sulphuric acid decolorizes it with the formation of iron sulphate. Some samples are practically insoluble in concentrated hydrochloric acid, while others dissolve more or less readily. Amongst other things, the age of the pigment seems to have a marked influence upon its solubility in hydrochloric acid, and it is not improbable that, on keeping, it undergoes some kind of physical change, although its chemical composition remains the same. You will recall a similar instance amongst the sulphide pigments; I refer to mercury sulphide, which when first formed is black, but on further treatment is converted into vermilion, the colour of which is familiar to you all. In the case of Prussian blue, however, the colour of the pigment remains the same, although certain of its other physical properties are slightly altered.

On warming with a solution of oxalic acid, Prussian blue dissolves, yielding a blue liquid or ink. Of late years, however, this blue has been largely supplanted by the various coal tar dyes for the manufacture of ink.

Now here is an interesting reaction. We will add a little caustic soda to some Prussian blue. A ruddy colour is obtained. This is our old friend, the hydrated oxide of iron. If now we neutralize the soda by addition of hydrochloric acid, the blue colour is immediately restored, because the soda gives back to the iron oxide the substances necessary to form the blue again. If we first wash the red oxide, however, and then add the acid, of course no blue can be obtained, and the oxide simply dissolves to form a soluble chloride of iron. It will be evident to you, therefore, that Prussian blue must not be tinted with lime, whiting, or any alkaline pigment, as a ruddy hue is sure to be produced.

In ordinary circumstances Prussian blue is a very permanent pigment, resisting exposure to moist air and to light. When used as a water paint, it fades slightly on exposure to light, but gradually recovers its intensity in the dark. When heated very strongly the carbon and nitrogen burn off and a red mass, consisting chiefly of anhydrous oxide of iron, remains behind.

The detection of Prussian blue in a mixture of pigments is an easy matter, and if you have followed all that I have just been saying, you will have no difficulty in understanding what follows.

A portion of the suspected pigment is warmed with caustic soda solution, when a ruddy colour will be produced if Prussian blue is present. Such a change would also occur, however, even in the absence of Prussian blue, if lead chromate were present, owing to the formation of the basic orange chrome. Although these two hues are very distinct when the pure pigments are being dealt with, yet in complex mixtures they are sufficiently alike to be misleading. To confirm, therefore, the presence of the blue, filter, and to the filtrate add a few drops of per-chloride of iron, together with sufficient hydrochloric acid to neutralize the caustic soda. If Prussian blue was originally present, it will be immediately formed again as a blue precipitate.

Prussian blue is seldom used alone. Its staining powers are great, and it finds extensive application in colouring other pigments. It is a very bad drier, and exerts a retarding action on the drying oils with which it associates.

Chrome Greens.[1]—These are very valuable pigments consisting of chrome yellow, Prussian blue, and bartyes, which work well both in oil and in water. They possess good body and colouring power, and are consequently used very largely for outdoor painting in oil, although they are not so fast to light as the zinc greens. Their small cost, however, is a great point in their favour.

Chrome greens are slowly darkened by sulphuretted hydrogen and by admixture with sulphide pigments, owing to the conversion of the lead chromate into black lead sulphide. Alkalies have a double action, converting the Prussian blue into hydrated oxide of iron, and the lead chromate into the basic salt. The mixture, therefore, assumes a ruddy hue. For this reason, the chrome greens should not be mixed with basic substances, as lime or whiting. If suitable precautions are taken, and perfectly neutral size is used, the chrome greens may be used in distemper work, but they must on no account be mixed hot, since on warming lead chromate becomes orange in the presence of water.

Acids are equally injurious; for, although they have no action upon Prussian blue and barytes, they dissolve out the lead chromate, and a bluer colour ensues.

Hurst[2] gives the following analyses of four different chrome greens, and a glance at them will suffice to show in what proportions the various constituents occur—

ANALYSES OF BRUNSWICK GREENS (CHROME GREENS).

	Pale.	Middle.	Deep.	Extra deep.
Water	1·00	0·80	1·00	0·80
Barytes	72·74	71·94	72·76	71·40
Gypsum	2·34	trace	trace	—
Prussian blue	0·93	0·44	4·54	6·91
Chrome yellow	14·27	25·73	17·66	17·87
Lead sulphate	8·07	1·04	3·28	3·15
	99·35	99·95	99·24	100·13

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[1] Not to be confounded with genuine chrome green, considered in Chapter III. These pigments are also known as *Brunswick Greens.* See Chapter X., p. 88.

[2] See Hurst, "Painters' Colours," etc., p. 170.

Zinc Greens.—These pigments are admixtures of zinc chromate, Prussian blue, and barytes, and are very popular on account of their brightness and relatively low cost. By suitably adjusting the proportions of the various constituents an astonishing variety of hues can be obtained, of various tints and shades, ranging from the lightest parrot green to the deepest blue green. They possess a slightly inferior body to the chrome greens, but are more permanent, since zinc chromate itself is more stable than the corresponding lead salt. Zinc greens are much faster to light than the chrome greens of equal intensity, as may be readily proved in the following manner[1]:—

Samples of the powdered pigments, containing equivalent amounts of Prussian blue, are spread side by side on paper, and exposed to the light for a time. The chrome green very soon develops a yellower hue, whereas the zinc green remains practically unaltered. A satisfactory explanation of these phenomena is not yet forthcoming.

Like the chrome greens, zinc greens are not fast to lime, for their Prussian blue content is not chemically combined with the zinc chromate, and is therefore still susceptible to the action of alkalies. Zinc greens are more apt to "blue" or "run" than are the chrome greens, which is due to the Prussian blue making its way to the surface of the paint, thereby imparting a chequered appearance to the coating. When mixed with oil the paint dries well, and gives very satisfactory results when applied to the surfaces of both wood and iron.

Ultramarine.—Ultramarine is one of the most important of the blue pigments with which the painter has anything to do. About a hundred years ago it was obtainable from natural sources only, and as these were very limited, the cost was generally prohibitive. It was obtained from the mineral *lapis lazuli*, the sapphire of the ancients, which occurs in small quantities in Persia, China, and Siberia, as well as in various parts of South America. The mineral was ground to a fine

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[1] See Zerr and Rübenkamp, "A Treatise on Colour Manufacture" (published by Chas. Griffin & Co., 1908), p. 252.

powder, mixed with resin, wax, and linseed oil, and kneaded in cloths under hot water. The blue colouring matter passed through the cloth, was allowed to settle, and after further grinding and careful drying, was sent into the market. It was listed at 80*s.* per ounce.

From a chemical point of view ultramarine is very complex, and widely different views have been expressed as to its composition and constitution. In 1806 Clément and Désormes gave the following analysis:—

Silica	35·8	per cent.
Alumina	34·8	,,
Soda	23·2	,,
Sulphur	3·1	,,
Calcium carbonate	3·1	,,
	100·0	

Consequently for many years it defied all attempts to prepare it artificially, and although a given measure of success has attended the efforts of chemists in this direction during the last decade, in so much that the pigment is now cheap and its consumption is measured by tons, nevertheless the progress has been the result of pure experiment, rather than that of experiment guided by theory. The methods adopted for the artificial production of the pigment are still somewhat tedious, and it is quite possible that they will be considerably simplified as our knowledge of the chemistry of the processes increases. It will be sufficient if I just outline to you very briefly the most common manufacturing processes now employed, known as the direct and indirect processes respectively.

(i) *The Indirect Method.*—Three kinds of ultramarine are manufactured in this way, viz. the sulphate pigment, which has a pale greenish blue colour; the soda pigment, poor in silica, used for the majority of purposes; the soda pigment rich in silica, used chiefly by paper-makers. The process is in each case conducted in two stages.

a. Calcination.—The composition of the mixture to be calcined will naturally vary according to the kind of ultramarine which it is desired to prepare.

For sulphate ultramarine:

	I.	II.	III.
Kaolin or porcelain clay (a hydrated compound of alumina and silica)	50	47	26
Sodium sulphate	41·5	19·5	57
Coal	8·5	8	—
Sodium carbonate	—	19·5	—
Sulphur	—	6	8
Resin	—	—	9
	100	100	100

As sodium sulphate contains sulphur, it will be clear why, as the proportion of the former decreases, many manufacturers take care that the proportion of sulphur should be increased.

For soda ultramarine poor in silica:

Kaolin	36·5	per cent.
Sodium carbonate	36·5	,,
Coal	4·5	,,
Sulphur	22·5	,,
	100·0	

For soda ultramarine rich in silica:

	I.	II.
Kaolin	33·0	33·3
Silica	3·5	—
Sodium carbonate	36·5	30
Sulphur	22·5	33·3
Coal	4·5	1·3
Resin	—	2
	100·0	99·9

As a general rule, it is found that the greater the percentage of sulphur, the deeper is the shade of the blue produced. Reduction of the sulphur and silica results in the formation of a lighter and more brilliant pigment.

The mixture, compounded as above according to the desired character of the finished product, is placed in crucibles some six inches in height, and four in diameter, and heated in a furnace for from seven to ten hours. On cooling, the burnt mass is removed. Its colour is somewhat variable, but, if the burning has been successful, it should be of a bluish green hue. If not properly burnt, the mass may be somewhat brown. It is now washed with water and ground as finely as possible, to assist in the extraction of all the soluble matter. After careful drying it is ready, either for the next operation, or for the market, under the name of **Green Ultramarine.** In this condition it is used by manufacturers of water paints, and is known to painters as "lime green," being fast to lime, and making beautiful and permanent green tints in lime colourings.

b. Colouring Stage.—The green ultramarine, obtained in the manner already indicated, is now heated in a furnace with brimstone or sulphur. There are several ways of carrying out this operation. Sometimes the green, powdered pigment is laid on trays to the depth of an inch, and sprinkled with sulphur. The furnace is lighted, and the heat continued until the sulphur begins to burn. The fires are then drawn, and when the sulphur has burned itself out, the crude mass is removed and "finished." That is to say, it is thoroughly well ground and washed, and by the process of levigation the different grades of the pigment can be separated. The finer qualities are used in different kinds of printing, the coarser, and consequently the cheaper, product being utilized by the painter.

(ii) *The Direct Method.*—This may be carried out in crucibles. A mixture comprising—

Kaolin	31·5
Sodium carbonate	28
Sulphur	34·5
Charcoal	6
	100

is ground as finely as possible, and heated in crucibles in a furnace to a bright red heat for several hours. Of course, the above recipe can be altered at will, according as a finished product rich or poor in silica is required. On cooling the burnt mass is removed, ground and finished in the way indicated above.

As I have already stated, all these processes for the preparation of ultramarine are unsatisfactory, in so far as the changes which take place are but imperfectly understood, and too much depends upon the duration and intensity of the heat required during burning, for which no definite rules can be given. Experience, therefore, seems to be the only guide, and this is ever uncertain in matters of this sort.

As a pigment ultramarine is fairly permanent in all ordinary circumstances. In contact with acids, sulphuretted hydrogen is evolved, showing the presence of a sulphide. It cannot, therefore, be safely mixed with lead or copper pigments, as discoloration is likely to occur owing to the formation of black sulphides of the metals.

The sulphate ultramarine is characterized by its pale greenish blue colour. The soda ultramarines are violet blue, the variety richest in silica being possessed of the darkest and deepest shade. Of the two the former is the less stable towards acids, being readily attacked by such weak reagents as acetic and tartaric acids. Nitric acid causes a precipitate of sulphur to form; but on prolonged boiling this dissolves, and a residue of gelatinous silica remains behind. Alkalies are without action upon any of the varieties of ultramarine, which are therefore used largely in the colouring of distempers, etc. When used for inside work, or exposed only to pure air, the result is very satisfactory. But the acid-laden air of our large towns and cities soon attacks the colour, producing effects far from pleasing.

When boiled with a solution of alum, ultramarines assume a more violet hue. The sulphate pigment is affected most, the change becoming less marked as the proportion of silica increases. The pigment with the highest silica content is largely used by paper makers.

As I mentioned to you a few minutes ago, chemists have held widely different views as to the composition of ultramarine. As will be seen from these analyses, quoted by Hurst,[1] the composition is somewhat variable. It is generally believed, however, that the ordinary blue ultramarine is a compound of silica, alumina, and soda, chemically united with a sulphide of sodium. The green ultramarine is believed to be a combination of the blue with salts of sodium, for, on boiling with

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[1] See Hurst, *opus cit.*, p. 211.

water, the blue variety is obtained, and sodium salts go into solution.

ANALYSES OF ULTRAMARINES.

	Sulphate.	Soap makers.	Calico printers.	Paper makers.	Green.
Silica	49·7	40·7	40·9	45·4	38·5
Alumina	23·0	25·1	24·1	21·2	28·9
Sulphur	9·2	13·0	13·7	11·6	8·3
Sulphur tri-oxide .	2·5	4·8	3·1	5·6	—
Sodium oxide . .	12·5	14·3	15·6	9·9	23·7
Water	3·1	2·3	2·6	6·3	—
	100·0	100·2	100·0	100·0	99·4

Yellow Ultramarine is the name sometimes given to barium chromate, which pigment we have already considered (Chapter VIII.).

X

PIGMENTS CONTAINING COPPER

Lime Blue.—Some years ago, before ultramarine could be prepared artificially in a cheap way, lime blue was largely employed for frescoes and for colour-washing. It is essentially a mixture of calcium sulphate and copper hydroxide, and is easily prepared in the following way :—

To a solution of copper sulphate, ammonia is added. A precipitate of copper hydroxide at once forms. If excess of ammonia is added, this precipitate dissolves, yielding an excessively blue solution. This is now mixed with milk of lime, which, you will remember, is calcium hydroxide suspended in water. This effects the precipitation of copper-hydroxide again, intimately associated with calcium sulphate, which is also insoluble in water. Neglecting the ammonia, which chiefly serves to keep the copper hydroxide in solution until the milk of lime is added, we may write the equation representing the change, as—

$$\begin{array}{c}\text{Copper}\\\text{sulphate}\end{array} + \begin{array}{c}\text{calcium}\\\text{hydroxide}\end{array} = \underbrace{\begin{array}{c}\text{copper}\\\text{hydroxide}\end{array} + \begin{array}{c}\text{calcium}\\\text{sulphate}\end{array}}_{\text{Lime Blue}}$$

The pigment is washed and dried at a low temperature, and is then ready for use. High temperatures must be avoided throughout the process, otherwise the copper hydroxide will lose water, yielding black copper-oxide.

As will be evident from its method of preparation, alkalies have no action on this pigment, hence its application to lime-washing. In common with all copper pigments, however, it is rapidly discoloured by sulphuretted hydrogen and sulphides generally, in which respect ultramarine has the decided advantage.

Verdigris.—Verdigris is the basic acetate of copper; that is to say, it consists of copper acetate combined with the hydrated oxide of the metal. It can readily be prepared in a variety of ways. The old French method consisted in exposing scrap copper to the action of the rejected skins of grapes, left after the juice had been pressed out for wine. These skins ferment, producing acetic acid, which dissolves the copper, yielding the acetate. After two or three weeks the copper is removed and dried, and the verdigris scraped off.

A few years ago, when verdigris was in greater demand than at the present time, this industry was in a flourishing condition in France and Belgium, where vineyards have for centuries been abundant.

The English method for the preparation of verdigris is somewhat different. Copper plates are wrapped in cloths soaked in crude wood vinegar, obtained by the distillation of wood. When the coating of verdigris is sufficiently thick, the plates are dipped into water and dried, after which the pigment is scraped off. The plates are then treated in a similar manner again and again, until all the copper has been converted into verdigris. The pigment obtained in either of these ways has now to be washed and carefully dried. The temperature of the latter operation must not be too high, as this is found to affect the brilliancy of the hue.

Verdigris has a greenish blue colour, which is more permanent in oil than in water. It readily dissolves in dilute acids, and turns black in the presence of sulphuretted hydrogen, owing to the formation of black copper sulphide. It is thus subject to the same limitations as the lead pigments, with regard to mixing with other colours. When heated strongly, black copper oxide is produced.

The commercial article exhibits considerable variation in composition, as will be evident from a glance at the following analyses of five samples, in which the percentages of copper oxide and water alone are given :—

	1.	2.	3.	4.	5.
Copper oxide	44·3	43·8	40·8	43·2	43·5
Water	23·5	18·0	13·0	29·2	25·2

Verdigris is often adulterated with barytes, silica, etc. Insoluble substances such as these can readily be detected and estimated by warming a given quantity of the pigment with dilute hydrochloric acid, which will dissolve all the pure pigment. The insoluble residue may now be filtered off, washed, and weighed in the usual manner. If the pigment dissolves with effervescence in the acid, the presence of a carbonate may be inferred. If the addition of a few drops of barium chloride to the acid solution produces turbidity, barytes or barium sulphate has been formed, indicating the presence of a soluble sulphate. If a blue residue remains after treating the pigment with acid, the presence of Prussian blue is to be suspected. Confirmation is readily obtained by a method which I explained to you when we were dealing with this latter pigment.

Scheele's Green.—Although this pigment is seldom if ever used, I mention it because of its chemical interest. It is a compound of copper oxide and the oxide of arsenic (sometimes known as "white arsenic") and is known to the chemist as copper arsenite. Sharples[1] gives the following analysis of the pure pigment:—

Copper oxide	50·0 per cent.
White arsenic	42·0 ,,
Water	8·0 ,,
	100·0

The composition, however, varies slightly according to the method by which the pigment is prepared. Berzelius, the great Swedish chemist, obtained it by boiling copper carbonate with white arsenic.

Sharples prepared Scheele's green by dissolving white arsenic in a solution of sodium carbonate and pouring the resulting solution into one of copper sulphate in water, at boiling heat. On the succeeding day the precipitate is washed and dried.

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[1] Sharples, *Chemical News*, **35**, 89 *et seq.*

By whatever process this pigment is prepared, it has a pale yellowish green colour, which, however, is not permanent. It was originally used in colouring wall papers, but the arsenic which it contains led to numerous cases of poisoning from this cause, so the pigment is not now used. It readily dissolves in dilute acids. Like verdigris, it is very susceptible to the action of sulphuretted hydrogen, and may not be safely mixed with sulphide pigments. When heated strongly, the white arsenic escapes as vapour, black copper oxide remaining behind. The presence of arsenic can readily be detected by means of Marsh's test, which I described to you in detail some time ago.

Emerald Green.—This pigment is known under several other names, the chief being **Paris Green**, and **Schweinfurth Green**, the last mentioned owing its origin to the fact that the pigment was first made in Schweinfurth in Germany. It is really an aceto-arsenite of copper; that is to say, it lies halfway between verdigris and Scheele's green. It is readily prepared by thoroughly mixing equal quantities of white arsenic and verdigris with water, and allowing to stand in a warm place. It is now washed and dried, when it is ready for use.

Owing to its poisonous nature, emerald green has not received the extensive use which it might otherwise have done by virtue of its fine colour, which is very difficult to imitate. It is only moderately opaque, and when used in oil has not a good body, and is very slow in drying. It is fairly permanent, but sulphuretted hydrogen rapidly discolours it. Like the other copper pigments, therefore, it may not be mixed with such colours as ultramarine, cadmium yellow, etc. Being soluble in acid, any insoluble adulterant, such as barytes, can readily be detected and estimated, as in the case of verdigris. The presence of arsenic can be proved by Marsh's Test.

Copper Carbonate.—The normal carbonate of copper has never been definitely obtained. The basic carbonate, however is found as the mineral *malachite* in Cornwall, Yorkshire, and elsewhere in the United Kingdom, as well as in Siberia, Persia, Australia, and many other countries. The natural ore is ground as finely as possible, and sent into the market under the names of **Malachite**, **Mineral Green**, and

Mountain Green. It works well both in oil and water, but is only moderately permanent. To this sample of malachite we will add a few drops of dilute sulphuric acid in a test-tube. You notice that the whole mass effervesces, and on gently lowering a lighted splinter into the tube, the flame is extinguished. The gas is carbon di-oxide. The blue solution in the test-tube contains copper sulphate, or blue vitriol, and if we were to boil off some of the water, on cooling the characteristic crystals would form.

$$\begin{array}{c}\text{Copper}\\\text{carbonate}\end{array} + \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array} = \begin{array}{c}\text{copper}\\\text{sulphate}\end{array} + \begin{array}{c}\text{carbon}\\\text{di-oxide}\end{array}$$

I will now bubble a little sulphuretted hydrogen into the solution. A black precipitate of copper sulphide is at once obtained, resembling lead sulphide. It will be evident to you, therefore, that malachite, and, indeed, all the pigments which owe their colour to copper, are subject to the same limitations as the lead pigments, in that they may not be mixed with sulphide pigments.

When gently heated, malachite decomposes, carbon di-oxide and water being evolved, and black copper oxide remaining behind.

A second basic carbonate of copper is found naturally as the mineral azurite. When ground up very fine it is used as a pigment under the name of **Mountain Blue.** As yet, however, it has not received a very extensive application.

Bremen Blue consists of a small quantity of copper carbonate intimately associated with copper hydroxide, which constitutes the bulk of the pigment. It is easily prepared in the following way :—

A solution of barium chloride in water is added to one of copper sulphate, whereby a white precipitate of insoluble barium sulphate is obtained, copper chloride passing into solution.

$$\begin{array}{c}\text{Copper}\\\text{sulphate}\end{array} + \begin{array}{c}\text{barium}\\\text{chloride}\end{array} = \begin{array}{c}\text{barium}\\\text{sulphate}\end{array} + \begin{array}{c}\text{copper}\\\text{chloride}\end{array}$$

On settling, the clear liquid is poured off, and milk of lime —that is, calcium hydroxide—is added until all the copper has been precipitated as blue hydroxide, containing a little carbonate, from which the lime is never entirely free. When sufficient lime has been added, the solution is colourless. The precipitate is allowed to settle, washed and dried, after which it is ready for the market. There are other ways of preparing this pigment, but I need not burden you with them now.

Bremen blue is used very largely for colouring the pulp of cheap wall papers. This is unfortunate, for the lime in the walls readily attacks it, rendering the paper blotchy, and, of course, the paper-hanger gets the blame, and may have the work to do over again with better-class material at his own expense.

Blue Verditer is another pigment composed chiefly of the basic carbonate of copper. It is prepared by adding a solution of sodium carbonate to one of copper sulphate. The reaction which takes place may be represented by the following equation—

$$\begin{array}{c}\text{Copper}\\ \text{sulphate}\end{array} + \begin{array}{c}\text{sodium}\\ \text{carbonate}\end{array} = \begin{array}{c}\text{sodium}\\ \text{sulphate}\end{array} + \begin{array}{c}\text{copper}\\ \text{carbonate}\\ \text{(basic)}\end{array}$$

The precipitate is treated with dilute caustic soda, which renders it still more basic, and imparts a bluer colour to it.

As will be seen from these analyses, given by Hurst,[1] the composition of blue verditer is somewhat variable:

1.	Copper carbonate	77·8	per cent.
	Copper sulphate	9·4	,,
	Copper oxide	12·4	,,
	Water	0·8	,,
		100·4	
2.	Copper carbonate	62·5	per cent.
	Copper hydroxide	31·2	,,
	Calcium sulphate	3·3	,,
	Water	3·0	,,
		100·0	

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[1] Hurst, "Painters' Colours," etc., p. 235.

Blue verditer is used by artists to a small extent, particularly in water colours, but it is not very permanent as a pigment. The so-called "refiners' blue verditer" receives its name from the fact that it is prepared from copper solutions obtained in refining silver and gold. In chemical composition it is, of course, the same as any other blue verditer.

Brunswick Green.—The old Brunswick green was a basic chloride of copper, now rarely manufactured. It was prepared by soaking copper turnings in a solution of ammonium chloride, kept in a warm place. The containing vessel was closed to prevent evaporation and access of too much air. After the lapse of about two months, during which time the contents were shaken up at intervals, the vessel was opened and the pigment removed.

Copper oxy-chloride mixes well both with oil and water, but is subject to the usual defects of copper pigments. It is now but rarely used, its place having been taken by the chrome greens, which consist of barytes, chrome yellow, and Prussian blue.[1]

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[1] See Chap. IX. These pigments are sometimes called "New Brunswick Greens," but the term "Brunswick Green" is misleading, for both emerald green and Bremen blue are known under that name as well. See "A Treatise on Colour Manufacture," by Zerr and Rübenkamp, published by Chas. Griffin & Co., 1908, p. 219. (Translated by Mayer.)

XI

ORGANIC COLOURING PRINCIPLES

HITHERTO we have confined our attention to a consideration of inorganic pigments, as these are the simplest and most readily understood, from a chemical point of view. It is true that such bodies as Vandyke brown and Cappagh brown contain a high percentage of organic matter, but it was convenient to treat them at an earlier stage, as they fell naturally into the places assigned to them. Now, however, we may pass on to a study of the chief organic principles, both of animal and of vegetable origin, which contain a negligible amount of ash, and owe their colour entirely to complex organic substances. The number of such principles is legion, and we must therefore content ourselves with a glance at the most important. We will deal with them in alphabetical order.

Annatto or **Anatta**, also known commercially as **Arnotto, Roucou**, and **Orleana**, is the reddish pulp surrounding the seeds of a South American tree called *Bixa orellana.* The fruit is bruised, macerated with water, and the colouring matter, which separates out on standing, is strained and dried. Sometimes a little oil is added in making it up into lumps. Annatto yields a bright orange colour, which is not very permanent. It is used in making some varnishes, but its most extensive application is in the colouring of butter and cheese. The commercial article usually contains, in this country at any rate, flour, chalk, and other ingredients, and is sold in lumps of the consistency of cheese. It is scarcely soluble in water, but readily soluble in alcohol, ether, oils, and fats, to which it imparts an orange colour. Strong sulphuric acid turns it blue.

When pure, annatto is of a red hue, but commercial samples are frequently coloured with Venetian red, red lead, and the like; whilst common salt and sulphate of copper are added to prevent decomposition. Pure annatto contains 28 per cent. of resinous colouring matter, and from 1·5 to 2 per cent. of ash. The following analysis of a commercial sample by A. W. Blyth[1] will give a good idea of the average composition of the annatto sold in this country:—

Water	24·2	per cent.
Resinous colouring matter	28·8	,,
Ash	22·5	,,
Starch, etc.	24·5	,,
	100·0	

Another, so-called "patent" sample analyzed by Blyth, yielded the following results:—

Water	13·4	per cent.
Resin	11·0	,,
Ash, (iron, chalk, salt, alumina, silica)	48·3	,,
Organic extractive matter	27·3	,,
	100·0	

In the latter case, you will observe, the weight of ash is double that obtained from the former, whereas the weight of the resin is only about one-third as much, showing very clearly to what a large extent adulteration had been effected.

Brazil Wood.—This, together with a number of other woods, e.g., *peach wood*, *sapan wood*, *Lima wood*, is obtained from a variety of trees known under the generic name of *Cæsalpinia.* They are frequently termed the "soluble red woods" because of the solubility in water of their colouring principles. The trees are found in Central America, the East Indies, and Peru. Like logwood (see below), when first cut from the trees the wood is colourless. It is therefore chipped and fermented in a similar manner to logwood, whereby the

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[1] See "Oils and Varnishes," by J. Cameron. Published by Churchill, 1886.

colouring principle, *brazilëin*, is developed. With mordants[1] a variety of colours may be obtained, but they are fugitive and have been largely superseded by the artificial alizarin dyes.

Camwood, *Barwood*, and *Sanders wood* are of interest in this connection as forming a group of "insoluble red woods," owing to the fact that their colouring principles are almost insoluble in water, even at boiling-point. They are obtained from several species of trees growing in the interior of West Africa, and are chiefly used in wool dyeing.

Cochineal.—Commercial cochineal consists of the bodies of females of the cochineal insect, *Coccus cacti*, which is found on certain species of the cactus plant, and is indigenous to Mexico and Central America. At the present time the cultivation of the cochineal insect has been extended to the Canary Islands, Algeria, Java, and Spain, so that quite a variety of different kinds find their way into the market.

The insects are collected shortly before the laying season, and are killed by steam, hot water, or by dry heat, their bodies being sold as colouring matter, 1 lb. containing some 65,000 insects. Cochineal finds its way into the market in three grades, known respectively as "silver grain," "black grain," and "granilla." Of these the first named is the best, the granilla being very inferior in quality.

Cochineal contains about 10 per cent. of a red colouring matter known as carminic acid, and is used for colouring sugar in confectionery, as a water colour for artists, and as a stain for microscopical work. With different mordants cochineal yields very beautiful colours which are fairly permanent under ordinary conditions, though somewhat susceptible to the action of alkalies. The scarlet colour is not infrequently modified by admixture with the yellow dye-stuff "flavine," obtained from quercitron bark (see below) by the action of dilute sulphuric acid.

Since the introduction of the coal tar colours, however, cochineal has ceased to hold such an important position in the

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[1] A mordant is an inorganic substance often required to fix or develop the colour of the dye. Its use is explained later. (See Chapter XII.)

world of dyeing, the so-called red azo colours being used to a large extent in its stead.

Indian Yellow.—**Purree** or **Indian Yellow** is a remarkable pigment obtained by evaporating the urine of cows, fed upon the leaves of the mango tree in Bengal, in earthenware vessels. The yellow mass is strained through calico, and sent into the market in the form of balls. These are a bright yellow inside, but a greenish brown on the outside. A single cow will pass about six pints of urine per day, from which approximately two ounces of purree are obtained. The annual production amounts to something like six tons.

As a pigment, purree is useful on account of its good colour, being used with both water and oil as media. But it is not perfectly permanent, the combined action of light and air causing it to fade. Owing probably to its alkaline nature, it spoils carmine and cochineal lakes when mixed with them. It may be used with advantage in fresco work.

Purree is frequently adulterated with lead chromate, but the presence of this body is readily detected by the addition of ammonium sulphide, which darkens it owing to the formation of black lead sulphide. Pure Indian yellow is unaffected by ammonium sulphide. It dissolves in hydrochloric acid, yielding a colourless solution. If a yellow liquid is produced, the presence of an aniline lake as adulterant is to be inferred.

Indigo.—Indigo is a most important dye-stuff obtained from various plants, known under the generic name of *Indigofera*, and cultivated in the East.

The leaves of the plant are macerated with water, whereby fermentation sets in, and a compound of indigo and hydrogen, known as hydrindigotin, which is colourless, dissolves in the water. At the same time the liquid becomes alkaline from the products of fermentation. It is now drained off and oxidized by exposure to air under agitation, whereby the hydrogen combines with oxygen to form water, and indigo is precipitated. After settling, the dye is boiled with water both to prevent fermentation and to remove any soluble impurities. It is then filtered, the residue being pressed into cakes and cut into cubes.

As obtained in this way, indigo is a variable product, and the amount of its colouring principle, indigotin, varies from 20 to 90 per cent., though a fair average is from 40 to 50 per cent. This makes the natural product a somewhat uncertain quantity, and it is being superseded by the synthetic indigo, prepared in Germany from certain coal tar products.

Indigo is a useful blue for distemper work, owing to its permanence and inertness, though it can scarcely be said to have met with extensive application in this direction. It works with oil, but is seldom used, being fugitive. For deep, neutral tones of blue, it is unsurpassed, and it is therefore used a good deal by the decorator, as it is permanent in water. The best qualities are obtained from Bengal and Guatemala. Poorer qualities come from Jamaica, Brazil, Mexico, Cuba, and Madras. When pure it burns easily, and is very brittle. It dissolves in concentrated sulphuric acid, but is reprecipitated on dilution with water.

Indigo is subject to considerable adulteration. If, when powdered and ground with water, a sticky paste is obtained, the presence of some kind of gum may be inferred. The amount of moisture expelled at 212° F. should not exceed 3·7 per cent., and the ash remaining after heating strongly will not be greater than 10 per cent., unless the sample has been adulterated with incombustible materials, such as sand, whiting, barytes, etc.

Before the manufacture of artificial or synthetic indigo, India was producing annually about 3500 tons of the natural product, the total output for the whole world being only some 4500 tons. Germany, however, is now exporting large quantities of the synthetic product, the value of which, in 1907, reached the enormous sum of £1,650,000. In connection with this, it is interesting to note that in the sixteenth and seventeenth centuries the importation of natural indigo into both Germany and England was prohibited by law, the dyers in Nüremberg being forbidden to use it under penalty of death!

Synthetic indigo is now used in the manufacture of lakes, which are very permanent.

Lac Dye.[1]—A similar dye-stuff to cochineal, known as **Lac Dye**, is produced by a relative of the cochineal insect, *Tachardia lacca*, the larva or caterpillar of which pierces the bark of various trees in India, and converts the sap into a hard resinous mass called "lac." When colonies of these larvæ have matured into perfect insects, the males impregnate the females, which latter become filled with a red colouring matter. When the lac, containing the bodies of these females encased in it, is collected, it is crushed and washed with a dilute solution of sodium carbonate, which extracts the pigment. Precipitation of the same is effected by the addition of alum or an aluminium salt, and the lake thus obtained is pressed into cakes. The resin finds its way into commerce as shellac, and we shall have more to say about it later.

As a dye-stuff, lac dye is similar in colour to cochineal, though less brilliant, and the colouring matters were believed to be identical in chemical composition until two chemists, Schützenberger and Robert E. Schmidt by name, independently assigned the colouring power of lac dye to a complex organic body, called laccainic acid, about two per cent. of which can be obtained in a state of purity from the dye.

It is said that the red cloth used in the English Army was for many years dyed with lac dye. The colour is more permanent than cochineal, but like most other natural dyes is being rapidly superseded by the coal tar colours.

Litmus is an interesting substance on account of its sensitiveness to the action of acids and alkalies, the former turning it red and the latter blue. It is therefore used by chemists as an indicator.

Litmus is the colouring principle of certain algæ found in the East Indies, America, and on the Canary Islands. The plants are dried and mixed with ammonium carbonate, potash, and lime, whereby fermentation is induced. After about three weeks, ammonia, chalk, and gypsum are added, and the pasty mass is pressed into cubes and dried.

Logwood.—This is the wood obtained from the centre or

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[1] See "Technical Notes on Lac," read by A. F. Suter before the Paint and Varnish Society on March 11, 1909.

heart of certain trees, known to the botanist as *hæmatoxylon campechianum*, which grow in Central America, and are cultivated in several of the West Indian Islands. When first cut, the wood is practically colourless, but on exposure to air it gradually oxidizes, assuming the familiar red hue of logwood. This is due to the formation of a complex organic body, consisting of carbon, hydrogen, and oxygen, and known as *hæmatein*, from the ancient Greek word signifying "blood."

In the commercial preparation of logwood, the timber is chipped and exposed in heaps to the action of the air until fermentation sets in, known technically as the "ageing" of the wood. During this process a small quantity of ammonia is set free, which assists the oxidation. The product is either used in the form of chips in the dye bath, or the red colour is first extracted by treatment with hot water, and subsequent concentration of the solution thus obtained. Logwood is valuable, not only on account of its own red colour, but because it yields numerous other colours with different mordants. Thus chromium salts yield a bluish black colour; tin, a reddish violet; and so on. The colours are fairly permanent.

Madder consists of the dried and ground roots of an Indian plant known as *Rubia tinctorum*. Formerly it met with extensive cultivation in France and Holland, and was a most important dye-stuff, being used for the production of Turkey red, in calico printing, and in wool dyeing. Very beautiful colours are obtained by combining madder with different mordants, all of which are permanent. Madder owes its colouring properties to the presence of two organic bodies, known as alizarin and purpurin. Both of these are now made from coal tar products, and the artificially prepared dyes are rapidly superseding the natural ones.

Mummy Paint.—There is on the market a brown paint used by artists, known as "mummy paint," and I mention it now rather as a scientific curiosity than as a substance of practical value. Genuine mummy paint should consist of dried, ground-up mummies, mixed with some liquid vehicle such as linseed oil.

Very recently two mummies, dating from 2500 B.C., have been analysed by P. Haas,[1] but the marked differences both in the outward appearance of the mummies, and in the results of the analyses, show that they must have been embalmed in different ways. One mummy, labelled A, yielded a dry, light brown powder, whereas the remains of mummy B were moist, and of a dark brown hue. After ignition, rather more than ten per cent. of ash remained, which contained compounds of lime, potash, soda, iron, and alumina.

Old Fustic, also known as **Brazilian Yellow Wood,** is obtained from the tree *Morus tinctoria*, known popularly as the dyers' mulberry tree. This tree grows to a height of about 150 feet in Brazil and the East Indies. In general it yields yellow colours with various mordants, which, being cheap and permanent, meet with considerable application. Old fustic is frequently used in conjunction with logwood to improve the hues obtained from the latter. Its principal colouring matter is known as *morin*.

Persian Berries are the dried, unripe fruit of various species of plants known under the generic name of *Rhamnus*, Their dyeing properties closely resemble those of quercitron bark. With tin mordants a very brilliant orange colour is given.

Sap Green is extracted from unripe buckthorn berries by boiling in water, straining, and adding a small quantity of alum.

Sap green is a dark, yellowish green pigment, used for colouring confectionery, etc. It is also employed as a glazing colour, since it is very transparent. It is not very permanent, however.

Sepia.—Certain small aquatic animals or cuttle-fish, known under the generic name of *sepia*, form the source of our pigment bearing the same name. These animals have a small gland or bag in which a blackish-brown liquor collects, of remarkably intense colouring power. When in danger, the animal secretes a portion of the liquid, which dyes the water for some distance round, and under cover of this darkness the sepia makes its escape. For use as a pigment the bag is removed and its contents dried. The commercial article usually contains fragments of the dried bag attached to it.

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[1] See P. Haas, *Chemical News*, December 17, 1909.

As this would be inconvenient when used for artistic work, the whole is boiled with soda, which dissolves the pigment, but leaves the skin or bag. On filtering and neutralizing the soda with acid, the pigment is re-precipitated, washed and dried.

Sepia mixes well both with oil and water, and possesses a wonderful colouring power. Its transparency enables the artist to use it, as a water colour, in such a manner as to exhibit a great variety of tints and shades. It is, therefore, of special service in monochrome paintings. Fortunately, sepia is a very permanent pigment, and is only slightly affected by exposure to light. It is very inert also, and may therefore be safely mixed with other colours. An alcoholic solution is employed by artists under the name of "liquid sepia."

It is said that the best sepia comes from Rome, though certain Chinese harbours are the principal sources of sepia. "Natural sepia" is the pure pigment, but "a coloured sepia" is on the market, and contains a little madder which imparts a somewhat ruddy hue to the sepia. Umber is sometimes added as an adulterant, but can readily be detected as it greatly increases the ash.

The chemical composition of sepia is very complex, and not fully understood. The following analysis, given by Prout,[1] is interesting :—

Black pigment	78·00	per cent.
Calcium carbonate	10·40	,,
Magnesium carbonate	7·00	,,
Alkaline substances, etc.	3·00	,,
	98·40	

Quercitron Bark.—This is the inner layer of bark of an oak tree, *Quercus tinctoria*, which grows in North America. It dyes similarly to old fustic, but gives brighter yellows with aluminium and tin mordants. When treated with dilute sulphuric acid, the commercial product "flavine" is obtained.

Turmeric is the colouring principle of the underground stem or "rhizome" of the plant *Curcuma tinctoria*. The plant

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[1] Quoted by Hurst, "Painters' Colours," etc., p. 245.

is a native of Southern Asia, and is cultivated on a large scale both on the mainland and on the islands of the Indian Ocean. It has been used since very early times as a condiment, a dye, and a medicine. In Europe it is employed chiefly as a dye, but also as an ingredient of curry powder. It dissolves in alcohol, and slips of paper soaked with the solution so obtained and subsequently dried are used as test-papers in chemistry, being turned a red-brown colour by ammonia and alkalies generally. There are several varieties of turmeric, showing slight differences in colour and in flavour. It is most successfully grown on light, rich, well-watered soils, an acre yielding about 2000 lbs. of the ground rhizome.

Turmeric dyes without a mordant, and is used for modifying red colours.

Weld or **Woad** consists of the dried stem and leaves of one of the wild mignonettes, known botanically as *Reseda luteola*, a native of South Europe, and frequently cultivated for the use of dyers. French weld is generally regarded as the best. The dyeing properties resemble those of quercitron bark, but the yellow colours with aluminium and tin mordants are brighter, purer, and more permanent. The colouring principle is known as luteolin, and can be prepared synthetically.

Young Fustic, also known as **French Fustet**, is a greenish-yellow wood, exhibiting brown-coloured stripes, obtained from the sumach tree, *Rhus cotinus*, which grows in Italy and Southern Europe. It is called "young" on account of the smallness of its branches as compared with the dyer's mulberry tree, which yields the so-called "old" fustic. The colours obtained with different mordants are similar to those yielded by old fustic, but they are not permanent.

In the following table[1] are given the reactions of the chief natural organic colouring principles with a few standard reagents:—

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[1] This table is abridged from that given by Zerr and Rübenkamp, *op. cit.*, p. 539.

REACTIONS OF NATURAL ORGANIC COLOURING PRINCIPLES.

Colouring principle.	Water.	Hydrochloric or sulphuric acids.	Alkalies.	Alcohol.
Annatto	—	Pale yellow S.	Orange S.	Light yellow S.
Brazil wood	Yellow-orange S.	Yellow-red	Carmine	Pale yellow S.
Cochineal	Yellow-red S.	Red	Purple-red to violet	—
Indian yellow	—	Gas evolved ; turns paler	Darkens	—
Indigo	—	—	—	Boiled gives Blue S.
Lac dye	—	Yellow S.	Red-violet S.	—
Litmus	Purple S.	Red S.	Blue S.	—
Logwood	Brown-red S.	Red S. and P.	Red-violet	—
Madder	Slightly soluble, red	Turns yellower	Blue-red	—
Old fustic	Yellow S.	Yellow P.	Red-yellow	—
Persian berries	Brown-yellow S.	Brown-yellow P.	Orange	—
Quercitron	Yellow S.	Brown-yellow P.	Turns paler	—
Turmeric	Nearly insol.	Red-brown	Red-brown	Orange S.
Weld	Green-yellow S.	Turns darker	Golden	—
Young fustic	Red-yellow S.	Turns paler	Less red	—

S. = Solution. P. = Precipitate.

XII

THE LAKES

The thorough study of the chemistry of the lakes is the work of an expert, and in this lecture I cannot hope to do more than give you a brief account of the way in which the lakes are prepared in just sufficient detail to enable you to understand the chemical principles involved.

Lakes are compounds of complex organic colouring matter, with a simpler inorganic substance. The origin of the word "lake" is interesting. Several centuries ago, Italian dyers were wont to use a "lac" in the process of dyeing fabrics, and the presence of metallic compounds, such as alumina, was found to be essential to the development and fixation of the colour. During the process, a scum was observed to collect on the top of the dye vats, and was known as "lacca." This was dried and sold to artists. Different natural colouring matters produced different laccæ, and hence arose the name "lake" as applied to any colour obtained in the same way. Eventually the composition of these lakes was determined, and now they can be prepared in any quantity and of almost any hue, without troubling the dyer. It is convenient for purposes of classification to divide the lakes into two groups, according to the source of the colouring matter. Originally the manufacturer was dependent upon the natural dyes, but these are being gradually displaced by those obtained from coal tar. We will deal with the former first.

I. Lakes from Natural Colours

Most natural colouring matters are acidic in character, and can therefore combine with basic bodies, such as the oxides and hydroxides of metals. The products thus obtained are coloured, and insoluble in water; they therefore possess two of the qualities necessary to render them serviceable as pigments. Theoretically, the amount of basic substance should be exactly sufficient to neutralize all the acid colour—neither more nor less—to form a true lake. Practically, however, this rule is not adhered to, an excess of base being usually employed in such quantities as to produce the desired shade. The greater the proportion of the base, the lighter will be the tint, for obvious reasons. As the colour and metallic base have such a strong affinity for one another, it is generally sufficient to mix solutions of the two, when the lake separates out. Sometimes, however, the addition of small quantities of sodium carbonate is necessary to effect the precipitation.

It is interesting to note the behaviour of the colouring principles in contact with different metallic salts. Some yield lakes of a similar colour, though varying a little in tint and shade, with bases of widely different metals. Such dyes are called "monogenetic." Fustic is a case in point, for it yields a yellow precipitate with salts of aluminium, lead, iron and copper. Many dyes, on the other hand, produce lakes of various colours according to the base with which they are combined. These are known as "polygenetic" dyes, and logwood may be quoted as a fair example. With aluminium sulphate logwood gives a crimson colour, with iron salts a blue-black is obtained, and so on.

One of the great beauties of the lakes is their transparent nature, which enables the artist to use them as a cover or glaze, to modify the colour of an undercoat of paint. It will be clear that in this way numerous effects can be obtained, which would be impossible with the more opaque pigments. You will remember that Vandyke brown is used in a similar manner, and it was the transparent beauty of this pigment which enabled the great painter, Vandyke, to obtain his wonderful effects.

Lakes may be rendered opaque by mixing with white pigments, such as gypsum or barytes. This, of course, is apt to affect the tint. It is essential that the lake should be insoluble in the vehicle, otherwise a coloured varnish is produced, devoid of body.

A short description of the chief natural dyes used in the preparation of the lakes has already been given. The following table will probably be of interest, as showing the colours of the lakes produced on combination of some of the dyes with different bases or mordants.

Dye.	**Mordant:** Compounds of			
	Aluminium.	Chromium.	Iron.	Tin.
Brazil wood—				
a. Soluble red	Red	Claret brown	Dark slate or purple	Bright red
b. Insoluble red	Brown-red	do.	Purple-brown	Red
Cochineal	Crimson	Purple	Grey	Scarlet
Logwood	Dark blue to black	Dark blue to black	Black	Dark purple
Madder	Red	Red-brown	Purple to black	Orange
Old Fustic	Yellow	Olive yellow	Olive green	Bright yellow
Quercitron bark	Yellow	—	—	Orange yellow
Weld	Yellow	—	—	Yellow

The great difficulty experienced by manufacturers in the preparation of these lakes is that of preparing successive batches of the same depth of colour. This arises from the fact that natural colours vary enormously from time to time, so that the same recipe will seldom give the same results twice running, particularly if some time has elapsed between the batches. This difficulty can only be overcome by direct experiment with the materials to be used. If more colouring matter is used than is required to unite with the base, the colour of the lake is not intensified, but the excess is washed away during subsequent processes, and is lost. If, however, the base is in excess, the tint of the lake is lighter in proportion. When once the correct quantities of the constituents have been ascertained, the rest is easy. Solutions of the dye and precipitant are placed in separate vats and mixed. After settling, the lake is well washed and dried at a low temperature. Generally they appear in the market as drops or *troches*, being made in this form by moulding in glue water, and drying in the usual way.

Of all the lakes prepared in this way, that known as **Carmine** is probably the most important. It is an almost pure lake and consists of cochineal, combined with alumina and lime, though its exact method of preparation is a trade secret. It is a deep scarlet powder, soluble in strong mineral acids, but insoluble in all paint vehicles. It dissolves in caustic soda, yielding a crimson liquid, from which the carmine can readily be recovered by addition of weak acids, such as acetic and tartaric.

When heated in a crucible, carmine burns, and leaves from 7 to 10 per cent. of a white ash, of variable composition. Lafar[1] has analyzed the ash and gives the following results :—

Copper oxide	0·35	per cent.
Tin oxide	0·14	,,
Alumina	40·48	,,
Iron oxide	trace	,,
Calcium oxide	44·20	,,
Magnesium oxide	0·61	,,
Sodium oxide	5·40	,,
Potassium oxide	3·20	,,
Silica	0·60	,,
Phosphorus pent-oxide	2·71	,,
Carbon di-oxide	2·31	,,
	100·00	

As will be seen, the ash is a very complex mixture, but undoubtedly the majority of the substances present are to be regarded as impurities, and in no way essential to the colour of the lake. The tin and copper have probably been derived from the vessels used in preparing the lake, and their action is not fully understood. Apart from the alumina and lime, the other constituents are of no importance.

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[1] Lafar, *Journal für praktische Chemie*, 1890, No. 3.

Carmine works well both in oil and in water. Unfortunately, it is not permanent, exposure to sunlight and air causing it to fade. It is frequently adulterated with other lakes and red pigments, but its solubility in ammonia serves as a ready check on its purity, as the adulterant will usually be left as an insoluble residue.

During the preparation of carmine the whole of the cochineal is not precipitated. The liquors poured off from the carmine are therefore strongly coloured, and are used for the preparation of the so-called **Carmine Lake.** These names are a little confusing, for carmine itself is a true lake. In order to produce the carmine lake, alum and tin chloride are added to the liquors, and then precipitated with potassium carbonate. After washing and drying, the lake is ready for the market.

Crimson Lake is similar to carmine lake, but contains a higher percentage of alumina. This is true also of the **Scarlet Lakes,** but these are tinted with a small quantity of vermilion.

Madder Lakes are prized by artists because of their brilliancy and greater permanence. By combining both madder and cochineal, bright **Carmine Red Lakes** can be produced. The madder lakes are soluble in caustic soda, but not in dilute ammonia. This serves to distinguish them from carmine. In dry air they are fairly permanent, moist air causing them to fade slightly. When boiled with dilute sulphuric acid, alizarin —the colouring principle of the madder—is set free in the form of a yellowish brown precipitate.

II. Lakes from Coal-tar Colours

The manufacture of colouring materials from coal tar, which at the beginning of the coal-gas industry was a waste by-product of no value, marked a new era in the world of dyeing and colour manufacture. When coal is heated in retorts, in addition to coke and gas, a tarry material is obtained, from which, by repeated distillation, a number of different and very valuable products can be isolated.[1] These,

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[1] See Chapter XV., where the subject is discussed in greater detail.

in the hands of the chemist, can be converted into the numerous dyes with which we are acquainted at the present day, though the processes involved are frequently very complex and expensive. It should be borne in mind, therefore, that the various dyes do not exist in coal tar *as such*, but they are prepared synthetically by the chemist in his laboratory from the coal-tar products.

It is gratifying to learn that the first true aniline colour, namely mauve, was discovered, in 1856, by an English chemist, William Henry Perkin,[1] who was then a lad only eighteen years of age. As is so frequently the case, this discovery was made by accident in a rough, home-made laboratory during the Easter vacation. Being desirous of preparing quinine, Perkin endeavoured to oxidize a complex derivative of toluene with potassium bi-chromate. Instead of quinine, however, a dirty, reddish-brown precipitate was obtained. This led the young investigator to try a similar reaction with aniline, and to his surprise obtained a dark-coloured body, which proved, on further examination, to be possessed of dyeing properties. Perkin's elder brother, Thomas, assisted in the preparation of mauve during the summer of the same year, in order to supply specimens for testing by the dyers. In August a patent (No. 1984, August 26, 1856) was secured, and a year later the new dye-stuff was placed on the market.

This remarkable discovery was followed by others in quick succession, and the impetus which was thus given to the new industry is absolutely unparalleled by any other of a similar nature within the memory of man. Alizarin, the well-known colouring principle of the madder, was prepared synthetically in 1868, and natural indigo is being rapidly displaced by the artificial product, as we have already seen. In fact, thanks to chemistry,[2] the death-knell of the natural colouring

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[1] See the OBITUARY NOTICE, by R. Meldola, *Journ. Chem. Soc.*, 1908, vol. 93, p. 2214.

[2] There is a sad side to this story. Fifty years ago, some 70,000 tons of madder, worth about 2½ million pounds sterling, were produced annually from the madder plant, but the introduction of synthetic alizarin, in 1869, ruined the industry. The indigo industry of India is sharing the same fate.

principles has been sounded, and every year sees larger and yet larger quantities of coal-tar derivatives making their way into the market.

The dyes obtained from coal-tar products may, for our present purpose, be grouped as follows:—

1. *Basic Colours.*—These are characterized by their power of uniting with acids, and include such products as magenta, aniline blue, Bismarck brown, etc. Certain weak organic acids, such as tannic acid, picric acid, and the like, yield coloured precipitates with these dyes, and are therefore used in the preparation of lakes. The precipitates are definite chemical compounds when pure, but as variations in the relative amounts of the constituents produce corresponding changes in colour, tint, and shade, the dye-stuffs are but rarely sold in a state of purity.

The great drawback to these colours is the fact that the organic acids prevent the oils, used as vehicles, from drying properly. For example, free tannic acid, when present in sufficient quantity, will almost completely hinder the drying of linseed oil, and picric acid behaves similarly. It is not surprising, therefore, that lakes compounded with these acids should tend to retard, to a greater or less extent, the drying of the oil used as vehicle.

For water-colours, on the other hand, these lakes may be very satisfactorily employed, as the same objection does not then apply. Work painted in this way may then be varnished on top with excellent results.

2. *Acid Colours.*—These are frequently of an acid character, although not necessarily so. When used for dyeing wool or silk, however, the vats contain a little free acid—hence the name "acid colour." The majority of these dyes contain nitrogen united with them in a particular manner, and are therefore known as "azo-colours," from the word "azote" by which the gas "nitrogen" is known in France. They are precipitated from solution by metallic salts, the three in most general use being barium chloride, lead acetate, and aluminium sulphate. Of these, the first named appears to be, on the whole, the most satisfactory, and the lakes produced with it

have the advantage of not being affected by sulphuretted hydrogen or by contact with sulphide pigments, as are those obtained by precipitation with lead acetate. They may be used with oil or water as vehicle, and the colours are permanent.

3. *Mordant Dyes.*—These are usually colourless, and require the presence of a second substance, known as a "mordant," to develop their colour and to fix it on to the cloth to be dyed. As with the polygenetic natural dyes about which I was speaking some time ago, so here, the colour developed depends to a large extent upon the nature of the mordant. Thus, when alumina is used as a mordant, alizarin gives a bright red colour, but with iron a violet, and tin a scarlet. Lakes prepared from these dyes are very permanent. The principal colouring matters of this group are alizarin and purpurin.

It is not surprising to learn that, owing to the complicated methods of manufacture, the dyes do not always possess the same colouring power and intensity. In order to supply a uniform commercial product, therefore, manufacturers standardize their colours against a recognized type by addition of other substances. The amount of the additions is determined by direct experiment, and the result is, that every batch of a given brand will give a certain, unvarying result in practical dyeing when employed under standard conditions.

Very frequently a commercial brand is a mixture of different dyes, the particles of which are indistinguishable by the naked eye. Particularly is this the case when brands are produced to match the buyer's sample, etc. By blowing some of the fine dye on to a wet filter-paper, the different grains stain the latter with different hues, and are thus readily detected. A single dye would, of course, merely produce one colour.

From what has been said, it will be evident to you that the process of manufacturing the lakes is very simple, that is as far as the plant is concerned, provided suitable dyes and precipitating agents are to hand. These are dissolved in water in separate vats, whilst in a third vat an opaque white pigment, such as barytes or gypsum, made into a milk with water, is heated to 120–150° F. The colouring matter is now run into the third vat, and after thorough mixing, the precipitating agent is added. The lake is allowed to settle, and when washed and dried is ready for the market.

Lakes are usually bad driers, and are therefore used very frequently in water, and varnished on top. As glazes, too, they have received extensive application in graining; for example, Victoria lake is used for rosewood, mahogany lake for mahogany, and so on.

I shall not attempt to burden you with a list of the numerous dyes and lakes now manufactured, for their name is legion. The very fact, however, that less than a century ago coal-tar colours were undreamt of, suffices to show what enormous strides science has made during the last few years, and he would be rash indeed who ventured to set a limit to the discoveries which the future may yet unfold.

XIII

PAINT VEHICLES

LET us now pass on to consider the various vehicles used by the painter to act as carriers and fixers of his pigments.

Vehicles may either be single liquids, or mixtures of two or more substances, according to circumstances. Those in most general use are the drying oils, turpentine, various spirits, benzene, naphtha, and water. We will consider them in the above order.

1. Drying Oils

Hitherto the only time that I have used the word "oil" has been in connection with the so-called "oil of vitriol," or sulphuric acid, although, as I mentioned at the time, it is a true oil in no sense of the word. The name was given to the acid in consideration of its oily appearance when flowing from one vessel to another. What, then, constitutes a true oil? Oils are greasy liquids of animal or vegetable origin, characterized by their insolubility in water, and the ease with which they dissolve in organic solvents such as alcohol, ether, benzene, and the like. They are combustible, usually lighter than water, slow to evaporate, and leave a greasy stain on paper. Chemically many of them consist of glycerine united with a fatty acid, and when acted upon by superheated steam, they split up into these two constituents. Caustic soda or potash will effect the same decomposition, but in this case the soda unites with the fatty acid to form a sodium salt, which is a soap. The reaction is therefore known as "saponification," that is "soap producing." Simultaneously, **glycerine** is liberated. This is a colourless, viscid liquid, possessed of a sweet taste, and is therefore used in the preparation of many sweets and lozenges. When pure, the specific gravity of glycerine is 1·270, but it has a great affinity for water, with which it mixes in all proportions. The solutions thus obtained do not freeze at 32° F., neither do they evaporate so readily on exposure to the air. For these reasons it is usual to add a little glycerine to the water in ordinary household gas-meters.

The paraffin and allied oils are the only ones which do not contain glycerine and fatty acids, and are not saponifiable in this way. They are very stable and contain carbon and hydrogen only. Many chemists therefore exclude them from the list of true oils, but popularly no such distinction exists. We shall refer to these again later.

Solid oils are known as fats, but of course there is no hard-and-fast line of demarcation between the two. For example, on a cold day olive oil readily becomes solid like mutton fat, but it is still called an oil. The majority of solid fats consist of glycerine united with stearic and palmitic acids, and are therefore known to the chemist as glyceryl stearate (or stearin) and glyceryl palmitate (or palmitin), respectively. The change which takes place on warming with caustic soda may be represented in the following way :—

$$\begin{array}{c}\text{Glyceryl}\\ \text{stearate}\\ \text{(fat)}\end{array} + \begin{array}{c}\text{caustic}\\ \text{soda}\\ \end{array} = \begin{array}{c}\text{sodium}\\ \text{stearate}\\ \text{(soap)}\end{array} + \text{glycerine}$$

It will be clear from this equation that a definite amount of oil requires a definite weight of caustic soda to effect its saponification, and that this weight will vary for different fatty oils. Thus, linseed oil requires from 13·4 to 14 per cent. of caustic soda, or from 18·7 to 19·5 per cent. of causic potash, to decompose it completely. These amounts are therefore known as the "saponification numbers," and are valuable inasmuch as they give a clue to the composition and purity of the oil under examination.

Though possessed of definite melting-points, fats and fatty oils have no definite boiling-points, for when heated to a temperature much above the boiling-point of water decomposition sets in. At higher temperatures darkening occurs, and acrid vapours are expelled which are very irritating to the throat and eyes. On exposure to air and light, all such oils and fats undergo change, although the rate of change varies enormously for the different samples. This affords a convenient method of classifying the former into two groups, namely—

1. Those oils which are but slightly acted upon by prolonged exposure to light and air. Such are olive oil, palm oil, castor oil and the like.

2. Those oils which, on exposure to air, set hard and dry. These, and these alone, are of value to the painter as carriers and fixers of his pigments. They are called **drying oils**, and are but few compared with the large number of oils that are known to science.

Lewkowitsch[1] enumerates no fewer than fifty drying oils, but of these the following only concern us as painters:—

Linseed oil.
Hempseed oil.
Poppy-seed oil.
Tung oil.
Walnut oil.

Here, again, it is difficult to draw the line, for some oils possess comparatively feeble, but decided drying powers, and thus lie halfway between the two groups. They are therefore classed as **semi-drying oils**, and the following are cases in point:—

Cotton-seed oil.
Maize oil.
Soya bean oil.

Rosin oil, although it is a wretched drier, is often used for paints, on account of its low cost. It is a favourite adulterant of linseed oil, and we shall therefore have occasion to refer to it again later.

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[1] See "Chemical Technology and Analysis of Fats," etc., by Lewkowitsch, published by Macmillan & Co., 1909, vol. ii., where an admirable account of the drying oils is given, and from which much of the information detailed in this chapter has been derived.

Linseed Oil.—By far the most important oil used by the house painter is that expressed from the seed of the flax plant, and known by the name of **Linseed Oil,** the first syllable of the word "linseed" being derived from the Latin *linum*, which is the generic name ascribed by botanists to the flax plant.

The last-named is cultivated both for its fibre and for its seed, the former being woven into linen. The principal countries where it is grown in large quantity are Argentina, India, Morocco, and Russia. The seed is small, of an oval shape, and brown in colour. It varies slightly in appearance according to the locality in which it is grown, and experts can usually determine, by mere inspection, from what source any well-known kind has been derived. That grown in the north of Russia, and known as Baltic seed, yields the best and finest oil; the Black Sea seed comes next, and a poorer quality is obtained from East India seed.

The following table will give you an idea of the enormous amount of linseed grown by the four principal countries:—

PRODUCTION OF LINSEED (EXPRESSED AS METRIC TONS[1])

Year.	Argentina.	India.	U.S.A.	Russia.	Total.
1900	389,951	295,674	475,000	533,877	**1,694,502**
1902	763,976	342,624	732,122	542,234	**2,380,958**
1905	591,912	347,400	711,944	421,000	**2,072,256**
1907	1,200,000	419,900	646,275	450,000	**2,716,175**

Very much smaller quantities of linseed are grown in Canada, Germany, Holland, France, England, and Ireland. The quantity imported into this country from different sources varies somewhat from year to year, as is evident from the following figures:—

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[1] A metric ton is 1016 kilograms = 2239·8 lbs., and is thus almost identical with the English ton (2240 lbs.).

Year.	Imports into Great Britain[1] (expressed as metric tons).
1900	309,108
1903	308,331
1904	505,519
1905	345,412
1907	372,537

The amount of oil contained in the seed varies both with the season and with the locality and origin of the seed. The average amount is from 30 to 35 per cent. of the seed, though only about 26 per cent. can be obtained by pressing, the total amount being extractable by solvents such as petroleum ether.

The following table shows the actual quantities of oil contained in various kinds of seed:—

Seed.	Oil.
Russian	32 to 38 per cent.
Indian	37 to 43 ,,
River Plate	35 to 36 ,,
N. American	36 to 38 ,,
Levant	37 to 42 ,,
Hungarian	36 to 38 ,,
Morocco	36 to 40 ,,

The bulk of the linseed oil of commerce is obtained by expression from the seed, the residual cake constituting a valuable food for cattle. Occasionally the oil has been extracted with organic solvents such as carbon bi-sulphide and petroleum ether; but, although a greater yield is obtained, the oil is not found to be so suitable for paints and varnishes, and possesses, in addition, a poorer colour and a more unpleasant odour.

Although several different processes are in vogue for the extraction of the oil by pressure, I need only refer to that known as the Anglo-American, which is extensively adopted and may be taken as representative.

The various stages of the process are five in number.

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[1] These figures refer only to imports from the four principal linseed-growing countries mentioned in the previous table. Imports of linseed from other countries are relatively small.

1. *Crushing.*—This is effected by means of a mill. The seed is fed in between two rolls and crushed in much the same way as the washerwoman mangles the clothes, save that the rolls are made of chilled iron, and not of wood. Usually the crushing machine carries five rolls, under which the seed is made to pass successively, and thus receives a very thorough treatment. The object of the crushing is to break the shell and flatten out any lumps so that, on pressing, the oil may readily escape.

2. *Heating.*—You all know what a raw egg looks like when its shell has been broken. The yolk is seen to swim in a colourless, slimy liquid, known as albumen. Now what happens if the egg is "boiled"? The albumen becomes solid or coagulated, and is then called "white of egg."

The crushed linseed, with which we have been dealing, contains a considerable quantity of albuminous material, and if the oil were now expressed, the albumen would escape with it, and render it unfit for many purposes. The seed is therefore heated in a "kettle" by means of steam which effects the coagulation of the albumen, and at the same time moistens the mass and improves its condition for yielding oil under pressure.

3. *Moulding.*—In order that the seed shall be in a suitable condition to submit to pressure, it is led from the kettle to a moulding machine, and pressed gently into a flat cake, of some 1½ inch in thickness.

4. *Pressing.*—The linseed cakes are now placed in a vertical pile, each cake between two plates of iron, and subjected to a pressure of approximately one ton on every square inch, for nearly half an hour. The oil trickles away from the edges of the cakes and is collected. The pressure is now doubled for about five minutes, and when any further exudation of oil has ceased, the cakes are removed and sold for feeding cattle.

5. *Refining.*—It will be evident to you, I think, that any process of refining a cheap oil, such as linseed oil, must be very simple and inexpensive. As it flows from the press, linseed oil contains a number of impurities mechanically

suspended in it, which it is desirable to remove. The oil is therefore stored in tanks and heated by steam coils to a temperature of 160–170° F. This serves to render the oil more fluid and to coagulate any small quantities of albumen which have been expressed from the cake. After standing for a considerable time the impurities settle, and a fairly pure oil remains. Sometimes this is sold without further treatment. Usually, however, a small quantity of dilute sulphuric acid is added, and the mixture is well stirred and then allowed to stand for twenty-four hours, when the acid settles to the bottom, leaving an upper layer of oil. The acid is drained away, and, after thorough washing with water, the oil is ready for the market, under the name of "Raw Linseed Oil." The function of the acid is to char and dissolve any albuminous matter still remaining. It also removes any other bodies which readily decompose, and thus the oil is rendered less liable to become rancid.

Properties of Linseed Oil.—The yellow colour and characteristic odour of linseed oil are familiar to every one of you. The oil is lighter than water, with which it does not mix; at ordinary temperatures it takes nearly 10 pints of the oil to weigh as much as 9 pints of water, its specific gravity ranging from 0·932 to 0·937. The Baltic oil is generally the heaviest of the three varieties, bulk for bulk. It dissolves in about forty times its volume of alcohol at ordinary temperatures, but is readily soluble in ether, petroleum, naphtha, and turpentine. When mixed with concentrated sulphuric acid, the temperature rises considerably, and the mixture becomes thick and dark. Sulphur di-oxide is evolved at the same time, owing to the fact that the oil abstracts part of the oxygen from the acid, which latter, you will remember, is formed from sulphur tri-oxide, which contains half as much oxygen again as the di-oxide. Linseed oil combines very readily with both bromine and iodine—more so, in fact, than any other oil, and the amounts absorbed are a measure of the quality of the oil, the better the quality the larger being the amount. On the average 100 parts of good oil can absorb 170 parts of iodine or 98 parts of bromine. The weights are known respectively as the iodine and bromine "equivalents" of linseed oil. This property is intimately connected with another, which makes the oil so valuable to the painter—I refer to its drying powers. Olive oil and colza oil may be left in contact with the air for a very long time without exhibiting any tendency to dry up. Pigments mixed with these oils, therefore, would be worse than useless as paints. Linseed oil, on the other hand, readily sets, yielding a body of resinous character. This is due to the fact that it absorbs oxygen from the air, though the chemistry of the process is still obscure. It will be clear that, from the painter's point of view, the quality of the oil is directly proportional to the amount of oxygen it can absorb, for the greater that amount may be, the more quickly will the oil dry.

The following numbers, given by W. Fox,[1] show the relative amounts of oxygen absorbed by equal weights of different oils:—

Baltic linseed oil	191
Black Sea ditto	186
American ditto	156
Bombay ditto	130
Calcutta ditto	126
Cotton-seed oil	24·6
Colza oil	17·6
Olive oil	8·2

From this table it will be evident to you why the Baltic linseed oil is the best for painters, and it will further be clear why such oils as olive, colza, and cotton seed are useless for the purpose. The explanation is not far to seek. Linseed oil is a compound of glycerine and certain unsaturated fatty acids, to which the name "linoleic acid" is generally given, although it is certain that, in reality, several acids are present. By "unsaturated" we mean that, although combined with as much glycerine as they can take up, all their powers of chemical combination are not used up or saturated. They can still unite with such substances as oxygen, bromine, iodine, etc. Non-drying oils, such as olive oil, consist of glycerine

[1] See *The Oil and Colourman's Journal*, 1884, p. 234.

and fatty acids which do not readily combine with oxygen, etc., and the semi-drying oils may be regarded as a mixture of the two. Their powers of drying will therefore depend upon the nature of their acid content, a measure of which is given by their bromine and iodine equivalents, as also by their oxygen absorption.

On warming the oil with a solution of caustic soda, glycerine is set free, and the soda unites with the fatty acids forming a soap. If dilute sulphuric acid is now added to the soap, sodium sulphate is formed, and the free fatty acids are liberated. These are insoluble in water, but dissolve with ease in alcohol and ether. At ordinary temperatures they are solid, but melt on warming from about 73° to 77° F. It is interesting to note that these acids are not as good driers as the oil from which they are obtained. It would appear, therefore, that the glycerine assists in the drying of the oil itself. Linseed oil, like wine, is greatly improved by storage. In fact, the effect of age on linseed oil can scarcely be over-rated. I cannot refrain from quoting a paragraph which caught my eye in *The Decorator* for August 23, 1909. It runs as follows:—

"The other day we were shown a bottle containing oil which, had we not been assured it was linseed oil, we should certainly never have guessed as being that material. It was absolutely star-bright, and there was not the slightest trace of cloudiness or solid matter suspended in it. It had a pleasant, mild odour. Its colour might be compared with that of the palest honey, and was as unlike the colour of ordinary raw linseed oil as can well be imagined. It was found, on pouring a little of this oil on a glass slide, that it dried very much more quickly than ordinary raw linseed oil, and that the film produced was much tougher than the film produced from the latter. This remarkable sample was nothing else than a portion of a quantity of linseed oil which had been kept for about five years. . . . The difference and improvement in the character of the oil was due simply and solely to storing and ageing. Those who have studied the question most deeply are strongly of the opinion that a large proportion of the troubles that arise to-day in connection with paints and painting are traceable to bad or imperfectly matured oil, and with this we cordially agree."

These remarks need no comment.

In the following table are given the physical constants of various samples of linseed oil, as determined by Lewkowitsch :—

PHYSICAL CONSTANTS OF LINSEED OIL.

Oil.	Specific gravity.	Iodine equivalent (per cent.).	Saponification No. with potash (per cent.).	Unsaponifiable residue (per cent.).
Raw linseed oil				
a. From finest Calcutta seed, 2 months old	0·9316	170·46	19·32	0·65
b. From finest Calcutta seed, 3 years old, protected from air and light . .	0·9324	174·0	19·25	0·70
c. From finest St. Petersburg seed, 3 months old	0·9334	177·3	19·22	1·10
d. From finest St. Petersburg seed, 7 months old	0·9345	176·2	19·31	0·98
e. From finest Baltic seed, kept 13 years from air and light	0·9410	175·8	19·52	1·10

Boiled Linseed Oil.—The power exhibited by the raw oil to absorb oxygen from the atmosphere is enhanced by heating the oil to a temperature of from 400° to 500° F., and maintaining it in this condition for a few hours. This is done by heating the oil in large boilers over a fire, the boilers holding anything from 100 to 600 gallons. They should be about one-third larger than the quantity of oil with which they are charged, in order to allow for expansion and frothing of the liquid. Great care must be exercised during the initial stages of the heating, in order to prevent the oil from boiling over. The danger is greater with freshly pressed oil than with that which has been kept for some time, owing probably to the presence of small quantities of water and albuminous matter suspended in the former, whereas in the latter they have had time to settle to the bottom of the storing tank, and do not therefore find their way into the boilers. After some time, which should not be less than two hours, the oil begins to boil quietly, and small quantities of driers are added in the proportion of about 5 lbs. to 1 ton of oil. It is advisable to add the drier in small portions at a time, as this not only minimises the risk of frothing over, but effects a better union with the oil. During the boil, water and several volatile organic substances which are very obnoxious are given off from the oil. The liquid assumes a dark-red colour, the higher the temperature the more intense being the colour. The quantity and composition of the driers have also a marked influence on the colour, and manganese di-oxide produces a darker oil than any other drier. I shall have something more to say a little later, however, with regard to the chemical action of driers, and we may conveniently leave any further consideration of their properties till then.

Although the method of boiling oil direct over a fire yields excellent results in careful hands, it is rather dangerous, and is gradually being superseded by steam processes. The oil is run into a tank fitted with a closed steam coil, and heated for about two hours at a temperature of from 203° to 206° F. This preliminary treatment is found to reduce the frothing which always occurs in the next stage of the process. This consists in running the warm oil into a boiler capable of holding one or two tons, and fitted with a lid and stirring gear. The outside of the boiler is heated by a steam jacket, and any fumes escaping from the oil leave the boiler through the flue (see Fig. 14). A current of air is next blown through the liquid, and causes a good deal of frothing. After the driers

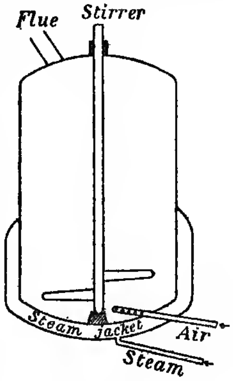

FIG. 14.

have been added, the oil is heated a few hours longer, after which it is run into settling tanks. The clear oil at the top is sent into the market as "boiled oil," and the remainder employed in the manufacture of putty and cheap paints under the name of "boiled oil foots."

Other plants are employed for the steam boiling of oil, but in principle they are the same as the one just described, and I need not burden you with an account of them now.

Genthe has patented a process for boiling oils under the influence of the light from his so-called "Uviol" lamp, about twenty of which are immersed in a tank containing one ton of raw oil. The whole is warmed to 176° F., and the lamps started. Air is now blown in, and the oil is stated to absorb about 5 per cent. of oxygen (see p. 161).

Properties of Boiled Linseed Oil.—Boiled linseed oil dries considerably more rapidly than the raw product, leaving a hard, lustrous surface, which, however, is liable to crack on exposure to air. It is usual, therefore, to add some raw oil to pigments, along with the boiled oil, in the mixing of paints, a more elastic coat being thus obtained. Boiled oil should be used for most outside work, as it resists the action of the air much better than the raw oil, and retains its gloss for a longer period. It may also with advantage be used with those pigments which are bad driers, although of course terebine and liquid driers may be employed.

The commercial boiled oil tends to darken rapidly on drying; in fact, simple exposure to sunlight serves to darken the oil, although, curiously enough, the raw oil is bleached in similar circumstances. Evidently, therefore, it is better to use the latter with very pale pigments. Although the better qualities of boiled oil are not possessed of this fault to the same degree, it is advisable not to use them for whites.

Boiled linseed oil may be applied to wood before polishing or varnishing, to bring out the colour and beauty of the grain. It should be of good quality, however, and a little terebine may be added to act as drier. Such treatment is excellent for the benches in a chemical laboratory, as it enables the wood to offer a stouter resistance to the corrosive action of chemicals.

Personally, I always use a mixture of the oil with turpentine, in the proportion of one to one, as this dries more readily than the pure oil.

The specific gravity of boiled linseed oil ranges from 0·937 to 0·952.

The Flash-Point.—The temperature at which the vapour of an inflammable liquid just catches fire is known as the flash-point. This has a very important bearing on the safety or otherwise of using different oils for various purposes. Thus, for example, an oil with too low a flash-point would be dangerous material to burn in an ordinary household lamp. A minimum flash-point has therefore been fixed, below which an oil may not be used for such a purpose.

It is clearly necessary for the painter to have some idea of the flash-points of the various liquid vehicles which he uses for mixing his paints, and a simple piece of apparatus is shown on the table here, by means of which fairly accurate determinations of the flash-points of liquids may be made. The liquid to be tested is poured into this nickel basin (B, Fig. 15) and is gently stirred with the thermometer T. If the liquid, like resin and linseed oils, has a high flash-point, the basin may be supported on a square of wire gauze, plugged with asbestos, and gently heated over the gas flame. If, on the other hand, the liquid has a low flash-point, like turpentine and petroleum, the nickel basin should be stood in a water-bath and warmed. A glass tube drawn out to a fine point is now connected with a separate gas supply, and a small jet of flame, about a quarter of an inch high, allowed to burn at its narrow end. This flame is frequently brought close to, but not touching, the surface of the liquid, and the temperature at which a small blue flame can be seen to flash across it is carefully noted. This is the flash-point. Such volatile liquids as benzene

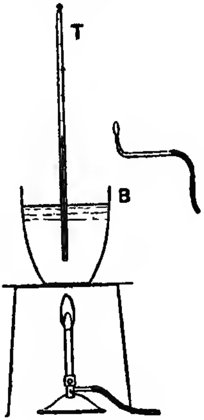

FIG. 15.

and naphtha catch fire at the ordinary temperature, and must therefore always be kept at a safe distance from a naked flame.

The approximate flash-points of different oils and spirits are given in the table—

Liquid.	Flash-point, °F.
Linseed oil	470
Rosin oil	310–320
Paraffin burning oils	100–120
Turpentine and rosin spirit	96–100
Petroleum burning oils	73–110
Naphtha	60–70
Methylated spirit	57–60

You will observe that the flash-point of rosin oil is very much lower than that of linseed oil.. Since the former is used very largely as an adulterant for linseed oil, its presence can readily be detected by its lowering effect upon the flash-point of the latter. This applies also to any other oil which is likely to be used as an adulterant, and the purity or otherwise of any sample of linseed oil can thus be established with ease.

Hempseed Oil.—The seeds of the hemp plant, *Cannabis sativa*, contain about 30 per cent. of oil, which is obtained by expression in the usual way. The plant is cultivated in France, Belgium, Germany, North America, India, Japan, Italy, and Algeria.

When fresh, the oil is of a light green hue, which on keeping becomes brownish yellow. It has a high iodine equivalent when pure, and its specific gravity ranges from 0·925 to 0·931. On the Continent it is used as a paint oil more frequently than in this country, and the lower qualities are said to be used in the manufacture of varnishes.

As in the case of the poppy, the hemp plant is cultivated in Manchuria, but the resulting oil is of an inferior grade, owing to the fact that the seeds are mixed with others containing a fair proportion of non-drying oils.

Poppy-seed Oil.—Poppy-seed oil is obtained by pressure from the seeds of one of the poppy family, known to the botanist as *Papaver somniferum*, which is grown extensively in Asia Minor, Persia, India, Egypt, South Russia, and the

North of France. The seeds yield from 35 to 50 per cent. of oil. The poppy is also cultivated in Manchuria, but as the seeds are collected with others which yield about 16 per cent. of a non-drying oil, the resulting product is a poor drier.

When fresh, poppy-seed oil is nearly colourless, and constitutes the so-called "white" variety. It is used by artists in preference to the darker linseed oil for mixing with light pigments. Fortunately it does not possess the narcotic properties which characterize the plant itself, and is employed as a salad oil, exhibiting little tendency to become rancid. An inferior quality of oil is expressed from the seed in the warm, and constitutes the "red" oil of commerce.

The cakes left behind in the presses are rich in nitrogen, and serve as food for cattle. Should they become mouldy they are reserved for manure.

Poppy-seed oil is usually contaminated with sesamé oil, the presence of which materially lowers the iodine equivalent, and thus affords a ready means of detecting the same. The specific gravity of the oil ranges from 0·924 to 0·927.

Tung Oil.—Tung oil is expressed from the seeds of the tung tree, which flourishes in China and Japan. The tree yields a nut enclosing three seeds with an oily kernel. The seeds are roasted, powdered coarsely between stones, and the oil obtained by treatment in primitive wooden presses. Three kinds of seed are recognized, namely, white, drab, and yellow. The average yield of oil amounts to about 40 per cent., although the total oil content of the kernels is 53 per cent.

The cold drawn oil is chiefly imported into Europe under the name of **White Tung Oil.** Black tung oil is chiefly used in home consumption, and is obtained by hot pressing. The oil is chiefly exported from Hankow in China, although, as will be seen from the following figures, the amounts seem very small compared with those of linseed oil produced by other countries:—

Year.	Tons of tung oil.
1900	19,653
1901	16,701
1906	28,685
1907	23,540

It is estimated, however, that the home consumption of tung oil in China is at least double the amount exported.

The cakes left behind in the presses are poisonous, and cannot therefore be used as a food for cattle. They are employed as manures for the soil, and also in the manufacture of black pigments.

The odour of tung oil is characteristic. Its drying powers are very pronounced, and a film on glass generally leaves a dry opaque skin, quite different from that left by linseed oil. The specific gravity is very high, namely 0·933 to 0·941, the Japanese varieties having the lower value. When heated to 480° F. for a few minutes, tung oil sets to a jelly, which is insoluble in the ordinary solvents. This is not due to oxygen absorption, since the change takes place in the absence of air. It is generally ascribed to what is known as "polymerization," that is to say, the tiniest little particles of the oil which can possibly exist by themselves, and known to the chemist as "molecules" (from the Latin, meaning *small masses*), have combined together, or polymerized, in a manner not yet thoroughly understood.

Both the saponification number and the iodine equivalent of the polymerized oil are different from those of the natural product.

Patents have been issued for processes which claim to produce varnishes from polymerized tung oil either alone or admixed with linseed oil, but I am not aware that they have proved successful commercially.

Walnut Oil.—This oil is expressed from the common walnut, the kernel of which contains from 63 to 65 per cent. of the oil. The nuts are placed in heaps for two or three months, which effects their complete ripening and partial decomposition. On subjection to pressure the "virgin nut oil" escapes. As this process fails to abstract the whole of the oil, the resulting cake is ground with hot water and again pressed, whereby the so-called "fire-drawn walnut oil" is obtained. The best qualities of walnut oil are colourless, and their drying power is equal to that of linseed oil. It is therefore used by artists for mixing with pale pigments. The paints obtained are less liable to crack than similar ones containing linseed oil as vehicle. If it could be obtained more cheaply it would certainly prove a serious rival to linseed oil in house painting. It is frequently adulterated with linseed oil, but the latter is readily detected by its raising the iodine equivalent of the oil abnormally. The specific gravity of walnut oil is practically the same as that of poppy-seed oil, namely, 0·925–0·927. The oil is apt to become rancid, however.

Rosin Oil.—This is not a true drying oil, and would not be considered here were it not for the fact that it is largely used as an adulterant for linseed oil.

I have already mentioned that, after the crude resin from the pine tree has been subjected to distillation in a current of steam; rosin is left behind in the boiler. This is transferred to a cast-iron still, capable of holding about 2000 gallons, and heated direct over a fire. The distillation occupies from 50 to 60 hours, and the following products are obtained :—

Gas	5·4	per cent.
Acid water	2·5	„
Rosin spirit	3·1	„
Rosin oil	85·1	„
Pitch	3·9	„
	100·0	

Two varieties of rosin oil are collected. That which comes over during the first stages of the operation, and particularly if the process is effected rapidly, is known as "hard rosin oil." It is a thick, turbid liquid, of a dark red hue, and when mixed with coal tar and grease, makes a good lubricator for wheels, etc.

The second portion of the oil which collects is known as "soft crude rosin oil"; it is thinner, lighter, and more acid in character. It is largely used for mixing with lime in the preparation of wheel grease, as it does not dry so well as the hard oil.

When alternately treated with sulphuric acid and caustic soda, and subjected to re-distillation, a refined product of a pale colour is obtained, which has no drying power at all.

The cruder varieties do dry in time, but a few weeks later the coat becomes soft and tacky, "giving again" as the painters express it; and this defect will manifest itself even if a good linseed oil paint is used for a top coat. Rosin oil is, therefore, a most undesirable adulterant in paints.

The specific gravity of refined rosin oil varies from 0·980 to 0·995. This is considerably greater than that of linseed oil, which ranges from 0·932 to 0·937, and, as I have already remarked, enables us thereby to determine whether or not a given sample has been adulterated with rosin oil.

In the accompanying table are given the characteristics of the oils treated of in this chapter. The values are only approximate, and represent the average results obtained by different investigators.

PHYSICAL CONSTANTS OF PAINTERS' OILS.

Oil.	Specific gravity.	Iodine equivalent.	Sapon. number (potash).
Linseed—raw	0·930–0·937	170–180	19·3–19·5
,, —boiled	0·937–0·952	170–171	—
Hempseed	0·925–0·931	148–156	19·0–19·3
Poppy-seed	0·924–0·927	136–143	19·0–19·8
Tung	0·933–0·941	155–166	19·0–20·0
Walnut	0·925–0·927	143–151	19·2–19·8
Rosin	0·980–0·995	—	—

XIV

PAINT VEHICLES (*continued*)

2. Hydro-carbons

Turpentine.—Another exceedingly important vehicle to the painter is turpentine. Originally this name was given to the complex resinous exudation from pine trees, but the term is now used to denote the volatile liquid obtained from the resin by distillation.

Crude turpentine, sap, or resin, occurs in the wood, bark, leaves, and other parts of pine and fir trees, which latter are widely distributed throughout the world. Russia alone has 500 million acres of forestry, consisting largely of pine trees, while France, Germany, Switzerland, Sweden, and Austria each carry on a large turpentine industry. Turning our attention to the New World, we find vast extents of pine forestry in various parts of America, and many millions of gallons of turps are exported from there every year.

You know that, on gently shaking a full flower on a dry summer's day, a yellow dust, known as pollen, falls to the ground. It is essential that there should be an exchange of this pollen between plants of the same kind if the latter are to be fertile and produce seed. Pollen is often carried from flower to flower on the bodies of bees and other insects, which visit the flowers for honey. In the case of the pines, the wind is the chief agency for the dispersal of the pollen. As showing the extent of the American pine forestry, you will be interested to learn that in March, 1879, a shower of pollen fell in the north-eastern part of Pennsylvania, covering an area of something like 2500 miles. It is believed to have been carried by the wind over a distance of 500 miles. I leave you to imagine what a vast number of trees would be required to produce such a large amount of pollen. There are three kinds of turpentine to be met with in our markets, namely, American, French, and Russian.

American Turpentine.—For the purpose of obtaining the crude turpentine in America, the trees are "boxed." This operation consists in cutting a cavity into the side of the tree, about one foot from the ground. Such a box will hold from two to three pints. Sometimes three boxes are cut in the tree, care being taken not to touch the heart wood, however, as this would certainly kill the tree. About March the sap begins to exude, and collects in the box and on the sides of the cut surface. The season lasts till September, and one man is able to attend to about 10,000 boxes. If the bark of the tree is hacked a little every fortnight, then about six pints of exudation can be obtained from each box during the season. That which collects in the box is known as the "dip," and that on the sides, as "scrape." The first year's product of a tree is called the "virgin dip," and is collected separately; that of other years is known as "yellow dip." After five or six years the trees are exhausted, and cut down. The process is wasteful, and unless suitable precautions are taken, the forests must become exhausted. In order to preserve the life of the trees, Schuler uses earthenware cups for the collection of the sap, and thus removes the necessity of cutting cavities deep into the tree. A little water is put into the cups, and the sap, being heavier, sinks to the bottom, whereby loss through evaporation is prevented.

The crude product obtained in this way is now distilled in the following way. It is run into a boiler, and heated over a fire to a temperature slightly above that at which water boils. A current of steam is now blown through the liquid, whereby the turps escapes as vapour along with the steam, and on passing through a spiral tube cooled externally with water, the two condense and the turpentine is run off into barrels. When no more turps escapes, the rosin left behind in the boiler is emptied out, and the latter is now ready for another charge.

Owing to the devastating manner in which this industry has been carried on, the supply of turpentine has considerably decreased, as is evident from the following data :—

1. TURPENTINE PRODUCED IN AMERICA.

Year.	Gallons.
1900	38,488,170
1905	30,687,051

2. TURPENTINE EXPORTED FROM THE U.S.A.

Year.	Gallons.
1901	20,240,851
1903	16,378,787
1905	15,894,813

Owing to this shortage, numerous attempts have been made to obtain the turpentine by direct distillation of wood, sawdust, roots, etc., obtainable from the pine-tree forests, and a large number of patents have been issued. It is said that in Georgia a ton of sawdust can be made to yield 14 gallons of turpentine, three or four barrels of resin, and a quantity of tar.

In New Orleans the richest pine knots are selected, and submitted to destructive distillation in iron retorts. A "cord" of wood is stated to yield 35 or 40 gallons of turpentine, 2 barrels of tar, and between 20 and 25 bushels of charcoal, in addition to a quantity of combustible gas, which is utilized as fuel.

A number of different species of pine tree are used in America as the source of turpentine, the most productive being the "long leaf" pine, known to the botanist as *Pinus palustris*, and the Cuban pine (*Pinus heterophylla*). It is stated[1] that in the near future the Mexican pine may be worked for turpentine, of which it yields a larger quantity than the American pine. It grows at an altitude of 5000 to 9000 feet, whereas the American pine grows at a height of 500 feet.

French Turpentine.—The French industry is carried on more scientifically, and hence more economically. The trees are tapped for five successive years, and are then allowed to rest for a few years, after which tapping is recommenced.

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[1] See Lewkowitsch, *opus cit.*, vol. iii., Appendix.

When the tree has become exhausted a final tapping is taken, which yields a large amount of the crude resin and kills the tree. The last named is therefore felled and another planted in its place. Upon distillation in a current of steam, turpentine is obtained, a large proportion of which is consumed in France. It appears that in 1904 the total export amounted to 118,000 cwts., of which 9150 cwts. were imported into this country. In 1905, however, we received no fewer than 28,154 cwts. from France, which is rather more than treble as much. The quantity of rosin obtained is nearly four-fifths of the crude resin used.

A vigorous pine standing alone will yield annually from 45 to 90 lbs. of crude resin; but if the trees are grown together in clumps or forests the individual yield is reduced to something like one-quarter of this amount.

Russian Turpentine.—Russian turpentine is decidedly inferior to the French and American products, and is obtained by distillation of the dead waste wood and roots of the Scotch fir. Its odour is strong and unpleasant, and renders it unsuitable for use in the manufacture of indoor varnishes. Attempts have therefore been made to effect its deodorization by distillation over lime, and by treatment with powerful oxidizers, such as potassium permanganate and ozone; but the results do not appear to be entirely satisfactory, although the products now placed on the market are decidedly superior to those offered a few years ago. Nevertheless, they are inferior in every respect to the American and French turpentines.

The quantity of Russian turpentine imported into Great Britain is given in the following table:—

Year.	Weight in cwts.	Value.
		£
1901	21,956	19,882
1902	27,875	24,249
1903	56,304	60,155
1904	52,709	58,147
1905	68,754	67,117

Properties of Turpentine.—Turpentine is a good example of another type of vehicle, which in its chemical properties is as different as possible from the drying oils just considered. It is neither greasy nor can it be split up into a base, like glycerine, and a fatty acid. It is really a mixture of various compounds of carbon and hydrogen only, which are known to chemists as hydrocarbons. The chief constituent of the French and American turpentines is known as pinene, which is a colourless liquid, boiling at from 311° to 313° F. Pinene combines with dry hydrochloric acid gas to form a solid crystalline body, known as artificial camphor, which is used in the preparation of synthetic camphor, which latter is identical with the natural product extracted from the camphor tree—another remarkable triumph for science.

Turpentine burns with a smoky flame, yielding carbon dioxide, water, and soot or free carbon. It readily dissolves in ether, alcohol, benzene, and the like, but is insoluble in water. Fats, oils, and certain gums and resins dissolve in it with ease. Caustic soda does not effect its saponification for the reason already given. The specific gravity of French and American samples varies from 0·864 to 0·870. They begin to boil at about 310° F., and are completely distilled over at 340° F. Fresh samples leave practically no residue behind, but those which have been kept for a long time generally yield a little resinous matter, which, however, amounts to less than one per cent. of the turpentine. The flash-point lies between 93° and 100° F. Their odour is far from disagreeable.

Russian turpentine has a somewhat higher specific gravity, namely from 0·862 to 0·873. It begins to boil at about 311° F., but is not completely distilled below 356° F., most of it boiling away at approximately 343° F. It is evident, therefore, that Russian turpentine is more complex than the French and American. As already stated, it has a stronger odour, and is more apt to induce headaches.

Turpentine is very liable to adulteration, such liquids as petroleum, naphtha, and rosin spirit being used. Their presence can readily be detected, however, by the determination of the specific gravity of the suspected samples. If it varies greatly from the mean, 0·867, adulteration is highly probable.

As we have already seen, the annual production of American turpentine has decreased considerably, and its price has therefore risen in proportion, causing the market to be flooded with substitutes. One of the commonest of these consists of a mixture of equal parts of turpentine with rosin spirit, the odour of the latter substance being masked by the addition of a few blocks of camphor. There are several ways by which the purity or otherwise of a sample of turpentine can be establishe dwithout the employment of chemical apparatus such as that necessary for the carrying out of distillations or the determination of the specific gravity.

(i) A drop of the pure liquid renders a piece of paper translucent for the time being, but on evaporation no mark is left. If shadowy marks remain, the presence of an adulterant may be regarded as proven.

(ii) The odour of the warmed liquid may be compared with that of a genuine sample under like conditions, and, unless the experimenter happens to be suffering from a bad cold at the time, almost all possible adulterants will betray themselves if present. Coal-tar naphtha is particularly recognizable by its persistent odour.

(iii) If a sample of pure turpentine is shaken in a tube, the beads of liquid rapidly settle. This is not the case with adulterated specimens, which, in addition, show more or less inclination to froth.

Here is a jar of chlorine gas. As you see, it has a greenish yellow colour, and is prepared by adding a few drops of acid to ordinary chloride of lime or bleaching powder. This basin contains a little warmed turpentine, and I will soak some filter paper in it, and introduce it into the jar. You notice that the whole mass suddenly inflames. The hydrogen of the turpentine is uniting with the chlorine to form hydrochloric acid, and the carbon is thrown out as soot. This experiment shows us that bleaching powder and turpentine ought to be kept at reasonable distances from one another, as otherwise explosions may occur. Nitric acid acts very energetically on turpentine, producing various oxidation products, and when concentrated, causes the mass to burst into flame. Like linseed oil, turpentine gradually absorbs oxygen from the air, becoming thick and resinous, part of the turpentine volatilizing during the process. When spread into thin layers with a brush, a large proportion of the liquid evaporates, leaving a resinous layer behind, which is thus exposed to very complete oxidation, and serves as an excellent binding agent for pigments. Turpentine is therefore largely used in thinning paints.

The rate at which oxygen is absorbed by different samples of turpentine depends upon a number of factors. The absorption takes place more rapidly with rise of temperature, and with exposure to sunlight. Thus Kingzett[1] found that whilst a given quantity of turps absorbed 220 volumes of oxygen gas in six days when exposed to direct sunlight, only twenty volumes were absorbed in thirty-six days when kept in the shade.

The different varieties of turpentine absorb under similar conditions, as perhaps we might expect, very varying quantities of oxygen gas. The experiments of Kingzett may again be cited. Calling the largest amount of oxygen absorbed by a given weight of turpentine, under standard conditions, 100, it was found that the following table could be drawn up:—

Variety of turpentine.	Volume of absorbed oxygen.
Russian	100
Swedish	100
Geneva	89·4
American	78·9
Adulterated Swedish	52·6
"Scotch distilled" American	42·1

The last two samples were probably adulterated with rosin spirit, about which I shall have something to say presently.

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[1] See "Nature's Hygiene," by C. T. Kingzett. Published by Ballière, fifth edition, 1907, p. 390.

It is this property of absorbing oxygen which has led to the utilization of turpentine and similar bodies for the preparation of a very valuable disinfectant known as "Sanitas Oil." A mixture of turpentines, chiefly Russian, and water is placed in tin-lined receivers, and heated to about 140° F. Warm air is now pumped in for from four to twelve days, according to circumstances, whereby the oxidized product, Sanitas oil, is produced, floating on the surface of the water.

As you know, turpentine is used very largely in the manufacture of varnishes, which are made by dissolving gums and resins in it. These must generally be heated to fusion before they become soluble in the turps, a process which is expensive both on account of the cost of the firing and the unavoidable waste of a portion of the gum during the operation. Kingzett has found, however, that copal, Sierra Leone, and kowrie gums readily dissolve in Sanitas oil without previous fusion, and it appears that this oil is now used to some extent for the purpose. This avoids the darkening in colour which generally occurs when the gums are heated, and thus favours the production of a pale varnish:

Rosin Spirit.—When crude resin is distilled by fire heat, a large quantity of rosin is obtained, as we have already seen, and about three per cent. of a light volatile liquid, known as **Rosin Spirit.** If the distillation is effected by the aid of superheated steam, the percentage of spirit yielded is some three or four times as great. It is purified by successive treatment with sulphuric acid and caustic soda, and is finally re-distilled. Obtained in this way, rosin spirit is a clear, water-like liquid, the colour of which varies with the degree of refining. Its specific gravity ranges from 0·876 to 0·883, and is thus seen to be heavier than turpentine, the specific gravity of which lies between 0·864 and 0·870. Adulteration of the latter with rosin spirit is thus readily detected. It flashes from 97° to 100° F., and in this respect is similar to turpentine.

When exposed to air, a portion of the rosin spirit evaporates, and the remainder oxidizes to a resinous mass. It is insoluble in water and alcohol, but dissolves in ether, petroleum, shale naphtha, and turpentine. On distillation, it exhibits no definite boiling-point, as does turpentine. Ebullition commences at about 240° F., and the temperature gradually rises to 430° F., showing that rosin spirit is not a single substance, but a mixture of several liquids, the more volatile of which are naturally the first to escape.

Rosin spirit is an excellent substitute for turpentine, although its odour is regarded by many as rather objectionable. It is very liable to contain traces of rosin oil, as is obvious from its method of preparation, and as this is a wretched drier, the value of the spirit becomes thereby very materially reduced.

If on distillation the whole of the spirit does not boil over below 490° F., the residue may be regarded as rosin oil.

Cheap varnishes usually contain rosin spirit, rosin itself being used as body.

XV

PAINT VEHICLES (*continued*)

Hydrocarbons (*continued*)

Shale Naphtha.—Shale is a slate-like material, which appears to have been formed during the course of ages from the remains of animals and plants, mixed with mud. The Scottish shales may be taken as typical, and are found in large quantities in the district lying between Glasgow and Edinburgh.

Like coal, shale is submitted to a process of distillation, whereby numerous valuable products are obtained. Inasmuch as the shale itself is entirely destroyed by the operation, the process is known as "destructive distillation," to distinguish it from simple cases such as that of turpentine, where the different constituents of the crude resin are merely mechanically separated by taking advantage of their different boiling-points.

The plant employed in the distillation of shale varies greatly according to the district in which the mineral is found; but every manufacturer endeavours to effect the process at as low a temperature as possible. The shale is heated in iron retorts, protected in some plants from direct contact with the furnace fire by means of fire-brick arch or wall, and the process is assisted by the injection of superheated steam. At Broxburn, near Edinburgh, the following products are obtained, though the percentage of each is subject to considerable variation:—

DESTRUCTIVE DISTILLATION OF SHALE.

Volatile matter	Crude oil	12 per cent.
	Ammoniacal liquor	8 ,,
	Gas	4 ,,
Non-volatile (spent shale)	Combustible	9 ,,
	Ash	67 ,,
		100

Of these products only the first concerns us directly as painters. The crude oil is submitted to repeated distillation, whereby the following products are obtained :—

Naphtha	5 per cent.
Illuminating oils	37 ,,
Lubricating oils	17 ,,
Paraffin wax	13 ,,
Waste	28 ,,
	100

The naphtha isolated in this way is sent into the market under a variety of names, such as **Solvent Naphtha, Shale Naphtha, Benzine,**[1] **Benzoline.** It is a limpid liquid, insoluble in water and alcohol, but readily miscible with turpentine, ether, benzene, and the like. Its specific gravity ranges from 0·730 to 0·760. It is very volatile and inflammable, readily igniting at ordinary temperatures, which is a great objection to its use. On evaporation no resinous material is left, which distinguishes it from turpentine and rosin spirit. It is a good solvent for most oils, and many resins and gums, and is largely used as a substitute for turpentine. It begins to boil at about 150° F., and is generally completely distilled over at 400° F. Acids and alkalies are without action upon it.

Coal-tar Naphtha.—When coal is subjected to the process of destructive distillation, the following products are obtained :—

1. *Coke.*—This is the non-volatile material left behind in the retorts, and consists principally of carbon, together with about ten per cent. of mineral matter. The yield of coke varies according to the nature of the coal and the temperature at

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[1] Not to be confounded with benzene, a coal-tar product. It is unfortunate that the same name is used for one of the distillation products of mineral naphtha. (See below.)

which the distillation is effected. The following table shows the average amount obtained from different samples of coal:—

Newcastle gas coal	67 per cent.
South Yorkshire silkstone	66 ,,
Derbyshire silkstone	64 ,,
Barnsley gas coal	64 ,,
Cannel coal	50 ,,

2. *Coal Gas.*—This varies in amount from 10,000 to 12,000 cubic feet per ton of coal.

3. *Gas Liquor.*—This is a watery product, consisting chiefly of solutions of ammonium salts, and in agricultural districts is frequently applied to the soil directly, as manure.

4. *Coal Tar.*—The product with which we are most nearly concerned as painters is coal tar, which begins to distil over a little below 200° F. The specific gravity varies from 1·1 to 1·2, and usually lies between 1·12 and 1·15.

From a chemical point of view tar is a very complex mixture, as will be evident from a glance at this table:—

COAL TAR.

1. Hydrocarbons, consisting chiefly of benzene, napthalene, anthracene, and their derivatives.
2. Carbolic acid and its derivatives.
3. Organic substances containing sulphur.
4. Nitrogen derivatives, such as ammonia, aniline, etc.
5. Organic substances rich in carbon, constituting pitch.

In order to effect the separation of these very valuable products the tar is distilled, and the vapours which pass over are condensed in separate receivers according to their temperatures. The following four fractions are now usually collected separately in this way:—

1. First runnings and light oil, boiling off at temperatures below 410° F.	5 per cent.
2. Carbolic oil, up to 464° F.	16 ,,
3. Creosote oils, up to 518° F.	
4. Anthracene oil, up to "pitching point" which varies according to whether hard or soft pitch is required	21 ,,
	42

The residue consists of pitch, amounting to approximately fifty-six per cent., the remaining two per cent. representing the average unavoidable loss.

The first runnings and light oils, collected together, consist of hydrocarbons analogous to benzene. They are distilled, the portion coming over first being collected separately, and constituting crude naphtha. This is treated successively with caustic soda to remove organic acids, and with sulphuric acid to remove organic bases, and is again distilled. The portion collected below 284° F. is used for the extraction of benzene; that between 284° and 338° F. constitutes "solvent naphtha"; the residue, being heavy oil, is worked up with the carbolic oils.

As obtained in this way, **Solvent Naphtha**, or **Coal-tar Naphtha**, is used largely in the india-rubber industry, and in the manufacture of varnishes. It is a colourless, transparent liquid, with a specific gravity ranging from 0·865 to 0·877. Like shale naphtha, it is very volatile, leaving no solid or resinous matter behind. It mixes readily with turpentine, petroleum, shale naphtha, and the like, being frequently adulterated with the two last named. Such adulteration always affects the specific gravity and flash-point, and is thus easily detected. When pure, the flash-point of naphtha is approximately 20° F.

Petroleum Spirit.—Crude petroleum is known in commerce under a variety of names, such as **Mineral Oil**, **Rock Oil**, and **Naphtha**, and consists of a mixture of hydrocarbons obtained from oil wells in different parts of the world. The bulk of the petroleum comes from Pennsylvania, in America, and from Baku, on the shore of the Caspian Sea, although it is also found in Galicia, Roumania, Hungary, Alsace, and in the Crimea along the Black Sea. In 1908, Canada produced over half a million barrels. In its crude condition, petroleum is a thick, oily liquid, of a brownish colour, which loses its more volatile constituents on exposure to air. This tends to make it thicken, and to pass into *asphaltum*.

Caucasian petroleum has a higher specific gravity than the American, and contains far less of the light, volatile constituents. Galician petroleum occupies an intermediate position between the two.

North American petroleum was apparently first made mention of in 1629. The earliest reference to the oil in South America appears to have been made eleven years later, namely in 1640, by Albaro Alonso Barba in his work entitled "The Art of Metals," translated into English in 1669. As the paragraph relating to petroleum is very quaint, I take this opportunity of quoting it to you:—

"*La Naphte* is a sulphurous liquor, sometimes white, and sometimes black also, and is that which is called Oyl of *Peter*, of admirable vertue to cure old pains, proceeding from cold causes. It will draw fire to it (as the Loadstone does Iron) with that force, that it will take fire at a great distance from the flame, as hath been confirmed by the miserable experience of the *Conde de Hercules de Icontrarii*, of the Country of Ferara, who having a well in his ground, the water whereof was mixed with *Petreol;* and by some breaches or cracks in the well, much of this water ran to waste; commanded it to be repaired; the Laborer that was let down into the bottom of the Well desired a Candle, the better to see his work, which was furnished him in a Lanthorn, and immediately through the holes of the Lanthorn the *Naphte* suckt the flame into it self and set fire on the whole Well, which discharged itself instantly like a great piece of Cannon, and blew the poor man into pieces, and took off an arm of a Tree that hung over the Well."

The name of Andrew Carnegie is intimately associated with the early stages of the petroleum industry. About the year 1864, in conjunction with some friends, Carnegie subscribed towards the purchase of an oil creek, known as Storey Farm, for the sum of £8000. The production of oil amounted to 100 barrels daily, and over 3 million gallons were stored in a huge reservoir built expressly for the purpose. The value of the petroleum was estimated at £200,000. The supply of the oil, however, far exceeded the wildest hopes of the shareholders, and huge quantities were run to waste from sheer lack of storage room and inability to cope with the overflow.

Such outbursts are now, however, relatively rare, and the oil is won by sinking bore-holes, about 6 inches in diameter, and sometimes as much as 2400 feet and upwards in depth. The well is usually lined with iron tubing as far as possible, in order to keep out surface water. If the wells do not flow spontaneously, a force-pump is let down, which brings the oil to the surface.

Very frequently the oil is accompanied by large quantities of an inflammable gas under tremendous pressures, amounting to 400 or 500 lbs. per square inch. This is used extensively for fuel and illuminating purposes in the immediate neighbourhood of its source, and some of it is burned in an insufficient supply of air to effect complete combustion, whereby a mass of soot or carbon is obtained, which serves as a black pigment such as "lamp-black," or "diamond-black."

The chemical composition of the gas is naturally somewhat variable, but the following analysis of a sample from the Pittsburg district may be regarded as fairly representative :—

Marsh gas	67·0 per cent.
Hydrogen	22·0 ,,
Ethane	5·0 ,,
Nitrogen	3·0 ,,
Oxides of carbon	1·2 ,,
Ethylene	1·0 ,,
Oxygen	0·8 ,,
	100·0

Since the wells in any district are somewhat scattered, it is found advantageous to collect the oil in central storage tanks, and transmit it by means of pipes under pressure to the refineries.

It is not necessary for me to go into details as to the carrying out of the refining process; suffice it to say that the oil is subjected to fractional distillation, the fractions being purified by successive treatment with caustic soda and sulphuric acid.

In the following table the differences between the yields of the various fractions of Russian and American crude petroleums are well shown:—

	Russian.	American.
Petroleum spirit	4	25
Illuminating oil	39	60
Lubricating oil	32	15
Residue and loss	25	
	100	100

When the petroleum spirit, mentioned in the table, is subjected to further fractional distillation, three important products are obtained, namely:—

a. **Petroleum Ether** or **Gasoline,** boiling at about 140° F. Its specific gravity is only 0·66 to 0·70, and it is used very largely as a solvent for caoutchouc and oils.

b. **Naphtha** or **Ligroin,** boiling at temperatures ranging from 176° to 230° F. Its specific gravity ranges from 0·700 to 0·730, and it is used as a solvent for oils and resins, as well as for burning purposes.

c. **Benzine** is a slightly heavier fraction, of specific gravity about 0·74. It boils up to 302° F., and is used as a turpentine substitute.

As a rule, however, the benzine or naphtha sold to painters is an indiscriminate mixture of fractions *b* and *c.* It flashes at ordinary temperatures, begins to distil at about 150° F., and completely distils over by 300° F.

Turpentine Substitutes are usually mixtures of benzoline and heavier paraffin products. A sample examined by Hurst had a flash-point of 97° F., and began to distil at 312° F. Its specific gravity was 0·791.

Petroleum spirit has been proved to make a very successful and satisfactory substitute for turpentine. The chief disadvantage lies in its rapid evaporation, but it is very doubtful if this affects in any way the permanence and durability of the paint film, although it certainly is inconvenient to the worker, particularly so in flat work. Its great inflammability introduces a risk of fire, and Allan E. Munby[1] recommends the use of paraffin oil as a thinner, as being preferable to petroleum spirit. It is doubtful, however, if practical men will readily fall in with this suggestion, for, when used in a paint, paraffin oil only dries with extreme difficulty.

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[1] "Introduction to the Chemistry and Physics of Building Materials," by A. E. Munby. Published by Archibald, Constable & Co., 1909.

XVI

PAINT VEHICLES (*continued*)

3. Alcohol

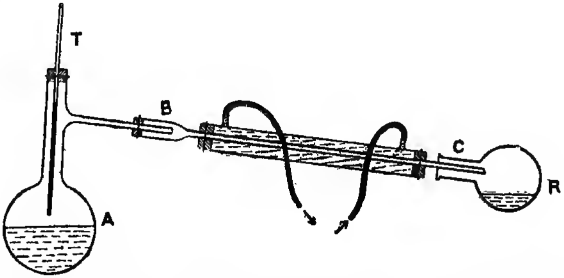
Methylated Spirit.—Methylated spirit consists essentially of a mixture of ethyl and methyl alcohols, together with small quantities of other substances intentionally introduced, in order to render the liquid unfit for drinking purposes. It thus escapes the heavy Government duties which are levied on the pure spirit and on alcoholic beverages generally.

Ethyl Alcohol, better known perhaps as "spirits of wine," is a product of the fermentation of sugar.

A few days ago a dilute solution of ordinary sugar was put into this flask, together with about an ounce of German yeast. You notice that the liquid mass is covered with foam, and if I plunge a lighted splinter into the flask the flame is immediately extinguished, for the flask is now filled with carbon di-oxide, which will not support combustion. We will now filter off the yeast, and subject the clear liquid to distillation (Fig. 16).

In the receiver a clear liquid has collected, which is a solution of alcohol in water. We will pour it on to quicklime in another flask, and distil again. This time, however, in order to avoid cracking the flask, we will not heat it directly over the gas flame, but immerse it in a pan half filled with water, and raise the latter to boiling. The lime removes the bulk of the water, and nearly pure alcohol collects in the receiver.

Obtained in this way, ethyl alcohol is a clear, colourless liquid, possessed of a pleasant odour and a burning taste. It rapidly evaporates when exposed to the air, leaving no solid residue. When pure it boils at 173° F., and distils over unchanged. It is very hygroscopic; that is to say, it absorbs moisture with great readiness, so that it is not easy to prepare it in a perfectly anhydrous condition. Its specific gravity should be 0·794 at 60° F., though, for the reason just given, this value is rarely obtained with the ordinarily so-called pure alcohol. Alcohol mixes with water in all proportions, a slight shrinkage being observed, and a small amount of heat liberated simultaneously. It mixes with ether, turpentine, and benzene, but not with petroleum. Whilst a good solvent for shellac and mastic, it has no action on the copals, kauri, and animi gums.



The liquid is poured into A and raised to boiling. The temperature at which the vapour escapes is noted by thermometer T. The vapour passes through the condenser BC, which consists of a tube surrounded by an outer jacket, and kept cool by a current of cold water. The vapour condenses and collects as a liquid in the receiver R.

FIG. 16.

The aqueous solution containing 49 per cent. of alcohol is known as "proof spirit," and has a specific gravity of 0·926.

Methyl Alcohol, the other main constituent of methylated spirit, is very similar in chemical structure to ethyl alcohol. It is obtained commercially in the dry distillation of wood, which latter is heated in retorts, the volatile substances being collected as in the destructive distillation of coal. The products are charcoal, tar, crude acetic acid, spirit, and gas. The last-named is used for heating the retorts, as well as a little charcoal. The tar is allowed to settle, and the watery liquid above, containing the acetic acid and spirit, is drawn off. Lime is now added, which combines with the acid, and the impure wood spirit is distilled off. This latter is a complex mixture, and requires careful refining to effect the isolation of pure methyl alcohol.

Pure methyl alcohol is a colourless, volatile liquid, boiling at 131° F., and of specific gravity 0·802 at 60° F. It is readily miscible with water, alcohol, turpentine, etc., and is a good solvent for resins.

The crude wood spirit, or wood naphtha, obtained in the way already indicated, contains about 80 per cent. of methyl alcohol, 6 per cent. of acetone, and 12 per cent. of water. The remaining 2 per cent. is composed of small quantities of other ingredients, which impart to the naphtha a disagreeable odour and taste, and thus render it unfit for drinking purposes.

Methylated spirit consists of 10 parts of wood naphtha and 90 parts of "rectified spirits of wine," which latter is the ordinary commercial form of ethyl alcohol, and contains about 14 per cent. of water. Half a per cent. of petroleum is now added to the mixture to render it still more undrinkable, although there are people whose tastes are so blunted by habitual intoxication, that they will drink even this filthy liquid.

As sold, methylated spirit is usually "64 over proof," that is to say, when 100 volumes of this liquid are mixed with 64 volumes of water, "proof spirit" results, which, when mixed with gunpowder and ignited, will just not set fire to the latter. When mixed with water a milky colour is produced, owing to the separation of petroleum and the other impurities, which are insoluble in water. As we shall see later, methylated spirit is used in the manufacture of varnishes, owing to its solvent action on the various resins. Such varnishes dry rapidly, owing to the volatile nature of the spirit.

So-called **Finish** is a solution of 3 ozs. of resin in a gallon of spirit.

4. Water

Obviously the cheapest vehicle which the painter has at his disposal is water. When a sample of pure water is boiled, the temperature remains constant at 212° F., and no solid residue remains behind. Water, therefore, cannot act as a binder, as linseed oil and similar vehicles. Further, the majority of gums are only partially soluble in water, and the true resins are quite insoluble, so that its use as a vehicle is considerably restricted.

Distemper.—Distemper is one of the cheapest preparations used by the painter and decorator, and consists of pigments diluted with water, to which some adhesive material such as glue has been added to serve as a binding agent.

Distemper is usually applied to plaster, stucco, brick, and stone surfaces, but not to wood. The great drawbacks to its use in this country lie in its susceptibility to the action of a moist atmosphere, and the fact that it cannot be washed. It may be used with advantage in dry buildings and in places where it is not likely to be touched, for it is extremely permanent, and can be made to any desired tint or shade. Examination of the ruins of Herculaneum and Pompeii, and of the ancient tombs of Egypt, shows that distemper may, under suitable conditions, last for centuries.

In America, lime preparations under the name of "kalsomine" are used in distemper, but in England whiting is the usual pigment. This is broken into small lumps, and rendered soft or muddy by the addition of water. Size is now added until the whole is of the consistency of cream, and by admixture with colouring materials the desired tint may be obtained, after which the whole is strained. The quantity of size required depends upon the condition of the whiting and that of the surface to which it is applied. If too little size is present, the material will rub off when touched. An excess of size is equally objectionable, since it causes the whiting to peel. Alum is frequently added to distemper, as it exerts a solvent or liquefying action upon the size. Unfortunately, it also attacks a number of the pigments used for colouring the whiting, and its employment is not, therefore, to be recommended.

If deep colours are desired, the whiting may be partially or entirely replaced by cheap permanent pigments such as ochre or rouge. This is not necessary, however, if pigments characterized by great staining powers are used, such as, for example, ultramarine and indigo.

As I explained to you some time ago, whiting is apt to be somewhat alkaline or basic in its reactions. For during the process of drying there is a tendency for a small portion of the carbonate to decompose with evolution of carbon di-oxide, lime being left behind. It is not safe, therefore, to colour distempers with such pigments as Prussian blue and chrome yellow. The most suitable pigments for this purpose are ochres, umbers, siennas, Venetian red, vermilion, lime blue, and indigo; and these in combination may be made to produce a large variety of hues.

Foreign substances are frequently added to distemper to modify their general properties, or to make them suitable for any special purpose. In the following table a list is given of the most important additions in common use, together with the purpose for which they are added :—

Substance added.	Result.
Turpentine Paraffin	Increased binding power.
Glycerine Sugar Treacle	Slower drying.
Carbolic acid Chloride of lime	Deodorizes and disinfects.
Vinegar	Neutralizes the alkalinity of the lime, etc. Renders size more fluid.
Alum	Renders size more fluid.
Spirits of wine	Size hardened and rendered less easy to remove.
Soap	Hinders undue absorption.

Water paints and distempers are frequently spoken of as being the same thing. Such, however, is not the case. A water paint is a kind of saponified oil paint, and when properly applied to a suitable surface, it yields a non-absorbent coating, which may be painted or varnished over without further treatment. Distempers, on the other hand, require the application of some priming material before covering with paint or varnish, even though they are what are known as "washable." This is because the distemper contains no oil, the particles being simply bound together by glue. If a little water is splashed on to a distempered surface, it leaves temporarily a dark-coloured patch. In the case of a water-paint surface, however, the moisture can be wiped off without leaving any mark.

A very good example of a water paint is **Duresco**, which I mention by name on account of its historical interest as being one of the first put on the market. Since its appearance numerous other water paints have been produced by different manufacturers, which are quite equal to duresco, if, indeed, they do not excel it in many respects.

Water paints contain such substances as barytes, oil, and glue. W. J. Pearce[1] speaks very highly in favour of duresco, as he finds it to withstand wet lime, putty, finish, plaster, damp, heat, and steam. He further states that in one instance a fungus grew on its surface for several months, and after its removal, the material was not found to be appreciably affected. These remarks may be taken as applying to water paints generally.

As oil is used in its preparation, a water paint is an oil paint in essence. It is saponified, however, by treatment with alkali, which renders it mixable and workable with water. It has a fulness and soft quality possessed by no other similar material, and can be used on new plaster with perfect safety. One of the characteristics of an oil paint is its power of closing the pores of any material over which it is spread, thus preserving it from the action of outside influences. Whilst this is just what we want in the case of wood, it is not always advisable to coat a wall with such an impervious layer, as it obviously prevents the so-called "breathing" or "respiration," and renders the plaster likely to blister and scale off. A water paint, on the other hand, is porous and allows a wall to breathe. At the same time it resists the action of rain just as well as an oil paint. Numerous distempers and water paints are now on the market under a variety of names, and I only regret that I have not time to tell you more about them. They form, however, a study in themselves, and one which I can heartily recommend to any of you who can find leisure to pursue it.

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[1] See "Painting and Decorating," by W. J. Pearce. Published by Chas. Griffin & Co., 1898, p. 133.

White Wash and Colour Wash consist merely of lime and water, coloured with pigments in the latter case. They are used for the sake of cleanliness and sanitation, rather than of decoration, in outhouses, cattle sheds, and the like.

In the following table are given the specific gravity, flash-point, and boiling-point, of the chief liquid vehicles, other than drying oils, used by the painter:—

Vehicle.	Specific gravity.	Flash-point °F.	Boiling-point °F.
Turpentine	0·864–0·870	93–100°	310–320°
Rosin spirit	0·876–0·883	97–102°	220–470°
Shale naphtha	0·730–0·760	Ord. temp.	150–400°
Petroleum	0·730–0·760	„ „	150–250°
Coal-tar naphtha . . .	0·865–0·877	20°	284–338°
Methylated spirit . . .	0·821	Ord. temp.	176–212°
Water	1·000	—	212°

XVII

DRIERS AND LINSEED OIL

THE chemistry of the action of driers is extremely interesting, though, at the same time, very intricate, and far from fully understood. A thorough study of the subject is a work for the expert chemist, and in this lecture I cannot hope to do more than treat the subject in a broad and general manner.

We have already seen that the drying of linseed oil is intimately connected with its absorption of oxygen,[1] and any substance which can assist the oil to combine with that gas with greater rapidity, will hasten its drying and thus act as a drier. Such substances may act in two ways:—

1. *Direct Oxidation of the Oil.*—The majority of metals are able to unite with oxygen in more proportions than one. Now it frequently happens that in the higher oxides, the extra oxygen is only comparatively loosely attached to the metal, and is readily given up to substances capable of chemically uniting with it. The oxide is then said to be reduced, a lower and more stable oxide being formed. The higher, unstable oxide is frequently called a per-oxide, a term with which we have already become familiar in connection with hydrogen per-oxide, which is frequently used as a picture restorer[2] for this very reason. Oxides such as these may therefore very reasonably be expected to act as powerful driers, and practice does not fail to bear out our expectation. The two metallic oxides of this class found to be most suitable for the purpose are manganese di-oxide and red lead, each of which has already received full treatment in connection with the oxide

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[1] See p. 116.

[2] See p. 45.

pigments. Many organic substances are likewise able to form per-oxides, which act in a precisely similar manner.[1]

But it is evident that, even under the most favourable conditions, such an explanation can only account for part of the drying, for the weight of the drier added only amounts to a few pounds per ton of oil, and can contain at best but a small fraction of the oxygen which the oil requires. For example, only 5 lbs. of oxide of manganese are added to a ton of oil, and if this proportion is exceeded the action is too intense, a hard and friable coat being obtained instead of a firm, elastic one. Nevertheless, 5 lbs. of perfectly pure manganese di-oxide contain less than 1 lb. of loosely attached oxygen, and a ton of good linseed oil can absorb from 4 to 5 cwt. of the gas,[2] which is more than 400 times as much. In order to meet this difficulty, therefore, a second and supplementary explanation has been offered, known as the "catalytic theory."

2. *Driers as Catalysers.*—Catalysers are substances which assist chemical reactions to take place with greater rapidity, without themselves undergoing any permanent change. They may thus be likened to the cane which acts as an incentive to the lazy schoolboy, or to the spur which quickens the slow horse. It is in this capacity that many of the driers may be supposed to act. When suspended in the paint they unite with the oxygen of the air to form high and unstable oxygen compounds, which are immediately reduced by the oil. They are then free to unite with additional oxygen, only to suffer reduction once more. And so the processes go on indefinitely until the oil has become completely oxidized. The drier thus serves as a carrier of oxygen to the oil, and inasmuch as it undergoes no permanent change of itself, we may term it a true catalyser. It will be evident that a very small quantity of the drier should, according to this theory, be

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[1] See A. Genthe, *Zeit. angewand. Chemie*, 1906, p. 2087, abstracted in the *Journal Society Chemical Industry*, 1907, p. 56.

[2] This statement is based on the observation of W. Fox in the *Oil and Colourman's Journal*, 1884, p. 234, that 1 gram of Baltic oil absorbed 191 c.c. of oxygen gas.

capable of effecting the oxidation of a large amount of oil—a state of affairs which we know in practice to be true. Furthermore, the efficiency of a drier will depend more upon the amount of metal that it contains than upon the nature of the metallic compound used. Thus, for example, 5 lbs. of manganese di-oxide contain as much metallic manganese, when pure, as 4 lbs. of manganese mon-oxide, and if used in these proportions the drying capacities of these oxides are practically equal, the extra drying action of the 1 lb. of loosely attached oxygen in the former being negligible in comparison with the catalytic action exerted by the metal. The same is true for red lead and litharge, the equivalent quantities being 10¼ lbs. of the former to every 10 lbs. of the latter. I know that this statement is contrary to our generally accepted ideas, for red lead is usually regarded as a better drier than litharge, but the recent researches of T. A. Davidson[1] show that such is not the case, and that, weight for weight, litharge is slightly the better drier.

Nor are we confined to the metallic oxides for driers. The salts of the metals are almost equally efficient provided equivalent quantities are taken, although minor differences certainly exist, due in part to a variation in the physical condition of the salt, and also to the chemical nature of the acid with which the metal is combined.[2] For example, as rosin is capable of absorbing oxygen from the air, metallic resinates—that is, metallic salts of the rosin acids—may be expected to exert a more than usually powerful drying action. Such compounds have therefore recently found their way into the market, and are now regarded with considerable favour. They may be prepared by fusing together a metallic oxide and rosin, the product being known as a "fused" drier, and is free from moisture. The so-called "precipitated" driers are similar in chemical composition, but are obtained by mixing solutions of sodium rosinate with a soluble metallic salt, whereby the drier

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[1] See "The Action of Driers on Linseed Oil," a paper read by T. A. Davidson before the Paint and Varnish Society, November 12, 1908.

[2] It is assumed, of course, that the salt is soluble in the oil, otherwise it can have no drying action.

is precipitated. For example, if manganese rosinate is required, the sulphate would probably be used, the reaction proceeding according to the equation—

$$\begin{array}{c}\text{Sodium}\\ \text{rosinate}\end{array} + \begin{array}{c}\text{manganese}\\ \text{sulphate}\end{array} = \begin{array}{c}\text{manganese}\\ \text{rosinate}\end{array} + \begin{array}{c}\text{sodium}\\ \text{sulphate}\end{array}$$

Precipitated driers always contain considerable quantities of moisture, up to about 6 per cent., and can thus be readily distinguished from fused driers. Compounds of the fatty acids of linseed oil and certain metals—chiefly manganese and lead—are also prepared in a similar manner, and sold under the names of "precipitated manganese linoleate," "fused lead linoleate," etc. From tung oil, Lewkowitsch[1] has prepared lead and manganese tungates.

These organic compounds of metals are known as "soluble driers," since they readily dissolve in turpentine and in linseed oil. Their solutions in either of these solvents or in a mixture of the two, are known as "liquid driers" or "terebines."[2]

Since it is the metals, rather than the acids with which they are combined, which are the principal catalysers, it is clear that expensive salts offer no advantage, and the complex mixtures compounded and boomed by various manufacturers are frequently far less effective than the cheaper and simpler driers. The last-named consist essentially of the cheapest salts of manganese and lead, and the chief are enumerated in the accompanying table. You will notice the enormous fluctuations in the percentage of metal occurring in the commercial products. The case of manganese borate is particularly noteworthy, and implies, of course, extensive adulteration, with consequent reduction in the drying power. The need, therefore, for painters to receive a definite statement as to the purity of the article they are purchasing, is very great, and ought to be insisted upon.

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[1] See Lewkowitsch, "Chemical Technology," etc., 1909, vol. iii. p. 107.

[2] Not to be confounded with tere*bene*, a medical preparation obtained by the action of sulphuric acid on turpentine, and used in bronchitis, and as a disinfectant.

TABLE OF COMMON DRIERS.

Name.	Colour.	Per cent. metal in pure drier.	Per cent. metal in commercial drier.[1]
Litharge	Buff	90·3	89·4
Red lead	Red	90·1	86·7–87·6
Lead acetate	White	54·6	52·4–53·3
,, linoleate	Brown	—	31·2
,, oleate	Yellow	—	22·6
,, rosinate, fused	Yellow-brown	—	15·6
,, ,, precipitated . .	Light brown	—	—
Manganese borate	Pinkish	—	7·8–23·8
,, carbonate	Buff	—	38·8-42·6
,, di-oxide.	Black	63·2	50·4–54·3
,, hydroxide	Brown	—	46·5
,, linoleate	Dark brown	—	7·8–8·9
,, oleate	Brown	—	8·1
,, oxalate	Pinkish	—	30·2
,, rosinate, fused . .	Dark brown	—	2·3–3·5
,, ,, precipitated	Pinkish	—	5·0–6·1
,, sulphate (anhydrous)	Pinkish	36·4	—

It frequently happens that a particular salt of a metal, whilst slightly inferior as a direct drying agent, possesses other properties which render it very useful as a drier in certain special cases. For example, lead acetate is generally considered to be weaker than red lead and litharge, but it has the decided advantage of not causing the oil or paint to become so dark, and is largely used in making the so-called "patent" driers. Ferrous sulphate (copperas) is frequently used as a drier, particularly in the manufacture of varnishes. It should be used with care, however, as the tendency is for it to harden the coat and thus render the latter liable to crack. It contains a good deal of water of crystallization, and must therefore be dried before use. It owes its drying power to the tendency exhibited by ferrous salts to oxidize in the air to the ferric

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[1] The numbers in this column are calculated from the results given by T. A. Davidson, *loc. cit.* The theoretical percentages of the metal cannot always be given, as the composition of the salts often varies according to the method of preparation, the amount of water of crystallization being particularly affected by the temperatures at which the salts are dried.

condition. The extra oxygen is then yielded up to the oil, and the process begins over again. The iron thus serves as a catalyser in precisely the same way as manganese, although its action is not so vigorous.

It is evident that chemically inert substances such as barytes, lamp black, etc., cannot function as driers in the ordinary sense of the word. Hurst[1] gives the analyses of three samples of "patent" driers. No. 1 is a fair drier, though the zinc sulphate and oxide of iron are of doubtful value, even when employed alone. In conjunction with a lead salt, however, the use of zinc sulphate is positively ridiculous, because insoluble lead sulphate is formed, which is worthless as a drier. Thus—

ANALYSES OF PATENT DRIERS.

	No. 1.	No. 2.	No. 3.
Lead carbonate	71·77	19·17	—
,, acetate	8·21	—	7·10
Zinc sulphate	5·18	—	—
Calcium sulphate	—	51·86	—
Barium sulphate	—	—	66·73
Iron oxide	2·20	—	—
Silica	—	1·20	10·07
Water	—	8·07	1·30
Oil	12·69	19·17	14·80

Lead acetate + zinc sulphate = lead sulphate + zinc acetate

We thus see that unless the mixing of driers is conducted along scientific lines, a large amount of good material may be absorbed in producing a most inefficient article. Drier No. 2 is exceedingly poor, whilst No. 3 is worse than useless, containing no less than three-quarters of its weight of barytes and silica—two of the most inert substances with which the chemist has to deal.

But even chemical analysis has its limits. Experience proves that a drier is not always equally soluble in linseed

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[1] See "Painters' Colours, Oils, and Varnishes," by Hurst. Published by Charles Griffin & Co., 1906, p. 437.

oil, even though the analytical results may be perfectly satisfactory. The hydrated oxide of manganese is a case in point, and the explanation lies in the fact that the physical condition of the particles plays an important part in determining the value or otherwise of the product. Hence it is desirable that chemical analyses should be supplemented by practical tests.

The case of turpentine is interesting. This substance is generally regarded as a drier. According to W. N. Hartley,[1] however, it does not function as a carrier of oxygen to the oil. It only assists in the drying by reason of the fact that it dilutes the oil, rendering it thinner, so that it can be spread over a larger surface and thus come in contact with a greater quantity of oxygen. But whilst this is undoubtedly true, we must not lose sight of the fact that turpentine readily absorbs oxygen from the air, forming, as many chemists believe, an organic per-oxide, although this latter body has not as yet been isolated. It is easy to see, therefore, that the turpentine may act as a catalyser[2] or carrier of oxygen to the oil to a certain extent, even though the bulk of its action is admitted to be the natural result of dilution.

The drying action of litharge is somewhat more complicated than would appear at first sight. We have already seen[3] that caustic soda effects the decomposition of linseed oil, expelling the glycerine, and combining with the fatty acids to form a soap, which is soluble in water. A precisely similar reaction takes place with litharge, although more slowly, resulting in the formation of an insoluble lead soap, which dissolves in the rest of the oil, leaving a bright coat on drying. This gloss greatly enhances the value of litharge, therefore, as a drier.

Chemical Changes induced by oxidizing Linseed Oil.—Before we pass on to consider the best methods of testing the efficiency of the driers, let us try and gain an insight into the nature of the chemical changes resulting in the setting or hardening of linseed oil.

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[1] W. N. Hartley, *Journal Soc. Arts*, February 10, 1893.

[2] The catalytic action of turpentine is discussed by Lewkowitsch, in his "Chemical Technology," etc., 1909, vol. iii. p. 139.

[3] See p. 117.

As we have already seen, linseed oil is a compound of glycerine and certain unsaturated fatty acids, which latter are known under the generic name of linoleic acid; this name having been given at a time when the chemistry of linseed oil was less thoroughly understood than it is at the present day, and when its various fatty acids were regarded as one, since they had not been individually isolated and identified. We now know, however, that linseed oil is a glyceride of at least four different unsaturated fatty acids, although their relative proportions have not been determined with certainty. Thus, Hazura and Grüssner suggest the following composition for linseed oil:—

Oleic acid	5 per cent.
Linolic acid	15 ,,
Linolenic acid	15 ,,
*Iso*linolenic acid	65 ,,
	100

Fahrion,[1] however, gives the following proportions:—

Oleic acid	17·5 per cent.
Linolic acid	26·0 ,,
Linolenic acid	10·0 ,,
*Iso*linolenic acid	33·5 ,,
Other substances	13·0 ,,
	100·0

Lewkowitsch regards each of these results as doubtful, and suggests that the proportion of linolenic and *iso*linolenic acids amounts to 15·4 per cent. only. Now, each of these acids is capable of absorbing oxygen, as also are their glycerides, although the amount of that absorption varies in degree, being least in the case of the oleic acid glyceride, that is, *olein*, and greatest in the glycerides of linolenic and *iso*linolenic acids, which latter are known as *linolenin* and *isolinolenin*, respectively. The best drying oil, therefore, will be the one which contains the greatest proportion of the last-named glycerides, which yield hard, tough solids on oxidation, whose chemical nature is not as yet understood. Here, then, we may perhaps find

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[1] Fahrion, *Zeit. Angewand. Chemie*, 1903, p. 1193.

an explanation for the marked differences in drying power manifested by the linseed oils obtained from various sources. In addition to linolin and olein, which are but poor driers, linseed oil usually contains a small percentage of saturated fatty glycerides, such as *stearin* and *palmitin*, which are of a non-drying nature. It will be obvious, therefore, that all these substances will modify the hardness of the film of the oxidized oil, since they themselves remain practically unchanged for an indefinite period.

From the foregoing it is clear that the drying powers of linseed oil itself, quite apart from external conditions such as temperature, etc., will be dependent upon a large number of factors. The following are the chief :—

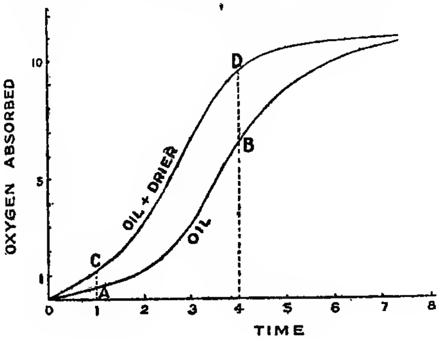
a. The particular variety of seed from which the flax plant is grown.
b. The soil in which the plant is cultivated.
c. The ripeness or otherwise of the seeds at the time of the oil extraction.
d. The method of oil extraction, whether by pressure or by a solvent.
e. The extent to which purification of the extracted oil has been proceeded with.
f. The age of the purified product.

No two different samples of oil may, therefore, be reasonably expected to behave exactly alike when placed under otherwise similar conditions, and the only fair way to test the efficiency of a drier is to compare it, using portions of the *same* sample of linseed oil, with other driers under standard conditions.

When two substances, capable of interacting chemically, are mixed, we usually find that the reaction proceeds vigorously at first, and then gradually slows up. When, however, linseed oil and oxygen are brought into contact, the absorption of oxygen is at first very slow, then it increases rapidly, and finally slows up again as the reaction nears completion. This is well shown by the curve (below) in which the absorption of oxygen by pure linseed oil is illustrated by the continuous line AB.

According to this, during the first two units of time, only one unit of oxygen was absorbed, whereas during the succeeding two units of time, nearly six units of oxygen were absorbed, making a total of seven.

How is this to be explained? A simple assumption meets the case. It is this: During the first few moments of contact the oxygen unites with the oil to form unstable organic complexes of the nature of per-oxides, which serve in some way as catalysers or carriers of oxygen to the remaining unoxidized portions of the oil. As oxidation proceeds, an ever-increasing amount of catalyser is formed, and the rate of oxidation is proportionately accelerated until the process nears completion, when of course it begins to slow up. Since the catalysers are formed from the oil itself, the process is known as "autoxidation," the prefix *aut* meaning "self."



In view of this theory of autoxidation, it is interesting to inquire in what way driers act upon the oil. The rate of oxidation of linseed oil containing a drier is shown by the line CD in the curve, from which it is clear that the action of the drier consists in shortening the initial slow period. This is precisely what we might expect, for if we add the catalyser to the oil instead of waiting for it, or a similar one, to be formed during the initial stages of oxidation, the reaction may very reasonably be expected to start away fairly rapidly right at the beginning.

Testing Driers.—It will now be evident, I trust, that, before a definite opinion can be pronounced as to the efficiency or otherwise of a drier, a series of experiments must be carried out under certain well-defined conditions. The time which a thin film of oil takes to set in such a way that it will just bear the dry finger being drawn across it without leaving a whitish mark, is known as the "setting value." The setting value of oil containing a drier indicates nothing by itself, as it is dependent upon so many variable factors. If, however, the same oil is used with different driers, but under otherwise precisely similar conditions, then a comparison of the setting values affords a very accurate method of determining the relative efficiencies of the driers used.

Let us for a moment consider what are the principal factors likely to affect the setting value of an oil independently of its containing a drier.

1. *Temperature.*—A rise in temperature assists the drying of the oil. For this reason it is often an advantage to paint and varnish exposed surfaces in warm weather.

2. *Light.*—The action of light is interesting. Sunlight assists the drying action, and also effects a certain amount of bleaching. It is not, however, the light itself which increases the rate of drying, for oil exposed to its action in sealed bottles, in the absence of air undergoes no change. It would appear, therefore, that the light stimulates in some unknown way the production of catalytic per-oxides, and thus shortens the initial slow period of oxygen-absorption, about which we have already spoken. Oil exposed under white or clear glass dries more rapidly than that under red glass.

All ordinary light, however, is accompanied by heat, but Genthe has prepared an electric mercury lamp which emits a uniform amount of light, with very little heat evolution. When enclosed in quartz glass it constitutes the so-called "Uviol" lamp, and experiments show that under its influence, raw oil and oil containing driers dry practically at the same rate.

Genthe[1] has patented a process for boiling oils under the influence of the light from his lamp, about 20 of which are

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[1] German Patent 195,663.

immersed in a tank containing one ton of crude oil. The whole is warmed to 176° F. (80° C.) and the lamps started. Air is now blown in, and the oil is stated to absorb about 5 per cent. of oxygen.

Prepared in this way the boiled oil is claimed to dry more rapidly than is usually the case, yielding a brilliant, varnish-like coating, free from stickiness.

3. *Moisture.*—This is an uncertain factor, but it is well known that a dry atmosphere is more favourable for outside painting than is a wet one. This is particularly the case with metal work, which is apt to condense a layer of moisture on its surface, and thus prevent an intimate contact being formed with paint or varnish afterwards applied.

Raw linseed oil dries more slowly in a moist atmosphere,[1] but when driers are introduced the subject becomes more complicated. Thus, for example, an oil containing a mixed manganese-lead drier is comparatively little affected in its rate of drying by the presence of moisture. Manganese driers are very curious in this respect. When more than about 0·05 per cent. of the metal is present in the oil in the form of a drier, drying takes place more quickly in dry than in moist air. Smaller quantities of manganese produce an entirely opposite effect.[2]

4. *Rate of Change of Air.*—The effect of this will be obvious, for a gentle circulation of the air brings fresh supplies of oxygen to the surface, and assists the drying action very materially.

5. *The Thickness of the Oil Film* is a factor which must not be overlooked. Obviously, if the film is thick the superficial layer oxidizes and sets first, whilst the underneath portion is still liquid. The determination of the setting value is thus rendered very difficult.

6. *The Surface to which the Oil is applied* has a good deal to do with the rate of drying. On metallic lead oil dries more rapidly than on glass, and a plausible explanation will at once suggest itself to you.

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[1] This is also true of the boiled oils, without regard to their age; see Lippert, *Zeit. angew. Chemie*, 1905, p. 94.

[2] See Lippert, *Chem. Zeitung*, 1900, p. 133.

Sufficient has now been said to show what a number of factors influence the rate of drying of an oil, and one need not be surprised at the consequent complexity of the subject. In order, therefore, to compare the drying powers of two or more driers, the need for carrying out the necessary tests under precisely similar conditions cannot be too strongly emphasized. The old method of noting the time taken by a thin film of terebine on glass to dry, and deducing therefrom conclusions as to its efficiency or otherwise, is grossly inaccurate and misleading. Any manufacturer who understands his trade can prepare terebines which will dry hard on glass in a very short time, and yet have no real drying efficiency. On the other hand, a terebine may be a very slow drier by itself, and yet work with great efficiency when mixed with oils, etc.

One of the most satisfactory and scientific methods of testing a drier is that detailed by Davidson in his interesting paper, to which reference has already been made.[1] Late in the afternoon mixtures of terebine and linseed oil are made up in the ratios of one part of the former to 5, 10, 15, 20, 30, 40, etc., parts of oil. These are placed in separate, stoppered bottles, and kept at a uniform temperature till the next morning, when they are ready for examination.

If a loose and flocculent precipitate is formed, the presence of lead is almost certain. A clotted precipitate indicates a faulty adjustment of the ingredients of the terebine, or faulty manipulation in its making, and is a bad sign. As a rule, manganese compounds do not give any precipitate unless present in excessive amounts. If both lead and manganese are present, the lead precipitate invariably carries down some manganese with it. Davidson remarks that he has come across extreme cases where the whole of the driers have been thrown down in clots, without having been absorbed by the oil. The resulting mixture had therefore no higher setting value than raw oil, and the value of the terebine was obviously nil.

The liquids are now filtered through paper into clean, dry bottles, and a portion of each is run on glass and put into an

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[1] See "The Action of Driers on Linseed Oil," by T. A. Davidson, read before the Paint and Varnish Society, Nov. 12, 1908.

air oven, kept at a constant temperature. After an interval of half an hour another set of tests is put in as a check. The first series is now examined from time to time by touching with the finger, until the film is sufficiently firm to bear the finger being gently drawn across it without leaving a whitish mark. It may then be regarded as set, and the time noted. Davidson finds it convenient to take a period of 10 minutes as his unit of time. If, therefore, a mixture takes 2½ hours—that is 150 minutes—to dry, its setting value is 15. His experiments were carried out at 100° F.; but the choice of such a temperature is, of course, purely arbitrary.

XVIII

RESINS AND GUMS

Resins.—In popular language, all exudations of trees are known indiscriminately as gums and resins. It is convenient, however, to distinguish between the two terms. Strictly speaking, resins are those products which are absolutely insoluble in water, but dissolve in organic solvents such as alcohol, turpentine, benzine, etc., whereas gums are either entirely or partially soluble in water. Of course it is difficult to draw a hard-and-fast line between the two groups, as is the case in every other system of classification, for substances always occur whose properties lie on the border line.

As a class, resins are brittle and lustrous. Those most suitable for varnishes are generally clear and nearly colourless. The majority are odourless, although a few, like benzoin, are characterized by an aromatic odour, which is by no means displeasing. For this reason several resins have been employed for centuries in the manufacture of incense. Chemically, resins are very complex, their constitutions being but poorly understood. They are more or less combustible, burning with a luminous, smoky flame, showing the presence of much carbon. They are almost all heavier than water.

As regards their solubility, the resins are both peculiar and interesting. Some of them, such as shellac, rosin, and sandarac, dissolve with ease in alcohol, benzene, etc., and are easily made into varnishes. Others are insoluble in all the usual vehicles until they have been fused by heat. They will then dissolve, and can be utilized for varnish making. Petroleum spirit is a poor solvent for resins, rosin and dammar being about the only two which dissolve in it.

Resin exudes from the tree in the form of drops. If it solidifies rapidly it naturally retains this shape. Mastic is a case in point, and it finds its way into the market in the form of small tears or drops. If solidification is slow the resin collects in knotty masses of various sizes and shapes. Such is the appearance of copal and dammar. Other resins, again, are artificially shaped before being sent into the market. Thus shellac occurs either in the form of thin flakes or as thicker "buttons"; gamboge is cast into cylinders; benzoin and elemi appear in blocks; and so on.

We will now consider the most important resins individually, and in alphabetical order.

Amber is a fossil resin of a yellow, semi-transparent appearance. It is occasionally found on the shores of Norfolk and the south-eastern counties, but the quantity is too small and uncertain to make its collection a profitable industry. The amber of commerce comes chiefly from the southern coasts of the Baltic, where it is washed ashore between Königsberg and Memel; and from Germany, Poland, Sicily, and Maryland in the U.S.A., where it is dug out of beds or mines. Amber was produced by a species of pine tree, and insects and vegetable matter are frequently found embedded in it, showing that it must at one time have been soft and viscous. The pieces found vary very much both in size and in quality. It is more valued in the East than in this country, probably because the Orientals regard it as a charm against disease. Nevertheless large pieces do not fail to realize very high prices. Amongst the royal jewels at Berlin in Germany is a piece of amber weighing 18 lbs. It is supposed to be the largest ever found.

The palest amber is most highly prized for ornaments, the darker varieties being used for varnish making. Its specific gravity ranges from 0·98 to 1·2. It is insoluble in water, ammonia, petroleum spirit, and benzene, but dissolves to a slight extent in absolute alcohol, ether, and turpentine. When just heated to fusion, and maintained at that temperature for a short time, amber is rendered soluble in the usual painters' vehicles, though not in alcohol. It then yields a very fine varnish, which gives a firm yet elastic coat, and offers a stout resistance to the action of the atmosphere. Its expense, however, militates against its extensive employment.

Amber is frequently adulterated with rosin; and insects, etc., such as occur in the genuine article are introduced into the mixture to increase the deception. Such adulteration can readily be detected, however, by determining the melting-point. Natural amber melts between 600 and 615° F., whereas the fictitious product has a much lower melting-point. Further, pieces of natural amber can readily be joined together after softening the ends with a solution of caustic potash, whereas fragments of the adulterated article unite only with difficulty after similar treatment.

When subjected to dry distillation amber yields inflammable gases, water, organic acids, and a volatile oil, known as amber oil, which forms about 23 per cent. of the resin. If the temperature is sufficiently high a solid residue of charcoal is left, amounting to 12 or 13 per cent. of the amber taken.

Animi is a pale, yellowish-brown resin, imported into this country chiefly from Zanzibar. It is a fossil resin, like amber, and is found in the surface soil, being collected during the rainy season, when the earth is soft and easily worked.

In its natural condition, animi is found covered with a red crust which is scraped off and unfolds the characteristic "goose skin" appearance of the pure resin, which is caused by the impression of the cellular structure of the tree in which it was originally deposited. Animi is an excellent varnish resin, and is used in making the best quality of coach varnishes. It is hard and brittle, with a specific gravity ranging from 1·04 to 1·07. It is very difficultly soluble in the ordinary solvents at the disposal of the painter, and is not attacked by caustic soda or by acids. Animi melts between 450° and 465° F., and loses from 20 to 25 per cent. in weight, yielding about 2 per cent. of water and some 18 per cent. of a brownish oil. The residue in the retort sets to a hard, transparent resin, soluble in turpentine, petroleum spirit, and benzene, as well as in hot linseed oil.

"Recent" or "virgin" animi is a similar resin, which is collected by Arabs from certain trees direct, or else picked up from the ground immediately beneath the same. It is inferior to the fossil variety, and is used in making poorer qualities of varnish.

Asphaltum is a blackish-brown solid, originally obtained from the shores of the Dead Sea. The most noteworthy source is the pitch lake at Trinidad, which yields two varieties known respectively as "Lake Pitch" and "Land Pitch." The former is the better, being soft, bituminous, and impregnated with gas, consisting essentially of carbon di-oxide and sulphuretted hydrogen. Land pitch appears to have been formed from Lake pitch by oxidation. It is harder, and free from gas. The natural products contain about 27 per cent. of water. The following analyses[1] of the water-free pitches may be taken as representative :—

	Lake pitch.	Land pitch.
Inorganic matter (ash)	36·56	37·74
Organic matter (not bitumen)	10·57	10·68
Bitumen	52·87	51·58
	100·00	100·00

Lake pitch softens between 180° and 192° F., and flows at from 189° to 210° F. Land pitch softens between 190° and 237° F., and flows at from 210° to 255° F. The natural product is refined by heating in stills, which expels the water, and causes a deposition of mineral matter, whereby "asphalt" results.

Asphaltum is readily soluble in coal-tar naphtha, and less so in turpentine. Such solutions may be used as black varnishes or paints, but the coat obtained is extremely brittle. This may be overcome by the use of oil and gums, when very serviceable japans and varnishes are obtained.

The Egyptians used it in embalming, under the name of

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[1] See "Chemistry for Engineers and Manufacturers," by Blount and Bloxam. Published by Chas. Griffin & Co., 1900, vol. ii. p. 124.

mumia, and it is recorded that the Babylonians employed it as a cement for building purposes.

Asphaltum is also made artificially by mixing together various kinds of pitch. This is useful for the preparation of cheap varnishes, provided it possesses the requisite drying power.

Benzoin or **Gum Benjamin** is the resin which exudes from incisions made in the stem or trunk of a small tree known to the botanist as *Styrax benzoin*, a native of Sumatra, Java, Borneo, Laos, and Siam. In Sumatra the tree is cultivated from seed, and in about seven years' time is ready to be cut. Each tree yields about 3 lbs. of crude benzoin annually, and the product of the first three years is the most valuable, being pale yellow in colour, soft, and possessed of a fragrant odour. As the tree advances in years the resin becomes darker in colour, and appreciably harder, so much so, that after about nine years it is not worth collecting.

The properties of benzoin vary slightly according to its source. The Siam variety is brittle, and possessed of a strong odour, something like that of vanilla. It is readily softened by heat, and is quite liquid at the boiling-point of water. According to Hager the specific gravity of Siam benzoin is 1·235.

Sumatra benzoin is somewhat greyer. Its odour is not so strong and it does not melt so easily as the Siam benzoin.

Benzoin is used to a slight extent in varnishes, to which it imparts its own odour. It is almost entirely soluble in alcohol, although turpentine and petroleum spirit dissolve but a small portion of it. With sulphuric acid a bright red colour is produced. When gently heated, from 9 to 20 per cent. of an organic body, known as benzoic acid, is liberated as white vapour, together with a small quantity of a volatile oil.

Copal.—Quite a variety of different resins are included under the generic name of copal, and, as might be expected, they vary very considerably in their properties. Some specimens are soft, and dissolve in ether, while others are hard and lustrous, requiring to be fused before they are capable of solution in the usual solvent vehicles. Much of the copal is imported from the West Coast of Africa, where it occurs at various depths up to about 10 feet under the soil. It varies in quality according to the district in which it is found. The following are the most important varieties on the market:—

Sierra Leone Copal is the finest quality imported from Africa, being hard and lustrous. Its specific gravity is 1·054, and its melting-point 400° F. After fusion it is soluble in the usual vehicles and yields a very durable and valuable varnish. If care is taken to use the almost colourless pieces, a pale varnish results.

Pebble Copal is found in rounded, water-worn pieces, closely resembling pebbles by the river side—hence its name. It is very hard, and has a specific gravity of 1·055, yielding a good varnish.

Demerara Copal is a product of the locust tree, which grows in South America, and is collected in much the same way as animi, whence its nickname "Demerara animi." It is frequently found in masses weighing 10 or more lbs., and in 1887 a lump weighing at least 60 lbs. was exhibited at the Manchester Exhibition. Its specific gravity is 1·03, and it melts between 450° and 465° F.

Java Copal occurs in resinous lumps with a milky appearance. It is not quite so hard as the African copals. Its specific gravity ranges from 1·03 to 1·04, and it melts at 347° F.

Manila Copal is the resin obtained from trees in the Philippine Islands, and exported chiefly from Manila. It is not a true copal, being very much softer. Its specific gravity is about 1·06, and it melts between 230° and 250° F. At higher temperatures a rose-red oil distils off, soluble in benzene and turpentine, and decidedly acid in its reactions.

The fused gum is much more readily soluble in the usual painters' vehicles than fresh copal, and is used in the manufacture of spirit varnishes and enamel paints.

Dammar.—This term includes several very similar, and often indistinguishable, resins which come principally from Siam.

White or *Singapore dammar* is obtained by incising a tree known to the botanist as *Dammara orientalis*, which grows in

Java, Sumatra, Borneo, etc. The resin is harder than rosin, but less so than copal. Its specific gravity ranges from 1·06 to 1·12. It is soluble in turpentine, petroleum spirit, and oil, but only partially soluble in alcohol.

The *Batavian dammar* is somewhat more soluble. Both yield a pale, hard varnish, which is used for coaches, cabinets, pictures, etc., and the microscopist frequently employs its solution in benzene for mounting his slides.

Rock dammar is a product of certain trees known by the generic name of *Hopea.* It is practically indistinguishable from the Singapore variety.

Sal dammar is obtained from the sal tree, which grows on the Himalaya Mountains, as well as in Borneo and Sumatra. Its specific gravity ranges from 1·10 to 1·12. It dissolves in benzene and turpentine, yielding a somewhat turbid solution.

Black dammar comes from India, where it is used for varnish making. As its name implies, it possesses a very dark colour, and is not used in this country for that reason. The trees from which it is obtained are known by the generic name of *canarium*, and yield, on the average, about 200 lbs. of resin each. During the hot season they are incised and set on fire below the cuts. This kills the tree, which is allowed to stand, and the resin which it now exudes for some years is collected. The specific gravity of black dammar is 1·09. It is soluble in turpentine, and when distilled yields considerable quantities of an oil resembling resin oil.

Dragon's Blood is a very suggestive name given to the resin obtained from the *Calamus draco*, a tree which yields the so-called rattan canes. The fruit, on ripening, is covered with a red resin, which is collected, melted, and cast into rolls or cylindrical sticks, rather more than a foot long, and about an inch in diameter. Most of the resin is imported from Eastern Asia, though small quantities of similar resins find their way into the market from Bombay and Zanzibar.

Dragon's blood has a specific gravity of approximately 1·2. It melts at 248° F. Though almost insoluble in turpentine, it dissolves in benzene, petroleum spirit, and shale spirit, and is used for colouring spirit varnishes a deep red.

Elemi.—Like the term Copal, Elemi is used to denote several resins. *Manila Elemi* is the most important, obtained from a tree known to botanists as *Canarium commune*, which grows in the Philippine Islands, being exported from Manila. When pure, it is white and soft, yielding on distillation 10 or 12 per cent. of an oil resembling turpentine. When heated to about 170° F. it begins to soften, and at 250° F. is quite fluid. Being soluble in alcohol and most painters' vehicles, it is used in varnish making, chiefly as a toughener. Its specific gravity is 1·2 when pure, but it is frequently adulterated.

Gamboge is a resin obtained from a Siamese tree known to the botanist as *Garcinia morella*. It is possessed of a reddish-yellow colour, and is obtained from the leaves and branches by bruising. The resin is allowed to thicken in cocoa-nut shells, and is afterwards made into rolls by pouring into moulds made of bamboo.

Gamboge is soluble in alcohol and ammonia, and is a drastic purgative. Water-colour artists use it as a pigment, and it is also employed in the colouring of varnishes. It is an ingredient of gold lacquers for brass work, which sometimes contain turmeric as well. Hurst gives the following analysis of a sample submitted to him, presumably from Siam:—

Moisture	2·50	per cent.
Mineral matter	1·05	,,
Resin, soluble in ether	66·05	,,
Wax, soluble in alcohol	4·31	,,
Gum	26·03	,,
	99·94	

Two Ceylon samples of gamboge analyzed by Christison yielded the following results:—

	I.	II.	
Resin	68·8	75·5	per cent.
Gum	20·7	18·5	,,
Woody fibre	6·8	0·6	,,
Moisture	4·6	4·8	,,
	100·9	99·4	

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[1] See J. Cameron, *opus cit.*

Gum Accroides is the resinous exudation of several Australian trees, and is used in preparing dark gold lacquers and yellow varnishes, both alone and in conjunction with gamboge. Several varieties are known, which are all soluble in alcohol, yielding yellow or red solutions. The specific gravity is about 1·20.

Kauri is an important resin found in New Zealand, and is a product of various species of pine tree. Like the copals, it is found at various depths below the surface. It is also obtained direct from the living trees, which bleed profusely when incised. The product thus obtained is distinguished as "young" kauri. In colour kauri varies but little, being a pale amber. Its specific gravity is about 1·05, and it melts at temperatures ranging from 360° to 450° F. When distilled it yields from 16 to 20 per cent. of oil, together with traces of water.

Lac[1] is one of the most important of all the resins, and we have already had occasion to refer to it in connection with the natural dyes. Lac has been known for centuries, and as early as 1563, a treatise was written upon it by Garcio de Orto, physician to the Portuguese Governor of India. Sixteen years later, namely in 1579, an Indian traveller, Christopher Acosta, drew attention to the fact that lac was frequently adulterated with a common resin and wax. Since those early days, the lac industry has become one of great importance. In 1901–2, the total export from India amounted to £640,352, and in 1907–8 reached the enormous value of £2,665,224, of which no less than £890,000 was purchased by the United States of America.

The lac trees are natives of the tropics, but they do not produce lac of their own accord, for the ordinary sap of the tree is quite a different substance. The secretion of lac is produced by a small insect known as *Tachardia lacca*, closely allied to the cochineal insect, which, in the larval or

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[1] See a most interesting paper entitled "Technical Notes on Lac," read by A. F. Suter before the Paint and Varnish Society on March 11, 1909, from which much of the information in this section has been culled.

caterpillar stage, punctures the bark of the tree, and assimilates the sap. A light yellow, resinous incrustation of lac collects around the bodies of colonies of these larvæ, completely encasing them. In the course of a few weeks the larvæ have developed into perfect insects, both male and female, the latter greatly preponderating in point of numbers. After impregnation, the abdomen of the females increases in size, and becomes filled with an intensely red fluid, known as *lac dye.* In another twelve or fourteen weeks a new brood of larvæ appears, which passes through an exactly similar cycle, with the production of fresh lac. As these cycles require only from four to six months for their completion, it will be clear that two, and even three crops, may be secured in a year, when the conditions are favourable.

As many as 87 different species of trees are known on which the lac insect grows wild. The palest variety of lac is obtained from *Schleicheria trijuga*, and under the name of *Nagali* is employed in the preparation of the finest **Lemon Lacs.** The product of *Butea frondosa* is much richer in colouring matter and is made up into **Garnet Lac.**

For a long time it was uncertain whether the irritation set up by the punctures in its bark caused the tree itself to produce lac, or if the latter was a product exuding from the insect. It has now been satisfactorily demonstrated, however, that the lac is the digested plant sap secreted by the insect.

The lac is collected by natives before the new brood of young larvæ has swarmed, and it therefore contains all the red colouring matter to which reference has been made. The natives simply cut off the twigs and leaves incrusted with the lac, and send them to the factory. Here the twigs are broken into short lengths, either by hand or machinery, and are termed **Stick Lac.** This is crushed and washed, the wood being entirely removed, and the lac is left as a more or less coarse, granular powder, known as **Seed Lac.**

Washing is the next process, which extends over 24 hours. The water becomes coloured with the dye at this stage, particularly if it contains a little sodium or potassium carbonate. The wet mass is dried by exposure to light and air, which effects a partial bleaching, and adulterants, such as rosin, are added, which lower the melting-point of the lac. Yellow arsenic or orpiment, ground to a fine powder, is sometimes admixed to render the lac opaque, and impart a rich straw hue.

The mixture is now melted in cloth bags, and squeezed out in the liquid condition into troughs of warm water. Pouring or ladling on to a revolving cylinder effects its solidification in the form of thin, irregular sheets, which are stripped off with a knife and sent into the market as ordinary **Shellac.**

Sometimes the molten lac is allowed to solidify in round, flat buttons, which, owing to their thickness, appear to be of a dark brown hue. This form is known as **Button Lac.**

Bleached Lac, or **White Lac**, is obtained by decolorizing a solution of shellac in an alkaline solution by means of bleaching powder. The result, however, is not very satisfactory, and white lac frequently contains appreciable quantities of the bleaching agents, which have not been properly washed out.

Good shellac has a pale orange colour, and is known as **Orange Shellac.** The specific gravity ranges from 1·1 to 1·2, the darker varieties showing the greater density. It is used as an insulator in electric work, and also in the manufacture of knotting varnish.

Mastic is the resinous exudation of the lentisc tree or shrub, which grows in the lands bordering the Mediterranean Sea. The tree grows to a height of some 4 or 5 feet, and will yield 8 or 10 lbs. of mastic per annum.

As imported into this country, mastic has usually the form of small tears or pear-shaped drops of a pale yellow hue. The resin is brittle, and softens when placed in the mouth—a property which serves to distinguish it from sandarac. It is, therefore, used in Turkey and elsewhere as a chewing gum. Its specific gravity varies from 1·05 to 1·06, and it melts between 221° and 248° F. Though soluble in alcohol and turpentine, it will not dissolve in petroleum spirit. It is used in making picture varnish—a combination of which with boiled linseed oil constitutes *megilp.*

Rosin is the solid residue left behind in the stills after the extraction of turpentine from the crude resin of the pine trees. The best qualities are pale in colour, and perfectly clear, containing a small quantity of water. Its specific gravity varies from 1·04 to 1·10. It softens at 177° F., or thereabouts, and at the boiling-point of water is quite fluid. Though only moderately soluble in alcohol, it readily dissolves in benzene and naphtha, and is used in making the cheaper kinds of varnish.

Sandarac, also known as **Gum Juniper,** is obtained by incising the bark of certain trees growing in North Africa. It is yellowish-white in hue, hard and brittle. At 300° F. it melts, and its specific gravity ranges from 1·038 to 1·044. After fusion it is readily soluble in oil, and is used in the manufacture of both oil and spirit varnishes. It is also one of the ingredients of incense.

In the following table are given the specific gravities of the

Name of Resin.	Specific gravity.	Melting-point, °F.
Amber	0·98–1·20	600–615°
Animi	1·04–1·07	450–465°
Asphaltum—lake	1·38	189–210°
,, —land	1·43	210–255°
Benzoin—Borneo	1·16–1·17	170–212°
,, —Penang	1·14–1·16	170–212°
,, —Siam	1·24	170–212°
Copal—Angola	1·06	—
,, —Demerara	1·03	450–465°
,, —Java	1·03–1·04	347°
,, —Manila	1·06	230–250°
,, —Pebble	1·055	—
,, —Sierra Leone	1·054	400°
Dammar—Batavian	1·06	260–300°
,, —Black	1·09	—
,, —Sal	1·10–1·12	—
,, —Singapore	1·06–1·12	260–300°
Dragon's blood	1·20	248°
Elemi	1·02	170–250°
Gamboge	1·03	—
Gum accroides	1·20	—
Kauri	1·05	360–450°
Lac	1·10–1·20	—
Mastic	1·06	221–248°
Rosin	1·04–1·10	117–212°
Sandarac	1·04	300°

various resins which we have just considered, together with their approximate melting-points. Many of the resins have no distinct melting-points, for, on being warmed, they gradually soften like pitch or butter, and it is impossible to fix upon any one temperature, and say that below this temperature the resin is a solid, but above it a liquid. Some of the resins, on the other hand, have a decided melting-point which can be determined with ease; but it is not always constant for different samples. This is true also of their specific gravities.

Gums.—As I have already explained to you, gums are those exudations from trees which set to more or less hard masses, and are either partially or wholly soluble in water. They are used in the making of water varnishes, and also as binding agents in water-colour painting and distemper work.

Gum Arabic is the product of several species of *Acacia*, widely distributed throughout Africa, Asia, and Australia. The name is unfortunate, as very little of the gum, if any, now comes from Arabia. It occurs in roundish pieces, sometimes colourless, at other times decidedly brown in appearance. It consists essentially of a compound of arabic acid (a complex organic derivative) and lime, known as *arabine.* When boiled with dilute sulphuric acid, sugar is obtained. It is completely soluble in water, the best varieties requiring only 1½ times their weight of that liquid. They then yield a sticky mucilage, of considerable value to the stationer and others.

Gum Tragacanth is the exudation from a group of trees known by the generic name of *Astragalus*, growing in Asia Minor, Syria, Persia, and elsewhere. It occurs both in form of leaf and in long round masses. It is not soluble in cold water, but swells up to a gelatinous mass when boiled for some time. Alkalies dissolve it, but not alcohol. It is not used to any extent as a varnish gum, but is applied as a thickener in calico printing.

A few other substances used in varnishes may be conveniently considered at this point, though strictly speaking they are not true gums.

Dextrine or *British Gum* is prepared by gently heating starch either alone or with a small quantity of acid. When pure it is a white, tasteless powder, soluble in water, yielding a sticky fluid, which is used largely as a substitute for gum arabic. It dries with a fair amount of gloss, and is therefore used in water varnishes. When boiled with water, particularly if a little acid is present, dextrine is gradually converted into sugar.

Gelatine is extracted from bones and hide-fibre—chiefly the latter. The hide is digested with dilute caustic soda to remove the fat, after which it is well washed and bleached. It is now subjected to the action of water and steam, whereby a solution of gelatine is obtained. This is strained whilst hot, and run into cooling troughs. When the mass has set it is cut into slices and carefully dried.

Gelatine contains from 0·5 to 2 per cent. of ash. It consists of carbon, nitrogen, hydrogen, oxygen, and sulphur, united together in a very complex manner, not yet understood by chemists.

Glue is a coarser form of gelatine, and is prepared from animal bones. These are steeped in dilute hydrochloric acid until they are thoroughly soft, owing to the removal of the calcium phosphate. They are then washed and steamed under pressure. The glue and fat are run off at intervals into settling tanks, where the fat rises and is skimmed off. The glue is boiled down, and dried in a similar manner to gelatine.

Size is prepared like gelatine, but from rougher material. Gelatine is used in making varnishes. It dissolves in water when boiled, forming a thick, sticky liquid, which sets on cooling. It may be rendered insoluble in water by the addition of a little potassium bi-chromate, and subsequent exposure to light—a property which renders it possible to prepare water-proof varnishes from gelatine.

Albumen is the main constituent of the so-called "white of egg," from which it can be obtained by drying. It is soluble in cold water, but on raising the temperature it coagulates, forming a white, insoluble mass, familiar to you all as the "white" of a boiled egg. It is used in calico printing and in water varnishes.

XIX

VARNISHES

VARNISHES are usually more or less transparent liquids applied to the surface of a body to protect it from the destructive action of air and water, and, at the same time, to add a lustrous and glossy finish.

Sometimes varnishes are coloured by the addition of dyestuffs, such as turmeric and gamboge. The various natural varnishes known as lacquers, owe their colour and opacity to their chemical constitution. The bulk of the varnish used, however, is nearly colourless, and therefore does not obscure the colours of the undercoatings of paint.

A varnish consists essentially of the solution of a gum or resin in a liquid vehicle, to which driers may or may not be added as circumstances allow. The solvents employed are the ordinary vehicles which we have already studied in detail. We may, therefore, pass on at once to a consideration of some of the methods adopted by the manufacturers of to-day for the preparation of varnishes.

Oil Varnishes.—Oil varnishes consist of a solution of resins in a drying oil, linseed oil being the one generally employed. I have already drawn your attention to the fact, however, that most of the resins are insoluble in linseed oil in their natural condition, and require a preliminary fusion. This is known in the trade as *Gum Running*, and is effected in large cylindrical vessels, known as "gum-pots," and made of copper. They are usually constructed of two pieces, namely, a cylinder of sheet copper, and a cast copper bottom. These are bolted together through their flanges, as shown in Fig. 17.

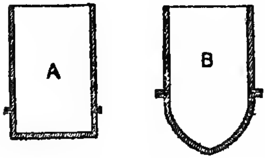

FIG. 17.

London gum-pots have a flat bottom, but those in the North of England are conical in shape, which latter device enables the gum-runner to ascertain more readily with his stirrer when the whole of the gum has been melted, as there are no corners for solid particles to get lodged in. The pot rests by means of its flange in a suitable hole in the top of the furnace, which top forms the floor of the gum-running shed. During the process of fusion acrid vapours escape from the resins, and are carried by means of a hood into a chimney. The operation is expensive, for the resins are often costly, and lose from 5 to 20 per cent. in weight. The actual temperature to which the resins must be exposed, and the length of time necessary, will naturally vary with the specimens used, and the particulars are retained by manufacturers as trade secrets. Attempts have been made to overcome this loss by trying to effect the solution of the natural resin in oil under pressure. The experiments, however, have not hitherto proved completely successful.[1] The unheated resins will usually dissolve with ease in turpentine; and linseed oil, as you know, will mix with the latter in any proportion; yet varnishes cannot be made in this way; for, though the liquid is clear at first, turbidity appears as soon as the turpentine begins to evaporate, linseed oil not being mixable with a concentrated solution of the resins.

During the process of running, a good deal of frothing always occurs, due probably to the escape of water from the resin. This is a source both of loss and of danger to the manufacturer, inasmuch as the frothings are liable to catch fire. To minimize this risk as far as practicable, the gum-pots are made considerably larger than is necessary to merely hold the fused gum manipulated in any single run.

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[1] But see the interesting paper entitled "Recent Progress in the Manufacture of Oil Varnishes without Previous Fusion," read by Ch. Coffignier before the Paint and Varnish Society on June 3, 1909.

Whilst the gum is being run, the oil is heated for an hour or two at about 500° F., and, when all is ready, the requisite quantity is poured into the gum-pot, under vigorous stirring. When the whole has been properly mixed it is run out into a large iron vessel or tank, of some 600 gallons capacity, and capable of holding the contents of several gum-pots. The temperature is maintained at from 450° to 500° F., until the varnish has become clear and stringy. It is then cooled somewhat and thinned with turpentine, after which it is stored for several months, or even a couple of years, to clear and age. During this time any insoluble particles sink to the bottom, and a more transparent and easily worked liquid remains.

For pale varnishes pale resins must obviously be used, and care must be taken not to allow the temperature to rise too high, otherwise darkening is the inevitable consequence.

The chief objects in using varnish are to protect the surface over which the varnish is spread, and to effect a lustrous and glossy finish, though this latter is regarded by some as being of minor importance. In fact, not a few decorators prefer egg-shell gloss or matt effects, and are therefore in the habit of "cutting down" an oil varnish surface with pumice and water in order to obtain a so-called "flat surface." Many painters imagine that one coat of varnish should be ample. A moment's consideration, however, will show that this is expecting too much. The first coat is thinned very largely by absorption into the varnished surface, as well as by partial evaporation of the liquid vehicle, and it is not until a second or a third coat has been applied that the varnish can be relied upon to adequately fulfil its function as a protector.

It may be urged that, in many cases, a painted surface is so hard and non-absorptive, that two coats of varnish should not be necessary, and, indeed, are not desirable. It must be remembered, however, that oil varnish is a very searching and softening material, and its first application very frequently softens and renders astonishingly absorptive a coat of paint which, to all appearance, was originally hard and impermeable.

The actual quantity of the varnish used should vary with the number of the coat. Thus, a first coat on bare wood may be comparatively freely applied, for absorption will be at its maximum. Succeeding coatings should, of course, be more sparing in character; but the careful painter will soon learn by experience what varnish to apply in special cases, and how best to apply it.

The amateur varnisher is sure to have trouble with his work at some time or other. This may be due to the use of faulty materials, in which case he may or may not be himself to blame. Usually, however, the trouble arises from the manner in which the varnish has been applied. The following points may, perhaps, prove of service to some.

Blooming.—This occurs mostly on exterior work, sized wood, and in new buildings which have not become thoroughly dry. Particularly is this to be feared where iron work has to be varnished, for the metal is very apt to condense moisture on its surface. It is advisable to varnish such, therefore, in a warm atmosphere if practicable. In any case, the surfaces should be rendered as dry as possible before the application of the varnish. Although blooming is often a sign of imperfect boiling in the varnish, it may occur with good material, particularly when applied over many of the red lakes now on the market under a variety of names such as, "Permanent Red," "Fast Red," etc.

Cissing is the name applied to a tendency manifested by paints and varnishes to curl up from the surface to which they have been applied. This may be caused by the presence of grease on the original surface, or by the excessive use of terebine. If the quality of the varnish is good and the surface carefully cleaned before the application by a vigorous rubbing down with a damp wash-leather, cissing is not likely to occur.

Cracking is a frequent source of annoyance to painters, and is not infrequently caused by the use of strong glue size under the varnish. Excess of terebine and the application of varnish to an undercoat not thoroughly hard, will produce similar trouble. If the cracks are very fine so as scarcely to be distinguishable by the naked eye, *silkiness* is produced.

Peeling is mainly due, in ordinary cases, to the use of an inferior varnish, containing a high percentage of rosin. It will also occur with good varnishes on glass surfaces, exposed to changes of temperature.

Pitting or Pinholing is generally caused by air bubbles in the varnish, though a greasy surface may effect the same trouble. By allowing the varnish to settle and let loose its air before continuing the work, the difficulty in the former case will be met. The remedy in the latter case is obvious.

Ropiness is due chiefly to bad workmanship. If the varnish is quick setting, a quick application is necessary.

Running usually follows in the wake of hurried work, and is due to an irregular spreading of the varnish over the surface to which it is applied. A little extra working will suffice to remove any running, provided the varnish has not set. In the latter case the varnish should be removed by rubbing with rag soaked in benzine, and the surface varnished again more carefully.

Tackiness may be caused in a variety of ways. Cheap varnishes containing rosin oil, which is a wretched drier, are almost sure to be tacky. Lack of cleanliness, and application of varnish to surfaces not thoroughly hard, will produce a similar effect, as will excessive cold or heat. If dirt or grease is the cause, a thorough cleaning off with a paint remover is often necessary. In other cases, coat thickly with a mixture of whiting and water, and after a day or two, wash off thoroughly and re-varnish.

Wrinkling.—If this occurs at all, it happens immediately after the coating has dried, and is due to too heavy an application of varnish. The best cure is to rub off and re-varnish more sparingly.

Yellowing is particularly noticeable when white surfaces have been varnished, and may be caused by excess of driers, but is more often the result of employing inferior varnishes. In dark rooms the yellowing is more in evidence, since light tends to act as a bleaching agent. Where pure white is required, it is better to use a white enamel, as even the palest varnishes have a creamy tint.

Sometimes varnish turns *whitish* from a variety of causes. It may be the result of its surface breaking up into powder, in which case the material itself is at fault. The remedy is obvious. A coating of rosin under the varnish is a second and frequent cause. New woodwork is often primed with spirit varnish to prevent suction. Now the spirit varnish contains rosin, and leaves a brittle coat behind, when the liquid vehicle has evaporated. The remedy in this case is twofold.

1. See that the spirit varnish does not contain rosin merely, in addition to the liquid vehicle.
2. Let the priming coat be just thick enough to sink into the surface of the woodwork, and not to leave a layer of brittle material in addition.

Enamels.—Enamels are compounded of oil varnishes and pigments, such as lead oxide, zinc oxide, iron oxide, etc. They receive their name from the fact that they dry with the formation of a skin having an enamel-like gloss. The varnish oils are ground up with the finely levigated pigment until free from grit, and thinned with turpentine. On account of the resins present, enamels offer a surer protection than the corresponding paints. Asphaltum is used in the preparation of black enamels. Charcoal should be avoided as it retards the drying. It should be borne in mind, however, that a quick-drying enamel will neither work so well under the brush, nor last so long as those which dry more slowly, for it soon cracks.

Spirit Varnishes.—Spirit varnishes consist essentially of solutions of various resins in volatile organic solvents, other than oil, such as methylated spirit and turpentine.

The method adopted in this country for their preparation is the essence of simplicity. The resins are mixed with the solvent and kept in a warm place or gently heated until completely dissolved. Great heat must not be applied owing to the volatility of the spirit, which would involve great loss, and to the danger arising from the inflammable nature of the evolved vapours. When methylated spirit is used it cannot be too strong, and should not be weaker than 64 over proof.

There is a tendency for spirit varnished work to crack. This is particularly the case with wooden surfaces, and is caused by the wood expanding more than the varnish. It may also be due to the varnish having been applied over an oil varnish or oil paint. Unfortunately there is no satisfactory remedy.

Certain hard woods exhibit a lack of "key" towards spirit varnishes, and chipping is the result. Thick spirit varnish is especially liable to chip and should therefore be avoided, at any rate in the first coating.

Water-Varnishes.—These are chiefly solutions of gum or gelatine in water. Glue varnish is made by dissolving glue in water, and if, just before use, a small quantity of potassium bichromate is added, the coat is rendered almost waterproof.

Natural Varnishes.—A number of trees occurring in the Far East yield a sap, capable of drying hard, and used largely in the production of lacquer ware, for which India, China, and Japan are noted. The trees only yield a few ounces of lacquer, and the tapping generally kills them, although, if care is taken, fresh tappings may be made at intervals.

Crude lacquer is a liquid of creamy consistency, which on prolonged exposure to the sun becomes quite black, and loses its power of drying. If, on the other hand, water is mixed with it two or three times a day, and evaporated off in the usual manner, the lacquer acquires the property of drying. These remarks apply to the Chinese and Japanese lacquers, which are identical. Indian, Ceylon, and Burmese lacquers are similar, the last named being a thick, viscid liquid, having an odour like turpentine.

XX

TESTING PAINTERS' MATERIALS

ALL through the ages it has been well recognized that good things are liable to adulteration and unworthy imitation. One need not be surprised, therefore, to find that painters' materials form no exception to the rule. A remarkable example of this is afforded by vermilion, to which reference has already been made in an earlier chapter (see p. 37). This pigment was originally known as *minium*, a term now applied exclusively to *red lead*, which latter was extensively used to adulterate the more costly vermilion, the name having passed from the pigment to its adulterant. It is therefore extremely important that practical painters and colour mixers should be able to test their materials in a simple but effective manner, and thus guarantee themselves against fraud, failure, and disappointment.

Complete quantitative analyses of paints, oils, varnishes, and the like, are work for the expert chemist, but such are rarely needed by the average painter. It is hoped, however, that the following remarks will enable even the amateur to test his materials with ease and certainty to an extent sufficient for all ordinary purposes.

1. **Chemical Purity of Pigments.**—The characteristic reactions of most of the common pigments, together with tests for their usual adulterants, have already been given in the preceding chapters, and reference should be made to these.

2. **Testing Liquid Vehicles.**—Liquids may readily be tested for specific gravity and flash-point, as these two constants are greatly affected by the presence of impurities. A simple method for the determination of the flash-point has already

been detailed (see p. 121). The specific gravity is most easily measured with a hydrometer (see Fig. 18). This instrument consists of an oblong glass bulb, weighted at one end with a small bulb of mercury, whilst the other end is attached to a glass tube or rod, bearing a graduated scale. The liquid to be tested is placed in a tall, narrow jar, and the hydrometer allowed to float in it, with the mercury bulb downwards, without clinging to the sides. The division on the scale exactly on a level with the surface of the liquid is noted, and the number corresponding thereto is the specific gravity required. Since, however, the specific gravity varies with the temperature, the experiments should be carried out at as near 60° F. as possible. This is the more necessary when very accurate results are required, as is the case when only small quantities of an adulterant are to be looked for, and correspondingly small changes in specific gravity may be expected.

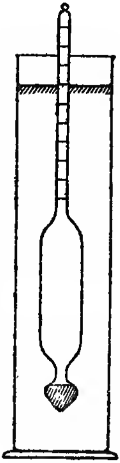
FIG. 18.

3. Analysis of Paint.—It is often necessary to determine the quality of the oil, and the nature of the pigment contained in a given sample of paint. If the latter is moderately liquid, on allowing to stand practically the whole of the solid pigment will settle to the bottom, and the supernatant oil may be poured off, and, if desired, tested for its specific gravity, in the manner already indicated. The pasty mass left behind should now be thoroughly mixed up, and a convenient portion (about ½ oz.) transferred to a glass beaker, and stirred with about 2 ozs. of ether. The mouth of the beaker is now covered with a glass plate, to prevent excessive evaporation of the ether, and the pigment allowed to settle. The liquid is then poured off, and a fresh supply of ether added. After the process has been repeated some two or three times, the pigment is transferred by means of a bone knife or *spatula*, to a pad of blotting or filter paper, and dried by gentle pressure, the filter paper being renewed as occasion requires. The dried pigment should now be exposed to the air in a warm place for a few minutes to expel the last traces of ether, when it is ready for examination, as indicated above (see § 1). As ether is excessively inflammable and volatile, it should never be used in the neighbourhood of a naked flame or fire.

If the paint is stiff to begin with, the oil required for examination cannot be obtained by merely allowing the paint to stand, as the pigment would take far too long to settle. It must be extracted with ether, a larger amount of the paint being taken, and treated but once, as indicated above, with ether. The latter is poured into a porcelain basin and allowed to evaporate, either of its own accord, or by floating the basin in a large vessel of tepid water. When the bulk of the ether has been expelled, and an oily residue remains in the basin, the latter is placed on the top of a water bath containing boiling water. For this purpose an ordinary water-tight tin can may be advantageously used (see Fig. 19) supported on a tripod stand, and heated by means of a Bunsen burner. The last traces of ether are thereby expelled, though the process may be considerably accelerated by allowing the oil to flow over the inside surface of the basin, thus exposing a relatively large and thin area to the atmosphere. When entirely free from ether (as may be ascertained by the smell) the oil must be tested for its specific gravity. As the quantity is too small to admit of testing with a hydrometer as shown in § 3, the following method may be adopted.[1]

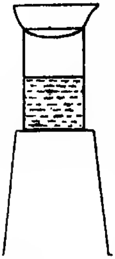

FIG. 19.

Prepare a mixture of equal parts of strong ammonia, of specific gravity approximately 0·88, and water, and determine the specific gravity of the mixture with a hydrometer in a tall glass jar. Add water or ammonia, whichever is required, in small quantities at a time, stirring well after each addition, until the specific gravity is exactly 0·932. Now take a drop

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[1] This is taken from "Simple Methods for testing Painters' Materials," by A. C. Wright. Published by Scott, Greenwood and Son, 1903, p. 103 *et seq.*

of the oil extracted from the paint out of the basin by means of a glass rod, and allow it to fall into the ammonia in the jar, care being taken to ensure that it takes no small bubbles of air with it. If the drop rises to the surface of the ammonia, its specific gravity is less than that of the ammonia, and is consequently not pure linseed oil (see p. 118). If, on the other hand, the oil sinks to the bottom, it may be regarded as pure, provided the odour of rosin oil cannot be detected. The actual specific gravity of the oil can obviously be determined by adding ammonia or water to the jar, as occasion requires, until the drop remains suspended in the liquid, without either rising or falling. It has then the same specific gravity as the ammonia, and this may now be determined by the hydrometer.

4. **Analysis of Varnish Paints and Enamels.**—The pigments and varnish contained in varnish paints and enamels may be extracted in a similar manner to that already indicated for the analysis of ordinary paints, save that benzene is used instead of ether.

5. **Spreading or Covering Power of a Pigment.**—It is not easy to determine with accuracy the covering power of a pigment, for this cannot be expressed in absolute numbers, as can the chemical composition. We are therefore forced to take a standard pigment, and compare all others with it, those which admit of being spread over a larger area being regarded as having a proportionately greater covering power. Equal quantities, by weight, of the pigments are thoroughly mixed with just sufficient oil to render them suitably fluid, and either spread out with palette knives or painted with similar brushes on panels or tiles in layers of uniform thickness. The spreading powers of the pigments are then roughly proportional to the areas covered.

In the following table[1] are given the relative covering powers of a series of white pigments, taking Orr's patent zinc white as the standard, namely 1000.

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[1] These numbers are calculated from the results obtained by Hurst, quoted in his "Painters' Colours," etc., p. 313.

Orr's patent zinc white	1000
Gypsum	960
Zinc white	768
Barytes	763
White Lead Co.'s white lead	747
Gardner's white lead	704
White lead (Dutch process)	507
Lead sulphate	427

Rash conclusions as to the value of a pigment should not be made on the ground of its covering power, for many otherwise excellent pigments give relatively low results when tested in this way, whereas not a few inferior pigments yield high values.

6. **Body.**—By "body" is meant the power possessed by a pigment of blocking out from view the surface over which it is spread—a property quite distinct from and independent of the covering power, although these two terms are often regarded as synonymous (see p. 22). Here again only relative values can be obtained, one pigment being taken as the standard. Equal weights of two or more pigments are separately mixed with equal quantities of oil, and painted or spread over equal areas of a dark panel. That pigment which most completely hides from view the surface of the panel is said to possess the greatest body.

To make a definite comparison which can be expressed in numbers, however, the pigments are mixed with varying quantities of oil, until the resulting paints possess equal body when painted with uniform thickness. The body of the individual pigments will then be directly proportional to the amounts of oil required. Thus, supposing one pigment, B, is mixed with 1 oz. of oil, and a second pigment, A, requires 1·25 oz. of oil to render the resulting paint equivalent in body, the latter pigment has the better body in the proportion of 1·25 to 1. Taking the pigment A, therefore, as the standard and calling its body 1000 units, that of B is given by $\frac{1}{1\cdot25} \times 1000 = 800$.

As it is not always easy to ensure that the paint is spread with uniform thickness in the two cases, and the value of the experiment depends almost entirely upon the accuracy with which this is done, the method should be varied as follows, a different set of experiments being carried out and the results compared in the two cases. The average value obtained will be very near to the mark.

Instead of varying the amount of oil, the weight of the pigments mixed with the *same quantity* of oil is varied, and the resulting paints spread uniformly over *equal areas of panel.* The body of the pigments will then be *inversely* proportional to their weights, when the resulting paints manifest equal body.

Thus, suppose 1 oz. of pigment A, when mixed with a certain amount of oil, yields a paint equal in body to that produced by compounding 1·25 oz. of the pigment B with an equal quantity of oil. The former pigment has the greater body in the proportion of 1·25 to 1. That is to say, if we regard as before the pigment A as the standard, and call its body 1000, that of B is given by $\frac{1}{1.25} \times 1000 = 800$, which is the same result, and serves as a check on the accuracy of the two methods.

Some pigments slowly lose their body or opacity after they have been mixed with oil. A notable example of this is white lead, and the explanation of the change has already been given (p. 60).

7. Permanence.—As is well known, many colours are extremely fugitive and therefore useless as pigments, whereas others are moderately permanent, and yet others as unalterable and inert as can be desired. The value of a pigment will thus be largely determined by its permanence, and it is not surprising that numerous experiments should have been carried out at various times by different investigators with a view to determining the relative permanence of the commonly used pigments.

A very simple, effective, and reliable method is to mix the pigments to be tested with water containing a little gum or glue, and paint them on to pieces of unglazed cardboard, such as Bristol board. Two or more of such cards are prepared, and one is placed in a dark, dry place, whilst the others are exposed to varying influences. One may be hung in a place where it is exposed to a maximum amount of sunlight and air. After a week or two the cards may be compared, and any change in hue, tint, or shade noted. Some colours may be altered in a few days, others in a few weeks, whereas others will undergo no change in several years. The condition of the air—moist or dry—should also be noted, since moisture has a very important action upon many pigments.

Other cards may be exposed to the action of sulphuretted hydrogen, ammonia, carbon di-oxide, etc., as these gases are to be found in the atmospheres of our great manufacturing towns and cities.

By far the most important series of experiments carried out on these lines, which have as yet received publication, are those detailed by Russell and Abney in their report to the Science and Art Department in 1888, and published in the form of a Blue Book, entitled " Report on the Action of Light on Water Colours."

The first series of experiments, which extended from May, 1886, to March, 1888, were made with strips of Whatman's paper, painted with various pigments ground in pure water, and exposed in glass tubes, open at both ends, to the action of light and air. The general results are given in the following table, the pigments being arranged in the order of their stabilility, the most fugitive being placed last. The pigments italicized were found to have distinctly altered either in depth or in hue by a much shorter exposure, namely, from May to August, 1886.

No change exhibited
Prussian blue
Chromium oxide
Terra verte
Burnt sienna
Venetian red
Indian red
Raw sienna
Chrome yellow

Yellow ochre
Burnt umber
Emerald green
Vermilion
Madder lake
Antwerp blue
Sepia
Cadmium yellow

Indian yellow
Vandyke brown
Gamboge
Indigo
Naples yellow
Crimson lake
Carmine

In another series of experiments the pigments were exposed in sealed tubes containing air and moisture. All the organic pigments were destroyed thereby, including even Prussian blue and Antwerp blue. When both moisture and oxygen were excluded, however, practically all the pigments remained unaffected, the principal exception being vermilion, which became black, as during the other trials. This latter change, however, is physical rather than chemical, as we have already seen in an earlier chapter (see p. 35).

8. **Durability.**—Although the terms "durability" and "permanence" are frequently regarded as meaning one and the same thing, it is advisable to distinguish between them (p. 10). Whilst permanence may be understood to refer to the hue, durability applies to the power of the pigment to wear well and protect the surface to which it has been applied, independently of any fading or discoloration which it may have undergone. Thus zinc oxide is much more permanent than white lead, its pure white colour remaining unaltered for an indefinite time. Owing to its comparative lack of durability, however, it is used chiefly for inside work, the more durable, though less permanent, white lead being used for exterior decoration.

The durability of a pigment is affected to a great extent by a variety of factors, not the least of which are the nature of the surface to which the paint is to be applied, and the conditions under which the paint will have to exist. Whilst, therefore, it will generally follow that the greater the chemical inertness manifested by a pigment, the greater will be its durability, this is not always the case, since paints which are specially suited for one class of work may be practically worthless under altered conditions. The best method of testing pigments, therefore, is to make up the paints carefully and give them longer or shorter trials on panels, etc., under conditions similar to those to which the paint will finally be subjected, when the most satisfactory mixture has been determined.

In making these trials, however, it is important that the following points be attended to, otherwise widely divergent and contradictory results may be obtained:—

(*a*) The surfaces painted should be perfectly dry, otherwise the film of moisture will prevent perfect adherence of the paint, which latter will tend to peel off. This is particularly the case where metal work, such as iron and steel, has to be painted.

(*b*) The different pigments should be mixed with liquid vehicles (oil, turpentine, etc.) from the *same* bottle or tanks, so as to avoid any error caused by variation in the quality of the same. The importance of using samples from the same stock of oil in the testing of driers has already been emphasized (see p. 159), and the same remarks apply with equal force in the present case.

(*c*) The durability of a pigment depends very largely upon the manner in which the paint is applied. The very best of paints when applied by a clumsy workman in thick uneven layers, will give most unsatisfactory results. Successive coatings should be applied, with reasonable care, uniformly, and of a thickness or thinness which experience proves to give most satisfactory results.

(*d*) A very important factor governing the value or otherwise of a pigment, is its state of fineness, and the degree of intimacy with which the pigment has been amalgamated with the liquid used as vehicle.[1] This is a point which is frequently overlooked, nevertheless there can be no doubt that even a pigment of inferior quality may, if thoroughly ground and incorporated with the liquid vehicle, yield a more durable paint than superior pigments less carefully treated.

Although by rubbing between the fingers a rough comparative examination of two or more pigments may be made, a more reliable guide is that obtained by the use of the microscope. A little of the powder is placed on a small glass slide, and viewed through a microscope carrying a $\frac{1}{4}$ inch objective, a little water or oil being used as a flux. If the microscope is fitted with a scale ruled to $\frac{1}{1000}$ths of an inch, the actual diameter of the particles can be measured. As these will vary considerably a number of measurements must be made, and the average taken. J. Cruickshank Smith has arrived at the conclusion that a pigment may be regarded as finely ground when :—

(1) The mean diameter of the smallest particles does not exceed 5·0 microns, that is 5 $\bar{\text{m}}$.[2]

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[1] See the interesting paper on "The Physics of a Pigment," read by J. Cruickshank Smith, before the Paint and Varnish Society, May 13, 1909.

[2] 1 $\bar{\text{m}}$. = $\frac{1}{1000}$ millimetre = 0·00004 inch; 5 $\bar{\text{m}}$. therefore equals 0·0002 inch.

(2) The mean diameter of the largest particles does not exceed 25 m̄.

(3) The estimated mean diameter of all the particles does not exceed 10·0 m̄.

In the case of enamel paints and materials of a similar nature the requirements as to fineness of grinding are much more stringent.

9. Colouring Power.—This is tested by comparison with a standard pigment, by mixing varying amounts with a definite quantity of some white pigment such as china clay, until the same tint has been secured as by the use of a known weight of the standard pigment with the same amount of china clay.

Thus suppose 100 grains of the pigment A to be tested yield the same depth of colour with 1 oz. of china clay as do 80 grains of the standard pigment B; the colouring power of A is $\frac{80}{100}$ of that of B. Taking the value of B as 1000, the colouring power of A is clearly 800.

The colours of the finely powdered mixtures are best compared by placing small quantities on a sheet of paper or cardboard (black if the colours are pale, white if they are dark), and flattening them carefully down with a palette knife until the two surfaces just meet along a line, but do not amalgamate (Fig. 20). By placing in a good light, a perfect comparison can be made.

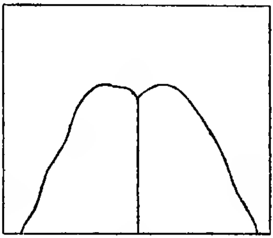

FIG. 20.

10. The Testing of Driers.—This has already been discussed in detail (see p. 161).

I regret that we cannot pursue this interesting branch of our subject further, for, as I remarked at the beginning of this lecture, a complete and thorough analysis of paints and varnishes is a work for the expert. It is hoped, however, that sufficient has been said to assist the practical man to guard himself against any serious fraud. Possibly, also, the interest of some of you may have been awakened to study the subject in more detail for yourselves. If such should be the case, I shall feel amply rewarded for any efforts I have made in the preparations of these lectures.

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THE END

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