THE BY-PRODUCTS
OF
COAL-GAS MANUFACTURE

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TABLE OF CONTENTS

CHAPTER I

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER VII

CHAPTER VIII

CHAPTER IX

CHAPTER X

CHAPTER XI

CHAPTER XII

COAL GAS BY-PRODUCTS.

INTRODUCTION.

THE gas which issues when a gas burner is turned on is not the only product furnished by the dry distillation of coal, the crude gas, as it leaves the retorts, containing substances the combustion of which has an unsalutary effect on the human organism, so that these substances must be removed from the gas before it reaches the consumer. The bodies in question are, chiefly, sulphuretted hydrogen, hydrocyanic acid and ammonia.

The distillation of coal is conducted at a very high temperature ; and some of the gaseous products thus formed do not remain in the state of gas at the ordinary room temperature. Consequently, a partial condensation of the gaseous mixture occurs on the way to the gasholder, coal-tar and gas liquor being deposited. Their complete separation is effected by suitable cooling, in order to prevent obstruction in the pipes. Naphthalene, in particular, tends to choke up the pipes to an unpleasant extent in cold weather, by crystallization. The substances to be regarded as the raw material of the by-products in coal-gas making are the coke and graphite left in the retorts, and the tar, gas liquor, sulphuretted hydrogen and hydrocyanic acid in the distillate. As coal gas there remain hydrocarbons, carbon monoxide and carbon dioxide.

The relative proportions of these various constituents depend on the temperature, the arrangement of the retorts and the length of the gasifying period. At present, coal is usually distilled at 1100-1300° C. With regard to the relative proportions of the constituents of coal, very extensive experiments were carried on by Drehschmidt in 1904 with the experimental plant at the Berlin municipal gasworks, at Tegel. Since this plant is constructed to scale and modelled on the lines of practice, the experiments furnish an accurate illustration of the percentage composition of the gasification products. The following table gives the maximum and minimum values in the case of sixty-eight kinds of coal and the gasification products of same. The moisture content of the raw coal was 2 per cent. The percentage of gas liquor is confined to the amount of water produced during distillation. The gasifiable sulphur could not be determined direct, but was calculated from the difference between the original sulphur in the coal and that found remaining in the coke.

The experiments show that the percentage content of cyanogen and ammonia is independent of the origin and composition of the coal; but that the sulphur, on the other hand, is generally more abundant in English coals. Before going into the treatment of the recovered substances, brief consideration may be given to the gas works, to gain some idea of how the substances mentioned above are eliminated from the gas.

	English Coals.		Westphalian Coals.		Silesian Coals.	
	Raw Coal.	Coal Substance.	Raw Coal.	Coal Substance.	Raw Coal.	Coal Substance.
	per cent	per cent	per cent	per cent	per cent	per cent
Carbon	63·12-79·33	75·32-86·21	68·24-74·18	81·19-84·63	59·22-72·69	75·27-86·22
Oxygen	5·00-14·84	5·53-17·16	6·62-8·97	7·61-10·48	5·58-12·60	6·29-15·63
Ash	4·15-20·82		9·17-18·11		4·99-21·32	
Hydrogen . . .	2·90-5·53	3·18-5·88	3·54-4·48	4·30-5·03	3·21-5·74	3·54-5·94
Sulphur . . .	0·89-3·11	0·97-3 93	0·59-2·48	0 69-2·73	0·74-2·20	0 78-2·79
Nitrogen . . .	1 00-1·77	1·10-1·94	1·26-1·59	1·42-1·89	0 81-1·50	1·02-1·76
Coke	64·0-78·1	59·9-75·7	67·7-73·9	63·7-70·9	65·0-79·2	58·7-78·0
Tar	4·2-6·8	5·2-8·0	3·4-5·7	4·2·6·6	2·8-8·2	3·2-9·0
Gas liquor . . .	3·6-13·3	2·3-13·3	5·0-7·4	4·2-6·6	4·2-11·9	2·5-12·8
Yield of gas per ton .	282·7-353·0 cub. metres	329·3 396·5 cub. metres	320·6-350·4 cub. metres	373·7-416·1 cub. metres	278·8-344·7 cub. metres	352·1·400·8 cub. metres
Volatile sulphur . .	0·9-1·68 per cent		0·18-1·33 per cent		0·22-1·22 per cent	
Sulphur in 100 c.m. of purified gas . .	23·4-172·9 grams		23·9-89·6 grams		19·6 172·0 grams	
Cyanogen per ton .	410 980 grams		630 980 grams		310-670 grams	
Ammonia per ton .	1760-3640 grams		2040-2900 grams		1460-3170 grams	

CHAPTER I.

PURIFICATION OF COAL GAS.

THE crude coal gas passes from the retorts through upcast and trapped pipes into a sloping receiver (the hydraulic main) in which the heaviest condensation products of the tar, and a portion of the gas liquor, begin to separate out. Next follows a tubular or annular apparatus in which the gas is cooled, by air, to a temperature of about 40° C. (104° F.), and is thus caused to part with the bulk of the contained water, part of the ammonia, and most of the residual tar. The gas is then put through a process of wet purification which removes the bulk of the ammonia, and part of the sulphuretted hydrogen and cyanogen, by absorption. On the counter-flow principle, the gas is introduced into the bottom of cylindrical vessels, down which water is allowed to flow from above. In order to present a large wetting surface to the gas, superimposed gratings are laid on bars at intervals in the interior of the cylinder, or else prismatic bars are laid over one another crosswise. In place of these upright cylinders, or scrubbers, inclined cylinders are now sometimes used. These are filled about one-third full of water, a horizontal rotary shaft carrying bars with faggots of wood bringing the gas into intimate contact with that liquid. By the aid of a suction and pressure apparatus, the gas is delivered to the purifying boxes for the dry treatment. These boxes are rectangular and are provided at the upper rim with a groove in which the lid engages, a tight joint being made by filling the groove with water. These boxes also are provided with gratings on which the purifying agent is loosely spread. The gas enters the box at a suitable point, flows through the interior and issues at the opposite side. To ensure complete purification, several boxes are arranged in series. In this case also the counterflow system has been found satisfactory, the fresh gas being brought into contact with the purifying material which has been most used, and the almost completely purified gas passing through fresh material. When the purifying material is no longer capable of taking up any more sulphuretted hydrogen, it is regenerated, the iron sulphide formed being reconverted into ferric hydroxide by atmospheric oxygen and moisture, whilst sulphur separates out. Repeated turning over with a shovel facilitates the process and prevents local heating through the heat generated by the reaction. The material regenerated in this way is used over again, until finally it has become so impregnated with sulphur that its value as an absorbent has sunk very low, whereupon it is put aside to be treated for the recovery of its valuable constituents. By the above treatment the gas is freed from most of its injurious constituents, and is then passed on to the gasholder, for distribution in the mains. Whilst the reactions in the wet purification process are simple, those of the processes in the purifying boxes are of a complex nature, and have been the cause of much divergence of opinion among experts.

In the wet process, ammonia, sulphuretted hydrogen and hydrocyanic acid pass directly into solution. A small portion of the sulphuretted hydrogen is oxidized by the oxygen present, so that oxygen compounds of ammonia are found in the gas liquor. Pfeiffer detected the following products in gas liquor from the Magdeburg gasworks :—

Total ammonia	1·935	per cent
Combined ammonia	0·642	,,
Free ammonia	1·293	,,

If the combined ammonia be allocated to the acids absorbed in the gas liquor, the following values are obtained :—

Ammonium carbonate	1·293	per cent
Ammonium sulphydrate	0·086	,,
Ammonium thiosulphate	0·130	,,
Ammonium sulphate	0·178	,,
Ammonium thiocyanate	0·147	,,
Ammonium ferrocyanide	0·034	,,

Information as to the distribution of these constituents in the different absorption apparatus is afforded by the researches of Lunge and Cox :—

Ammonia in Grms. per Litre, as:	From the Hydraulic Main.	From Another Part of the Hydraulic Main.	From the 1st Atmospheric Condenser.	From the 2nd Atmospheric Condenser.	From the 3rd Atmospheric Condenser.	From the 4th Atmospheric Condenser.	From the 1st Washer.	From the Last Washer.
Ammonium sulphide .	2·60	3·14	17·36	35·71	112·93	60·30	11·37	8·81
Carbonate .	2·75	1·16	17·14	41·14		61·43	22·86	8·57
Thiosulphate	0·40	0·27	trace	0·59	1·16	2·53	0·73	0·44
Sulphate .	0·03	0·13	—	—	—	—	—	—
Thiocyanate	0·36	0·41	0·03	trace	—	—	0·36	0·09
Chloride .	7·04	0·60	0·54	0·71	0·91	0·48	0·40	0·17
Ferrocyanide	—	—	0·07	0·14	0·43	1·29	—	—
Total . .	13·29	13·14	35·13	78·29	115·43	126·00	35·71	18·00
Percentage of stable salts	59	56	1·8	1·85	2·2	3·4	4·2	4·0
Sp. gr. at 15·5° C. .	1·011	1·012	1·035	1·075	1·115	1·120	1·022	1·010

The amount of these salts naturally varies according to the origin of the coal, the sulphur compounds containing a higher percentage of the ammonia in the case of coals high in sulphur. The construction and arrangement of the retorts also affect the ammonia content of the gas liquor. Thus, Carpenter obtained the values shown on next page for horizontal, sloping, and vertical retorts respectively.

Since the absorption of the hydrocyanic acid, in the wet process as detailed below, is effected previous to the absorption of the ammonia in purifying the gas, it naturally produces changes in the percentage composition of the gas liquor. On this point information is afforded by the values obtained in comparative experiments by Linder, which show

Gas Liquor from Retorts.	Ferrocyanide Cal. as HCN, Grms. per Litre.	Chloride, as Cl. Grms. per Litre.	Ammonia Grms per Litre.			CO_2 Grms. per Litre.	H_2O Grms. per Litre.	HCN Grms. per Litre.
			Total.	Readily Decomposable.	Stable.			
Horizontal	0·17	3·13	34·68	2·21	32·47	40·37	3·84	0·34
Sloping .	trace	5·25	25·54	5·23	20·31	36·96	1·95	0·17
Vertical .	trace	6·21	17·16	4·32	13·28	13·86	4·06	0·50

that the removal of cyanogen as a preliminary treatment, lowers the percentage of cyanogen, hydrocyanic acid and ammonia, but considerably increases the proportion of sulphate. Only small quantities of the cyanogen compounds present in the gas are absorbed during the wet purification, the reason being that the gas contains sufficient carbon dioxide to prevent the formation of ammonium cyanide. Leybold found that 8·02 per cent of the total hydrocyanic acid was removed in the cooling process, and 6·55 per cent in the scrubbers.

The main object of the dry treatment is the removal of sulphuretted hydrogen; and it is only of late years that importance has also been attached to a thorough absorption of the hydrocyanic acid as well, on recognizing the latter as being an injurious constituent of coal gas. At the same time it considerably improves the value of the spent purifying materials, and helps to recoup the cost of purifying the gas through the sale of the eliminated constituents. The older methods of freeing gas from

Constituents of Gas Liquor: Grms. per Litre.

	Without Removal of the Cyanogen.	With Removal of the Cyanogen.
Ammonium ferrocyanide	·12	1·01
Chloride cal. as HCl	7·76	3·26
Carbon dioxide	25·51	20·57
Sulphuretted hydrogen	6·61	2·68
Hydrocyanic acid	0·68	0·03
Ammonia:		
readily decomposable	21·76	14·68
stable	5·76	4·47
total	27·52	19·15
Allocation of the Sulphur:		
as sulphide	72·8 per cent	38·5 per cent
as sulphate	0·7 per cent	26·9 per cent
as thiocyanate	23·4 per cent	22·4 per cent
as sulphite and thiosulphate	3·1 per cent	12·2 per cent

sulphuretted hydrogen employed milk of lime, this being afterwards replaced by dry quicklime. This method, however, was abandoned as long ago as the sixties and is now employed only in England. The first effect of quicklime is to absorb the carbon dioxide in the gas, the carbonate thus formed then combining with the sulphuretted hydrogen to form calcium sulphydrate. The hydrocyanic acid is chiefly retained in the form of calcium thiocyanate. Laming introduced materials containing ferric oxide as absorbents for sulphuretted hydrogen, using an artificial preparation which still contained some lime. Later on, however, it was found that the material could be regenerated by exposure to air, even without addition of lime. As already mentioned, considerable divergences of opinion prevailed on the subject of the absorption processes; but since a discussion of these views would be outside the scope of the present work, further reference in this connection may be confined to Berteslmann's review of the question.

According to the view of that authority, "the absorption of sulphuretted hydrogen by the ferric hydroxide of the purifying material is largely accompanied by the formation of iron sesquisulphide. A portion of the ferric hydroxide is reduced by the conjoint action of sulphuretted hydrogen and ammonia, so that ferric sulphide is formed, together with free sulphur, the extent of this reduction varying directly with the amount of ammonia present.

"The hydrocyanic acid in the gas is not absorbed by materials which do not contain ferrous oxide, the absorption not commencing until the hydroxide has been reduced by sulphuretted hydrogen and ammonia.

"Regenerated material absorbs hydrocyanic acid, owing to the formation of ferrous hydroxide in the regenerative process, which hydroxide is not fully converted into the ferric condition. The cyanogen is contained in the purifying material as iron cyanide compounds and ammonium thiocyanate.

"Thiocyanogen is formed in the purifier by the absorption of hydrocyanic acid in presence of oxygen and ammonia, and consequently more thiocyanogen is formed when air is added to the crude gas than when such air is lacking. Moreover, thiocyanogen compounds are formed during the regeneration of the purifying material if the latter be rich in free ammonia and becomes strongly heated spontaneously in the process of regeneration."

The absorbent capacity of various natural and artificial materials used in gas purification is set forth in the following Table:—

Purifying Material.	Water.	Sulphur.	Berlin Blue.	Ammonium Thiocyanate.	Ammonia.
	per cent	per cent	per cent	per cent	per cent
Lux's . .	26·52	29·95	2·27	3·78	1·66
Dauber's .	24·72	27·82	2·70	8·06	2·82
Dauber's .	29·84	29·58	4·86	7·19	1·01
Schröder & Stadelmann's .	16·48	28·48	4·26	6·58	2·84
Matoni's .	26·36	28·26	5·40	2·41	0·41
Good bog ore	26·00	25·04	10·32	2·24	0·38

About 10-20 per cent of the total hydrocyanic acid remains in the purified gas, chiefly because a reaction between a solid and a gaseous body is here in question. Since, in addition, about 15-25 per cent of the cyanogen content is lost in treating the purifying material, attempts have been made to effect the absorption of cyanogen by the wet method. The first step in this direction can be traced in a process (German Patent 9409) for the conversion of trimethylamine into hydrocyanic acid, the methylamine being distilled by passing it through red-hot pipes, an operation which results in the formation of hydrocyanic acid, ammonium cyanide and an illuminating gas. The ammonium salt is then decomposed by passing the mixture through dilute sulphuric acid; and the hydrocyanic acid is absorbed by means of caustic soda or potash.

The next Patent dealing with the absorption of hydrocyanic acid by the wet method is that of Knublauch (Ger. Pat. 41930). This process is based on the absorption of hydrocyanic acid by a liquid containing an iron salt in solution, together with alkalis and alkaline earths. When these substances are present in certain relative proportions, the carbon dioxide and sulphuretted hydrogen passing through along with the gas are absorbed to only a minimum extent, and the quantity of iron sulphide formed in the operation is in perfectly definite relation to the potassium ferrocyanide and entirely independent of the carbon dioxide and sulphuretted hydrogen traversing the liquid. This means that, under certain conditions, it is possible to absorb nearly the whole of the cyanogen, without enriching the absorbent material with carbon dioxide and sulphuretted hydrogen.

The Patent Specification, which relates to an improved method of recovering cyanogen compounds, states that the gases obtained by the dry distillation of coal, coke, brown coal, bituminous shale, peat or wood, as also blast-furnace gas, are brought into intimate contact with a liquid (water or saline solution) containing one or more of the substances in group A (see below), together with one or more of those in group B, or else—given a sufficiency of ammonia in the gas—one or more of the group B substances.

Group A. Alkalis, ammonia (gas liquor), alkaline earths, magnesia and the carbonates of the said bases.

Group B. Iron, manganese and zinc, as also the native or artificially prepared oxides, hydroxides, and carbonates of these metals.

The proportions to be employed per molecule of the cyanogen present in the gas, are approximately 1 molecule of alkali, alkaline earth (magnesia) or their carbonates, with less than one molecule of the metallic compounds mentioned under group B. If ores or metals be used, the quantity should be increased in accordance with their lower activity, the amount of alkali, however, being still approximately 1 molecule.

The object of this process was to absorb all the cyanogen in a soluble form; but, owing to the readiness with which iron oxidizes, this could not be effected completely, small quantities of Prussian Blue being always found in the iron sulphide sludge. The Knublauch process never made headway in practice, the reason probably being that the demand for cyanogen salts was then too small. To this inventor, however, belongs the credit of having, by his careful researches, pointed out the way to absorb cyanogen by the wet method. A few years later, W. Foulis embodied a modification of the process in his English Patent 9474/1892, according to which the hydrocyanic acid is recovered, in the form of potassium ferrocyanide, or the corresponding sodium salt, by treating ammonia-free coal gas with freshly prepared ferric carbonate, held in suspension in bell scrubbers. This form of scrubber was afterwards replaced—in the same inventor's Patent 15168/1895—by scrubbers in which the charge was kept in motion by mechanical devices, an arrangement more suitable for sludgy liquids. For carrying out the process, 5 gals. of a solution of ferrous chloride—containing about $1\frac{1}{2}$ lb. of Fe per gallon—are treated with a solution of 15 lb. of calcined soda in 30 gals. of water. After stirring the whole thoroughly, the precipitate of ferrous carbonate is allowed to subside, the supernatant liquid being poured off and the deposit washed until all the sodium chloride has been removed; 27 lb. of calcined soda, or 35 lb. of potash, are then added, the volume of the suspension is made up to 40 gals. with water, and the charge is placed in the scrubber. A report of the results obtained with the process, in practical use, at the Hague gasworks, was published by Rutten ("Journal of Gas Lighting," 1902, vol. 80, p. 879) who used ferrous sulphate instead of ferrous chloride, and employed as absorption vessel a Kirkham scrubber, the first chamber of which was charged with heavy tar oil for the purpose of retaining the naphthalene. Whereas both Knublauch and Foulis prescribed the removal of ammonia from the gas before absorbing the hydrocyanic acid, the gas in the Hague trials was merely freed from tar before being passed through the absorbent charge. When the first chamber was found to be saturated with hydrocyanic acid, it was emptied, and the liquid from the second chamber was pumped into the first one, that from the third into the second, and so on, the operation being repeated as soon as the first chamber became saturated again. The counterflow principle was thus observed; and it was found that the absorption of hydrocyanic acid was practically complete. In the case of a crude gas containing, on the average, per 100 cubic centimetres:—

Hydrocyanic acid	185 grams
Ammonia	325 ,,
Carbon dioxide	4000-6000 ,,
Sulphuretted hydrogen . . .	1500 ,,

8·5 per cent of ammonia and 37·67 per cent of cyanogen were found in the sludge of a slightly oxidized preparation. Jorrissen and Rutten also found that, in the absence of carbon dioxide, all the cyanogen can be recovered in the soluble form, and that the presence of ammonia does not lead to the formation of thiocyanate. In this cyanogen sludge, the cyanogen is present as Prussian Blue and as potassium ferricyanide. The failure of Knublauch's attempts to absorb the cyanogen merely as salts in soluble form is attributable to the presence of carbon dioxide, on which account Bueb proceeded in such a way as to prevent the formation of soluble salts entirely, and to obtain the cyanogen in the sludge only, whereas in the previous methods both the sludge and the solution required to be treated for the preparation of cyanogen salts. Bueb's process (Ger. Pat. 112459) is worked with a solution of iron salts, of such high concentration that no absorption of ammonia takes place, and the amount of iron is very large in proportion to the ammonia. The hydrocyanic acid is thrown down as insoluble ammonium ferrocyanide. The absorbent liquid is prepared from a cold-saturated solution of ferrous sulphate, containing about 280 grams of sulphate per litre; and the apparatus consists of a horizontal cylinder the liquid contents of which are kept in motion by mechanical stirrers. This cylinder is set up between the tar separator and the ammonia scrubbers, and consists of several chambers, the first two of which are used for absorbing naphthalene by means of a charge of heavy tar oil containing up to about 3 per cent of benzol. The next four chambers are filled one-third full with the cold-saturated solution of ferrous sulphate. In order to present a maximum wetting surface to the gas, a shaft passing horizontally through the cylinder is provided with wood faggots in the naphthalene chambers and sheet metal discs in the cyanogen absorption chambers. The shaft is set in rotation by a worm and worm-wheel gear. The gas passes first of all through the chambers charged with heavy tar oil, where the naphthalene is retained: and from these it enters the cyanogen absorption chambers. The scrubbing liquid does not flow through these chambers continuously, but is stationary. After the liquid in the first chamber is completely saturated with hydrocyanic acid—which takes about nine hours in large plants—it is run out, the liquid from the second chamber being pumped in in its place, whilst the liquid in each of the other chambers is advanced a stage, and the final chamber is recharged with fresh liquid. The method of working is therefore exactly the same as in the Foulis process. The absorption of the cyanogen is based on the following reactions.

The ammonia decomposes the sulphate into hydroxide, sulphate of ammonia being formed:—

(1) $FeSO_4 + 2NH_3 + 2H_2O = Fe(OH)_2 + (NH_4)_2SO_4$

Sulphuretted hydrogen acts on the hydroxide, ferrous sulphide being formed:—

(2) $Fe(OH)_2 + H_2S = FeS + 2H_2O.$

In presence of ammonia and hydrocyanic acid, the ferrous sulphide is converted into ferrous cyanide, ammonium ferricyanide being also formed.

(3) $FeS + 2NH_3 + 2HCN = Fe(CN)_2 + (NH_4)_2S.$
(4) $2FeS + 6NH_3 + 6HCN =$
$(NH_4)_2Fe_2(CN)_6 + 2(NH_4)_2S.$

Both these cyanogen compounds are insoluble in water and are precipitated as sludge. If, however, they are allowed to remain in prolonged contact with the liquid, they are gradually converted, by the further action of hydrocyanic acid, into soluble ammonium ferrocyanide, according to the equations:—

(5) $Fe(CN)_2 + 4HCN + 4NH_3 = (NH_4)_4Fe(CN)_6$

and:—

(6) $(NH_4)_2Fe_2(CN)_6 + 6NH_3 + 6HCN = 2(NH_4)_4Fe(CN)_6$.

As is evident from these reactions, the Bueb process also furnishes small quantities of cyanogen in a soluble form in practice. The sludge obtained is dark brown to black in colour and contains an amount of cyanogen equivalent to 18-20 per cent of potassium ferrocyanide. According to the researches of Hand, Ost, and Kirchten, the insoluble salt has the formula: $(NH_4)_6Fe[Fe(CN)_6]_2$. The ammonia present in the sludge is partly combined with iron cyanide and partly as sulphate, and amounts to about 5-7 per cent. Owing to the impossibility of entirely excluding oxygen, a small quantity of thiocyanate is also formed, according to the equation:—

$$2NH_3 + 2H_2S + O = (NH_4)_2S + H_2O + S.$$
$$(NH_4)_2S + S = (NH_4)_2S_2$$
$$(NH_4)_2S_2 + NH_3 + HCN = (NH_4)CNS + (NH_4)_2S.$$

The free sulphur is deposited from the ferrous sulphide and water in presence of air. Feld has confirmed that the formation of thiocyanate takes place chiefly in the chamber nearest to the gas outlet, and that there is very little further increase when the liquid is transferred to the penultimate chamber.

A combined system of cyanogen absorption, analogous in some respects to the Solvay soda process, has been developed from the Foulis and Buëb processes by Feld. According to his German Patent 151820, he uses as the absorbent liquid a saline solution, the oxides, hydroxides, sulphides or carbonates in which are capable of displacing ammonia. To these solutions he adds sufficient ferrous salt to ensure that for each atom of iron present the liquid will contain at least 4 atoms of a monovalent salt or 2 atoms of a divalent salt. The gas must be rich in ammonia, and when this is not the case an ammoniacal saline solution is used. This process is intended to prevent the formation of thiocyanogen entirely. The ammonia and carbon dioxide of the flowing gas transform the salt into the carbonate, and this reacts with the ferrous hydroxide and cyanogen to form ferrocyanides. In carrying out the process in practice, use is made of the Buëb ammonium cyanide washer, into which the gas enriched with ammonia is passed. The process was formerly used at the Billwarder gasworks, in Hamburg, but as it has now been discontinued in practice, there is no need to describe it further.

Up to the present no practical process has been evolved for the absorption of the cyanogen as cyanide, though Feld patented a process of this kind (Ger. Pat. 141626). The gas, freed from tar, is passed through hot solutions of compounds of iron, manganese or lead, to remove the sulphuretted hydrogen, the carbon dioxide having been previously absorbed by a hot solution of basic magnesium salt. The cyanogen is next absorbed in a cold, neutral or basic carbonate solution, or by hydroxides or oxides of magnesium, zinc, aluminium, manganese or lead, the hydrocyanic acid being liberated from the solution by distillation, and absorbed in the form of any cyanide. No practical experience with this process is at present available.

The last method of cyanide absorption by the wet process that need be mentioned consists in converting it into thiocyanogen. However, since the thiocyanogen compounds are far less valuable than those of cyanogen, this method is of interest only to gasworks which have to deal with coals very high in sulphur, for which reason it has found application in some English gasworks. It is based on the conversion of the cyanogen into thiocyanogen by means of polysulphides in presence of ammonia. With this object the gas is washed with an aqueous suspension of flowers of sulphur (10 per cent by weight). The following reactions take place:—

$$(NH_4)_2S + S = (NH_4)_2S_2.$$

$$(NH_4)_2S_2 + NH_3 + HCN = NH_4CNS + (NH_4)_2S.$$

Up to 90 per cent of the cyanogen is absorbed as thiocyanogen; but the presence of large quantities of carbon dioxide is said to have an adverse effect. Patents for processes of this kind have been taken out by: Smith, Gidde, Salomon and Albright (Eng. Pat. 13653/1901); Carpenter (Eng. Pat. 22710/1902), and the British Cyanides Co. Lim. (Ger. Pat. 136367).

An attempt has been made, in the foregoing, to give an idea of the manner and the chemical condition in which the originating materials for the by-products of gas-making are obtained. These by-products are: coke, retort graphite, ammonia, sulphate of ammonia, sulphur, ferrocyanic acid and thiocyanic acid.

CHAPTER II.

COKE.

COKE is the first product obtained in the retorts as the distillation residue from coal. In large gasworks, the retorts are emptied by mechanical appliances, and the glowing coke is removed by belt conveyers, which pass through water in order to quench same. In small works it is wheeled in barrows to a large heap where the quenching is performed.

Gas coke forms a porous mass, ranging from silver-grey to a dark colour. It is very brittle and hard. Its chemical composition has not yet been identified. It does not, however, form a mixture of pure carbon and ash constituents—the non-volatile mineral constituents of the coal—but is a mixture of high-molecular compounds of carbon with hydrogen, nitrogen, oxygen and sulphur. Apart from the ash, the composition naturally differs according to the kind of coal; and it also depends on the coking temperature employed, the proportion of carbon increasing with the temperature. The porosity depends on the method of distillation, that is to say, on the position of the retorts. Thus, as a rule, vertical retorts furnish the densest coke, because in these it sinters together more, under the influence of its own weight. The range of percentage of the various constituents of gas coke, referred to dry and ash-free matter, are as follows:—

Carbon	92·70-96·09 per cent.
Hydrogen	0·60-1·22 ,,
Oxygen	0·29-3·60 ,,
Nitrogen	1·04-1·70 ,,
Sulphur	0·88-1·62 ,,
Heating value	7708-8022 cal.

The ash content fluctuates considerably, and ranges between 3·72 and 11·60 per cent. The above figures are taken from a Table compiled by Bunte from samples of coke from the gasworks of Berlin, Hamburg, Breslau and Munich, in 1897.

The examination of coke is directed to its fragility, the determination of the volatile constituents, sulphur, ash, and, above all, the heating value.

The test for ascertaining the fragility of coke is applied in the following manner: One portion of the sample is separated by sifting, and the remainder is dropped from a certain height on to a paved floor, and then sifted again. The amount of the screenings gives an idea of the fragility of the coke.

The determination of the ash, volatile matters and sulphur need not be gone into here, since it does not present any special features.

The heating value may be determined by means of empirical formulæ or by accurate experimental examination. Dulong ascertains the heating value from the chemical composition by means of the formula :—

$$H = 81C + 290 (H_1 - O/8) + 25S - 6W.$$

in which : H represents the heating value in calories per kilogram ; C is the percentage of carbon in the substance ; H_1 the percentage of hydrogen ; O the percentage of oxygen, S that of sulphur, and W the percentage of moisture present, both originally and as produced by the combustion of the sample.

The recognized method of determining heating values is by means of the calorimeter, which is a steel bomb filled with oxygen under pressure. The substance under examination is powdered, and compressed into a tablet, in which an iron wire, of known carbon content, or one of platinum, is embedded at the same time. This wire is raised to incandescence by the aid of an electric current, and thus ignites the tablet which has been placed inside the bomb. The heat thus liberated is transmitted to water in which the bomb is immersed : and the rise in the temperature of the water forms a measure of the heating value of the substance. The water is kept in constant motion to ensure a uniform distribution of the heat ; and the whole apparatus is placed in a second vessel containing water, in order to protect it from the influence of external heat. However, since the heat is transmitted to all parts of the apparatus and not merely to the water alone, it is necessary to take into consideration the "water value," as regards heat, of such parts. If the water value of the vessel be taken as X, and the weighed quantity of water be represented by Y, the correction for radiation—according to the formula of Ostwald—being set down as Z, the initial water temperature as T_1 and the maximum temperature of the water during the experiment as T_2, then the heating value, expressed as heat units (calories), will be: $\text{Cal.} = Y (X + Y) (T_2 - T_1 + Z_1)$. From this result there must be deducted the heat generated by the iron wire and the nitrogen; and since the heating value is referred to 1 kilo. of substance, this value must be recalculated accordingly. Moreover, the evaporation value of the water of combustion must be deducted, for which purpose the quantity of the water of combustion must be determined—which can be effected in the same experiment, the bomb being constructed in such a way that the contents can be completely emptied out and collected after the combustion process. The water produced is retained by a calcium chloride tube, and the carbon dioxide by a potash apparatus arranged in succession to said tube. With this object the bomb is heated to 105-110° C., and, after the pressure has become equalized, dried air is passed through it for a short time. The increase in weight of the calcium chloride tube gives the weight of the water of combustion formed; and for every kilogram of water of combustion, 606·6 cal. must be deducted from the heating value found by the formula.

The coke coming from the retorts is not homogeneous in character, and is in lumps of different sizes. In order to obtain a product of uniform appearance, the large lumps are broken, either by hand or, more generally, in coke-breaking machines after the style of that illustrated in Fig. 1. This machine consists of a shaft provided with interchangeable teeth or cutters to which the coke is fed down an inclined plate, which also forms an abutment. The broken coke is passed over mechanically operated screens of different mesh, and is thus classified at once into various sizes. The coke fines (fragments below ¼-inch diameter) can be worked up in a briquetting machine.

The ash from the fuel used in heating the retorts also contains unconsumed particles of coke, which can be separated by hand, and constitute the so-called "coke breeze," which forms an inferior, cheap grade of coke, of about one-third the value of gas coke.

There is no need to dilate upon the use of coke as a heating agent, but a good deal is consumed by the gasworks themselves as fuel, particularly for charging the producers.

In the gasworks of large towns the consumption of gas varies considerably at different times of the day, but increases very quickly at short intervals towards evening, and this increased consumption cannot be met at once by the retorts alone. It may, however, be dealt with quickly by mixing the coal gas with water gas, the output of which can be regulated more easily. Another important factor in the case of water gas is the amount of floor space required, it being possible to produce more than five times as much water gas with a plant occupying only one-third the

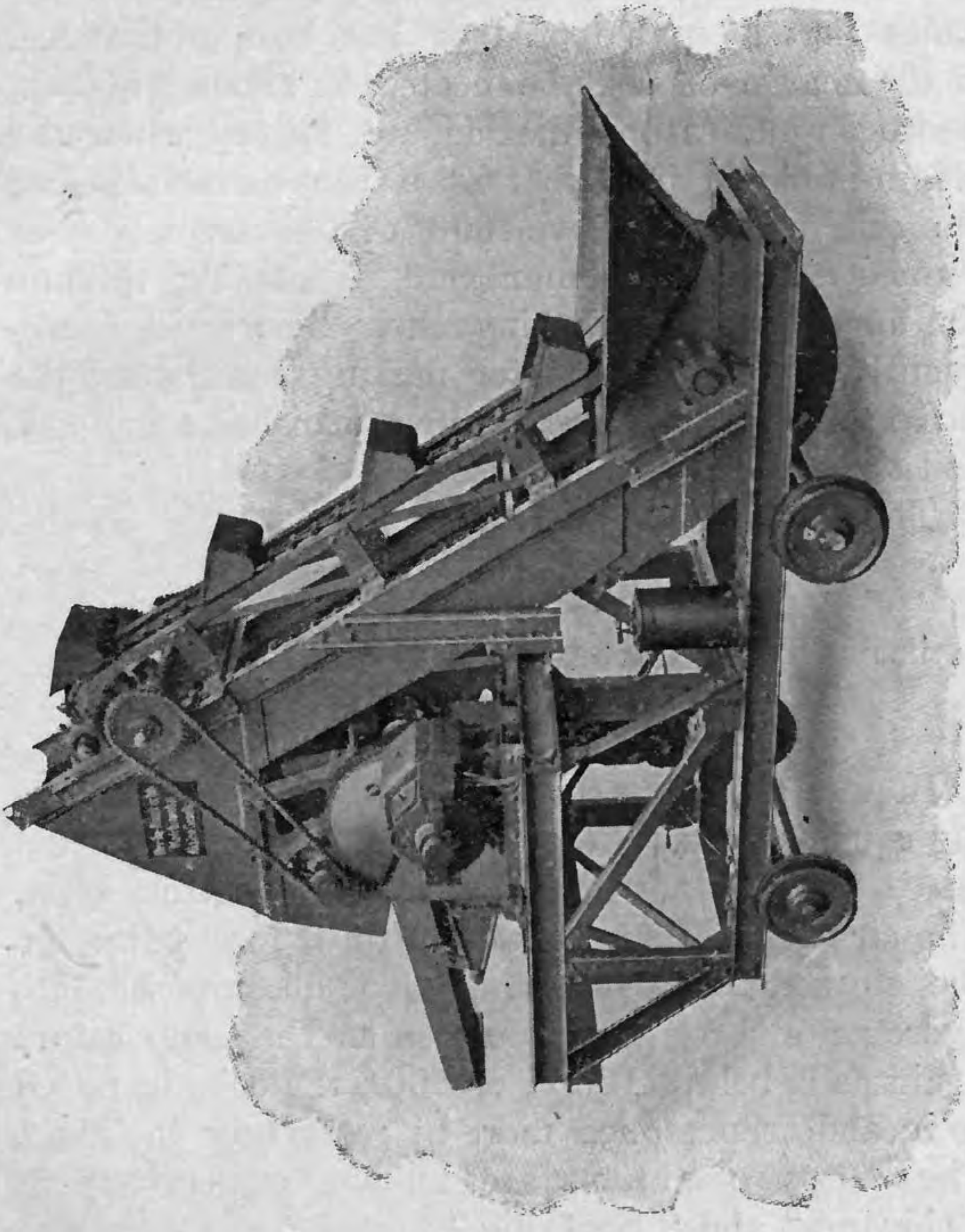

FIG 1.—Coke breaker.

floor space required by the retorts used in making coal gas.

Water gas is made by passing steam through glowing coke; but though the process dates back about a century, it is only within the last few decades that a usable product has been obtainable. If the charge of coke be heated to about 500° C., hydrogen and carbon dioxide are formed when the steam is blown in; whereas if the temperature of the coke be raised above 1000° C., the carbon dioxide formed is reduced to monoxide in passing through the upper layers of glowing coke. There are, consequently, two processes for making water gas; the carbon monoxide process, which furnishes a fuel gas, and the carbon dioxide process.

Thus, at 500° C., the reaction is:

$$C + 2H_2O = 2H_2 + CO_2,$$

whilst at 1000° C. it is:

$$C + CO_2 + 2H_2 = 2CO + 2H_2.$$

In practice the process is carried out on the following general lines. Coke is ignited in a retort and raised to incandescence by means of a bottom blast. The air is then shut off, and steam is forced through the glowing coke, by which it is decomposed into hydrogen and oxygen. So soon as the temperature again falls below 1000°, or 500°, the coke is raised to incandescence once more by restarting the blast. These two operations are known respectively as "blowing" and "gasifying".

Schäfer gives the following as the percentage (by volume) of a water gas:—

Hydrogen	50	per cent
Carbon monoxide	40	,,
Carbon dioxide	4-7	,,
Nitrogen	3-6	,,
Oxygen	1	,,

The heat of combustion of such a water gas amounts to about 2500 cal. and its heating value is about 12 per cent lower than that of coal gas.

CHAPTER III.

RETORT GRAPHITE.

RETORT graphite or retort residue is formed by the decomposition of the hydrocarbons produced in the distillation of coal in the retorts, a portion of the gases being decomposed into their constituent elements by the high temperature. The carbon formed in this way is also deposited on the firebrick walls, and furnishes a hard mass which resembles graphite and will even give out sparks when struck by a piece of steel. This graphite is a very bad conductor of heat, and therefore has to be taken out of the retorts at intervals of four or five months. The thickness of the deposit is sometimes considerable, that from English coals being not infrequently $2\frac{1}{2}$-3 ins. thick. The mass is cleared away either by purely mechanical means or by burning, the latter being generally preferred, because the extreme hardness of the deposit renders the material of the retorts liable to injury when mechanical means are employed. To burn out the graphite, half-moon bricks are placed in the hot, empty retorts, so as to form troughs, the openings in which are closed, together with the retort heads, whilst the cap of the upcast pipe is opened.

The air flowing through the retorts then burns the deposit and loosens its hold on the walls, which operation takes from four to sixteen hours. When cold the loosened graphite can be completely removed by mechanical means.

The specific gravity of retort graphite varies between 1·72 and 2·35 according to the pressure which has prevailed in the retorts. The degree of hardness also varies considerably. The ash content is about 2·5 per cent.

Bunsen proposed to use retort graphite for carbon electrodes for electrical purposes, and thus opened up a large market for the article. In fact practically all carbon electrodes and rods are made of retort graphite. The raw material, however, is not perfectly homogeneous, and the shape of the retorts is adverse to the production of any but comparatively small plates and rods. On this account, and because the direct treatment of the raw material would give rise to a good deal of waste, the crude graphite is first hand-picked and cleaned, and is then ground down to a coarse powder. This is next worked up into a plastic mass, along with lampblack and coal tar, in a mixer, and from this mass the carbon rods are shaped in hydraulic presses under a pressure of several hundred atmospheres, the plates being treated in a similar manner. The resulting mass, however, has not yet attained its full strength, which is imparted by baking in circular kilns similar to those used in brickmaking. The heat of the kiln decomposes the coal tar, and the resulting graphitic carbon binds the grains of the retort graphite together. The product is used for the carbon rods of arc lamps, chiefly on account of its very low combustibility. Most of the works engaged in the manufacture of electric carbons are situated in the district round Nuremberg, though the largest firm, Gebr. Siemens & Co., is in Berlin.

CHAPTER IV.

GAS TAR.

THE third product met with between the retort and the gas holder and having to be extracted from the gas, is tar. This tar is deposited in three chief places; the hydraulic main, the air condenser and the water-cooled condenser, a portion of the gas liquor also separating out at the same time. On this account, the gas tar and gas liquor, together with that from the scrubbers, are collected in one pit, where their different density causes them to separate into two layers, the specifically heavier tar being at the bottom. By means of a siphon, which reaches down to the bottom of the pit, the tar is drawn off from the supernatant liquor and is then pumped up into a high-level tank.

A full description of the treatment of this tar is beyond the scope of the present work; and it need only be mentioned that the entire dyestuff industry employs gas tar as the raw material for the preparation of all the crude products of that industry. All that will be dealt with here is the direct utilization of the crude tar, and its fractional distillation into light, medium and heavy oils, anthracene oil and pitch.

The yield of tar obtained in gasworks depends on the origin and character of the coal, and ranges (see Table below) between 4 and 8 per cent, coals rich in oxygen usually furnishing the highest tar output. The following data were compiled by Bunte as the result of a large number of experiments:—

Origin of Coal.	Retort Temperature.	Percentage of Tar.	Percentage of Gas Liquor.
Wesphalia . .	1360-1385° C.	4·09	4·44
Saar district .	1205-1290° C.	5·33	6·90
Bohemia . .	1240-1350° C.	5·79	9·06
Zwickau . .	1180-1240° C.	5·22	11·86
Bohemian cannel	1180-1350° C.	8·81	6·45

Gas tar is a thick, deep-black greasy liquid, but is not a homogeneous substance, being a mixture of highly divergent hydrocarbon compounds. In addition to water it contains hydrocarbons of the methane, ethylene and acetylene series; naphthylenes; terpenes; naphthenes; aromatic hydrocarbons of the benzol, naphthalene and anthracene homologue series; phenols; aromatic acids and sulphur compounds; basic and non-basic aromatic nitro-compounds and free carbon.

Krämer has found samples of German gas tar to contain:—

Benzol and its homologues, C_nH_{2n-6} . . .	2·50 per cent.
Phenol and its homologues, $C_nH_{2n-7}OH$.	2·00 ,, ,,
Pyridin and chinolin bases, $C_nH_{2n-7}N$ . .	0·25 ,, ,,
Naphthalene, C_nH_{2n-12}	6·00 ,, ,,

Heavy oils, C_nH_n	20·00 per cent.
Anthracene, phenanthrene, C_nH_{2n-8} . .	2·00 ,, ,,
Asphaltum (soluble constituents of the pitch), $C_{2n}H_n$	38·00 ,, ,,
Carbonaceous matter (insoluble constituents of the pitch), $C_{3n}H_n$	24·00 ,, ,,
Water	4·00 ,, ,,
Gas (loss on distillation)	1·25 ,, ,,

This Table is merely intended to give an approximate idea of the relative proportions of the various constituents of gas tar.

The tar from coal distilled in vertical retorts is richer in light oils, and is also more fluid. The influence of the retort arrangement on the various fractions of the tar is shown by the results obtained by Buëb with New Leverson and Leverson Wallsend Coals:—

	Tar from Vertical Retorts.	Tar from Horizontal Retorts.
Water . . .	2·17	3·50
Light oil . .	5·85	3·10
Medium oil . .	12·32	7·68
Heavy oil . .	11·95	10·15
Anthracene oil .	15·96	11·54
Pitch	49·75	62 00
Loss in distillation	2·00	2·03

In the examination of tars obtained by distilling coal in vertical and slanting retorts, Kärting obtained the following values for the several fractions :—

Temperature.	From Vertical Retorts.	From Slanting Retorts.
	per cent	per cent
0-100° C.	8·8 of oil, 5·7 of water	1·0 of oil, 0·85 of water
100-170° C.	1·2 ,, —	1·6 ,, 1·85 ,,
170-230° C.	13·5 ,, —	10·27 ,, —
230-270° C.	7·3 ,, —	7·5 ,, —
Over 270° C.	29·3 ,, —	18·80 ,, —
Residue	34·1 ,, —	58·13 ,, —

According to the use for which it is intended, the tar is examined for water content, percentage of ash, heating value, specific gravity and carbon content. Gas tar itself is not a homogeneous substance, a whole series of bodies separating out, in accordance with their specific gravity, especially on prolonged standing.

For this reason, it is essential to employ great care in obtaining a good average sample for the purpose of judging the value of a tar. The best method of sampling is to mix the tar in the vessel by blowing air through it, and then taking samples from different places. Ahrens and Senger recommend, as an efficient tar sampling device, a tube which is long enough to reach to the bottom of the tar vessel, and is traversed by a rod provided on its lower end with a conical or flat valve member, so that the sampler can be closed by a pull on the rod. In taking samples, the tube, in the open condition, is worked slowly down as far as the bottom of the vessel, and is then closed at its lower end by pulling on the rod. In this way a complete sample of the several layers of tar in the vessel is obtained. By repeating the operation in different parts of the vessel an average sample is obtained.

For determining the percentage of water, Maiwald recommends distilling 100 grms. of the tar in a copper still, capable of holding 200 grms. and connected to a Liebig condenser, 50 grms. of benzol being added to the tar to prevent it from frothing up and boiling over. By the time the still temperature attains 190° C. all the water will have passed over. The distillate is collected in a measuring cylinder, in which the layer of oil separates from the water, so that the percentage amount of the latter can be read off direct. Merchantable tar should not contain more than 4 per cent of water; and if found to have more than this amount, an allowance should be claimed on account of the unnecessarily increased cost of carriage.

According to Senger, 500 grms. should be distilled in a 1 litre copper still, without addition of benzol, the frothing of the tar being prevented by the application of heat from above, by means of a ring burner arranged under the upper rim of the still. Conducted in this way the operation requires no supervision, and is completed in about three or four hours. In the Maiwald method the distillation is finished in half an hour.

The heating value is determined by means of the Berthelot bomb, in the same way as for coal. According to Allner, it is advisable to soak the tar up in cellulose cubes, in order to obtain complete combustion of the carbon, the heat of combustion of the added material being determined beforehand and deducted from the result furnished by the calculation. Bertelsmann, however, has found no difficulty in effecting the direct combustion of the tar.

The specific gravity is determined by the method of Lunge. A small weighing glass is used as pyknometer, and a notch, about 2 mm. wide and of the same depth, is filed in the edge. The following weighings have to be performed :—

The tare weight of the vessel = a;

The weight of the vessel filled with water at 15° C. = b;

The weight of the vessel filled about two-thirds full of tar = c;

The weight of the vessel now filled up completely with water = d.

Then: $$\text{Sp. gr.} = \frac{c - a}{b + c - (a + d)}.$$

Before making this determination, it is necessary, of course, that the tar should be freed from water. This can be effected by leaving the tar to stand in a covered glass beaker for about twenty-four hours at 40° C., under which conditions the tar and water separate from each other. The supernatant water is then poured off, the final traces being soaked up with filter paper.

In determining the value of c, the vessel should be allowed to stand in hot water for some considerable time, to expel all air bubbles from the tar.

For determining the carbon content, Köhler prescribes heating 10 grms. of the tar with a mixture of 25 grms. each of glacial acetic acid and toluol for some time, and then passing the whole through a tared filter, the residue being washed with benzol until the washings are free from colouring matter. The carbon remains on the filter and is determined by weighing.

Krämer and Spilker warm 1 part of tar with 3 of aniline, and pour the mixture on to a plate of unglazed earthenware, which absorbs the liquid constituents of the tar. The residual carbon is then transferred to a tared watch glass by means of a spatula and weighed.

For the determination of the various fractions in tar, Krämer and Spilker recommend a method adopted directly from practical working on the large scale, 5 kilos. of the tar under examination being placed in a cast-iron still, holding about 8 kilos., and distilled in a partial vacuum, the fractions being collected at definite intervals of time.

The ash content is ascertained by warming 1 grm. of tar in a platinum dish, then igniting it, and when the flame has subsided, heating the residue in a muffle until of constant weight. The ash seldom exceeds about 0·05 grm.

As already mentioned, the tar collected in the tar tanks still contains a large amount of water, from which it must be separated. According to the method of the Deutsche Continental Gas Gesellschaft (Ger. Pat. 191342/1907), the mixed tar and water is allowed to flow down an incline of 45° in a thin stratum.

During this operation the tar and water separate, the tar collecting in a pit at the bottom of the slope, whilst the water floats on the surface. Schlosser's tar-separator is based on the same principle, the tar being allowed to flow over the edge of a high-level tank on to a vertical corrugated plate, below which is a collecting tank in which the tar and water form separate strata.

Another method, frequently employed in large gasworks and tar distilleries, consists in the application of centrifugal force. Burmeister and Wain proposed to use a centrifugal tar separator constructed on the same principle as the milk separator. The drum is run at a speed of about 2000 revolutions per minute, and the tar, which is fed into it as a continuous stream, at a temperature of about 30-40° C. (86-104° F.) separates from the water, which rises to the top, inside the tar, and is retained in the central space of the drum by a partition, over which the tar flows outward, the two liquids being thus forced apart.

One very simple method consists in merely warming the tar, in which case the temperature should not exceed 50° C. (122° F.), in order to prevent loss. In this state of increased fluidity a separation of the tar and water takes place automatically.

According to Klönne (Ger. Pat. 196240/1906), tar can be freed from water by forcing it between rollers, which are heated if necessary, this treatment freeing the imprisoned particles of water from the adherent tar by pressure and friction.

The Weil method (Ger. Pat. 217659 and 218780/1908) is performed in a partial vacuum. The tar flows, as a continuous current, round a system of pipes heated by waste gases. To prevent loss of readily volatile constituents, a condenser and washer for their absorption are arranged in the rear of the vacuum pump.

In a large number of systems the device for removing the water from the tar is placed in direct connection with the distillation apparatus. A method of this kind is that patented by the Rütgerswerke A. G. (Ger. Pat. 161524/1904) in which, by the application of heat from above downwards, the floating water is got rid of first, then that emulsified with the tar, and finally the chemically combined water. The flue gases from the retorts are utilized as the heating agent.

The crude tar obtained in this way is used for painting cast-iron articles, for making lampblack and for roofing-felt. For application to metal surfaces the tar is made fluid by heat, and then laid on the metal direct, producing a lustrous and durable black coating. This paint is used on cast-iron pipes intended to be exposed to corrosive vapours, for example in chemical works. Kuhlmann also recommends gas tar as an acid-resisting paint for stone and brickwork; but it is not much used as a preservative for wood. One of the most important direct applications of gas tar is in the manufacture of roofing felt. This is a very simple process, the millboard or felt being boiled in water-free tar or passed continuously through hot tar solutions, whilst the surplus tar is removed by pressing the material between rollers. It is more economical to carry on the work in closed cylinders, instead of open pans, in order that the readily volatile constituents may be recovered by condensation. The crude tar may also be replaced by a mixture of tar pitch and heavy oil, in which case the roofing felt will have to be frequently recoated with the same preparation during the first few years it is in use.

Crude gas tar is also used for making lampblack; but a better product can be obtained from the heavy oil. Of late years, tar has also found advantageous employment for dressing the surface of highways, in order to render them dustless and more durable.

Crude tar, from which the constituents boiling up to 150° C. have been distilled off, is made into artificial stone (Dörrite stone) with dried and crushed gravel, furnishing a product characterized by great hardness and strength.

The possibility of producing an illuminating gas by passing coal tar through red-hot pipes has not found any practical application; but, on the other hand, this tar is utilized as fuel, having a heating value of about 8500 cal. The tar flows through a nozzle to the burner and is forced into the combustion chamber by a mixture of steam and air.

As already mentioned in the introductory chapter, gas tar is likewise used for absorbing gases; and it also serves to absorb naphthalene in naphthalene and cyanogen washers.

The bulk of the tar, however, is distilled, for the purpose of fractionating it into the four grades: light oil, medium oil, heavy oil and anthracene oil, pitch being left behind in the retorts as residue. The relative yield under the same treatment naturally differs with tars of divergent origin. The following percentage values are given by Krämer and Spilker for the yields obtained in distilling the gas tar from: (1) Upper and Lower Silesian gas coals; (2) Zwickau coal, with addition of paraffin coal; (3) English coal; (4) Saar gas coal, with addition of paraffin coal:—

No.	Retort Pitch.	Water.	Light Oil.	Medium Oil.	Heavy Oil.	Anthracene Oil.	Total Distillate.
1	55·1	3·0	2·1	12·0	9·2	18·0	41·3
2	52·2	4·9	2·5	12·9	11·2	15·2	41·8
3	59·9	3·1	3·4	9·4	7·0	17·0	36·7
4	59·4	4·1	3·8	10·8	8·6	12·1	35·3

The first runnings, which distil over between 9 and 100° C., contain water and volatile gases—the light hydrocarbons absorbed by the tar, and also sulphuretted hydrogen, ammonia and carbon dioxide.

The light oil comes over between 100 and 180° C. It contains phenols, bases, sulphur compounds, nitriles, neutral oxygen compounds, olefines, paraffins, unsaturated and cyclic compounds, and aromatic hydrocarbons. The medium oil, which distils over between 180 and 240° C., consists chiefly of naphthalene and phenols. The next distillation product, the heavy oil, comes over up to 300° C., and, in addition to naphthalene, consists mainly of creosote oils. Anthracene oil, the final distillate, comes over at temperatures up to 400° C., and contains crude anthracene, which is solid at the ordinary temperature. The filtrate from this deposit is redistilled and furnishes an additional quantity of crude anthracene, together with carbolineum, which latter is used as a preservative for timber. The pitch forming the residue in the still, is a product of varying consistence and is composed of carbon compounds of unknown composition, mixed with carbon.

The apparatus used for tar distilling varies considerably in appearance, but not greatly in principle. A distinction may be drawn between three main systems of distillation: with direct fire heat or flue gases; with indirect steam; and vacuum distillation. Recently, continuous distillation has also come into favour.

The water-free tar is distilled in iron stills, preferably of wrought iron, which material is more easily workable than cast iron and is also able to withstand greater fluctuations of temperature. The more general use of cast iron is, moreover, precluded owing to the narrow limits of size possible with this material; though wrought iron is more liable to suffer from the heat. In order to protect the still from direct contact with the heating flame, a protective casing is provided under the still bottom, so that only the hot gases come in contact with the apparatus, which is, therefore, to some extent, in a kind of air bath. The flues must be arranged in such a manner that, during the whole of the distillation process, down to the pitch—which, it is true, occupies about two-thirds the total volume of the tar—the heating gases only come in contact with those parts of the still which are filled with liquid.

Tar stills differ considerably in shape, both vertical cylinders, as high as they are wide, and horizontal cylinders, being used. In the case of upright cylinders the bottom is domed (concave) and the upper end is of similar shape, this latter being provided with an outlet for the liberated gases. The reason for using a domed bottom instead of a flat one is that the former is able to give better under the influence of the high and considerably fluctuating temperature, whereas a flat bottom would soon get out of shape and make the complete removal of the pitch from the still a difficult matter. Very often the still is made in one piece, in which case the dome at the top is provided with a manhole for charging and cleaning out the still. In another form of still the whole dome is detachable, and the flanged joints have to be repacked every time a fresh charged is distilled. The best packing material is asbestos. In the case of horizontal stills, the question of distortion does not have to be considered. A cock for drawing off the pitch is provided at the deepest point of the still, which is usually set on the brickwork so as to have a slight tilt. Internally, the still is provided with stirring mechanism—adapted to the shape of the still—in order to facilitate uniform heating of the liquid, and also to prevent the charge burning on to the still walls; but these stirrers are not set to work until the higher distillation temperatures are reached and the residual charge has become very thick. A better method of keeping the charge in motion is by blowing in dry, superheated steam, because this facilitates distillation at the same time. In place of vertical stills, the horizontal pattern is used, especially in Scotland, the cylinders being about 21 ft. in length and 8 ft. in diameter. The still is protected from direct contact with the fire by an arch, the flame passing through about twenty openings in the sides into flues which surround the cylinder up to about its middle line. The stirring mechanism used consists of a shaft carrying horizontal rods, on the ends of which are attached short chains which scrape along the bottom of the still, in alternate positions, so that one chain scrapes along a part which has been left untouched by the preceding one. In large works a still charge is about 20 tons, but in smaller works, 12- ton stills are used. Though the larger sizes are the more economical in working, it is not desirable to go above a capacity of 18-22 tons, since this quantity can be finished off in about twelve to fourteen hours, whereas larger charges require night shifts. The heavy oil and anthracene oil are mostly distilled by the aid of steam and a partial vacuum.

In all the foregoing stills the tar must first be freed from water before distilling; but latterly methods have arisen in which the heat produced during distillation is utilized for removing the water from the crude tar at the same time. Thus, Respier drys the tar in a column still, of exactly the same type as that for distilling ammonia liquor (q.v.) and mounted on the cover of the dehydrating retort. The tar is run into the column through an intermediate member situated between the three lower and the two upper chambers. The gaseous distillates, water and light oil issue through a pipe connection mounted on the cover, and pass away to a condenser. In addition to this continuous dehydrating retort, are three stills for the separation of medium, heavy and anthracene oil respectively. The method of working is as follows: In starting operations, crude tar is slowly heated to about 200° C. in the dehydrating retort; and the disengaged gases flow through the column. Crude tar enters through a lateral pipe and is heated by the exhaust gases so that the bulk of its contained water and light oil are expelled, this tar then passing into the retort, where the final traces of this fraction are distilled off. The dehydrated tar is drawn off, at a rate corresponding to the rate of feed, into a storage tank, whence it is passed into one of the other retorts, for fractional distillation into medium, heavy and anthracene oil. The distillation of these fractions is carried on *in vacuo*, and proceeds in a very simple and rapid manner. The dehydrating retort dries sufficient tar daily for two or three 18-ton stills, and the whole operation is performed in about ten to twelve hours.

In another method, according to Rispler, the gases issuing from the still are cooled by crude tar, the heat thus transferred serving at the same time to free the crude tar from water and light oil. The apparatus is arranged in the following manner: A completely closed, rectangular iron tank is fitted up with a coil, composed of straight pipes with short bends, which coil is traversed by the still gases. Over this coil is a pipe bent to the same shape, but perforated; and through this pipe the crude tar flows in a thin stream on to the heated coil, and parts with its water and light oil, which escape to the condenser through a connection in the cover of the tank. The dehydrated tar, on the other hand, collects in the bottom and runs off through a connection to the still. The mouth of this outlet is closed by a bell seal, to prevent any vapours being carried along by the tar. The medium and heavy oils are distilled by fire heat: but in distilling off the anthracene oil, a partial vacuum is used, and superheated steam is forced through the mass.

The prevention of the risk of fire in tar distilling is the subject of a process patented by Opitz and Klotz (Ger. Pat. 188,635/1906), in which superheated water is employed as heat transmitter. An endless coil is arranged so that one portion is situated in a heating stove and the remainder inside the still. The hot water ascends through the coil, gives up its heat in the still and flows back, in a cooled state, to the heater. Unless the heater is underneath the still a pump has to be connected up with the coil so as to keep the water in proper circulation and utilize its heat effectually, For complete distillation it is necessary that the water should be raised to a temperature of 400° C., a result which is possible of attainment, since, by increasing the pressure, the critical temperature of water can be raised without converting it into steam. With this object the coil, which is made of special steel tubing, must be tested to stand a pressure of 1000 atmospheres ; and by this means the water can be heated to 400° C., which is sufficiently high for the distillation of all the tar fractions. By providing suitable gauges and safety appliances, any desired temperature up to the above maximum can be produced and automatically maintained. In consequence of the advantageous manner in which the transference of heat is accomplished, this process is economical in operation ; and by the separation of the heating chamber from the distillation chamber the risk of fire is considerably lessened.

For the last stage of distillation, the recovery of creosote oil, a vacuum (up to 15 mm. mercury gauge) is used with great success. At the same time, steam is introduced into the still, to prevent the contents from burning on to the walls. The employment of the vacuum makes the process work more regularly, and, in particular, prevents obstruction of the condenser.

Continuous fractional distillation, *in vacuo*, has been considerably improved by Krey, who arranges two receivers behind the condenser, with interposition of a bulb provided with a three-way cock and air-tight bell seal with gauge glasses. Both receivers are connected to the air-pump, and are also provided with gauge glasses to enable the progress of the distillation to be observed. Distillation is conducted without vacuum until the creosote oil stage is reached. By setting the three-way cock accordingly, the fractions can be collected separately. After each fraction has been collected, the receiver must, of course, be emptied into a vessel underneath. When the vacuum is employed, the two receivers must be brought to the same pressure before reversing the cock—a result which can be controlled by means of the pressure gauge.

Of late years continuous distillation has made great progress. In this system, a continuous supply of fresh tar is introduced and the corresponding quantity of pitch is removed. Numerous proposals have been made in this connection.

Hirzel (Ger. Pat. 115,921/1899) uses a column still of similar pattern to that employed in distilling ammonia. The various cells are heated to 155-160° C. by a coil through which superheated steam under a pressure of $6\text{-}6\frac{1}{2}$ atmospheres is passed. The tar is screened, to free it from solid fragments, and is then fed into the top of the column, whilst the soft pitch runs out at the lower end into a montejus apparatus. The distillate escapes through an opening in the cover, and after condensation is run into a trap in which the heavy oils are separated from the light oil and water, these two latter being separated in turn in a second trap. The heavy oil and light oil are collected in a common tank.

The distillate at 160° C. contains all the constituents which come over up to 300° C. in the ordinary process of distillation, but no anthracene oil, this being contained in the soft pitch. The distillate can be fractionated in the usual way. Hirzel separates the naphthalene by means of a refrigerator, and distils off the anthracene oil with superheated steam at 250° C., separating it from the water after cooling. The advantage of the Hirzel process is that the distillation temperatures are considerably lower, the heavy oils coming over at 155-160° C. instead of at 300° C., and even the anthracene oil being recovered at 250° C. instead of 400° C. Owing to the lower temperature, the distillates are in a much purer condition.

The Lennard continuous distillation process is based on continuous condensation. The crude tar is preheated by the anthracene-oil distillate and thus serves at the same time as a condensing medium. The warmed tar is passed through a scrubber, in which it gives up its contained water and ammonia, together with a little light oil which is then recovered in a condenser. The dehydrated tar is collected in tanks and forced from these, in a constant stream, to the still. This latter consists of a cast-iron coil of many turns, mounted in a special furnace which is heated by producer gas or by means of an oil burner, in order to obtain a constant temperature. The preheated tar flows through this still at a temperature of about 300° C., passing thence to a scrubber which is heated to the same temperature and into which superheated steam is blown in order to extract the volatile constituents from the tar. The residue collecting in the bottom of the scrubber consists entirely of pitch. The distillate is then fractionated by cooling it in stages, and the various fractions are collected separately.

The only other systems which need be mentioned here are: the Wernecke process (Ger. Pat. 201,372/1907), in which the tar is allowed to flow over a number of annular troughs, arranged in steps in a hopper-shaped vessel, in order to obtain more complete utilisation of the heat; and the Böckelmann and Sachse vacuum process (Ger. Pat. 154,755/1903).

CHAPTER V.

THE GAS LIQUOR.

THE gas liquor consists of the constituents which collect in the form of an aqueous liquid, together with the tar, in the hydraulic main and condensers, and as the tar-free drainings from the ammonia washer. The liquor obtained by condensation, as mentioned in the preceding chapter, is separated from the tar in the tar pit, and is run into a collecting pit with the washing water.

Gas liquor is yellowish to deep orange in colour. In addition to ammonia, it smells of sulphuretted hydrogen and tar. Chemically speaking, gas liquor consists of ammonia, ammonium salts and volatile constituents of tar, especially pyridin and phenols. The ammonium salts may be divided into two groups according to the relative difficulty experienced in decomposing them. To the readily decomposable salts belong: ammonium sulphide, ammonium cyanide, ammonium sulphydrate and the three forms of ammonium carbonate. The more stable salts are: ammonium chloride, sulphate, sulphite, thiosulphate, thiocarbonate and ferrocyanide.

It is not advisable to store gas liquor very long, because, as Lindner has shown, in these circumstances the proportion of the more stable salts increases. In such case the consumption of lime also increases, thus adding to the cost of production.

TESTING GAS LIQUOR.

The most valuable constituent of gas liquor is the ammonia. Attempts to recover the cyanogen compounds have not proved successful in practice, owing to the small proportion present, especially when the cyanogen washing process has been carried out beforehand. Before proceeding to recover the ammonia it is necessary to know both how much is present in the free state and how much is combined as stable salts; and it is to ascertain these data that the examination of the liquor is chiefly directed. The amount of the stable salts indicates the quantity of lime that must be added for their decomposition. There is no need to go into the examination for the acids with which the ammonia is combined, these being unimportant and non-essential.

The total ammonia is determined by distillation in presence of lime. Caustic soda should not be used for this purpose, because this reagent also liberates as ammonia the nitrogen of the cyanides and thiocyanates present, and thus gives results in excess of the truth.

The distillate is cooled, and then collected in acid of known strength, the excess of acid being afterwards titrated with equally strong caustic soda. The percentage of ammonia is obtained from the difference between the original volume of the acid and the excess as found by the titration, 1 c.c. of normal acid corresponding to 0·017 grm. of ammonia.

To determine the ammonia in combination as unstable salts, that is to say salts which split up at 100° C. into ammonia and free acid, the same apparatus is used as in the total ammonia determination; but a correspondingly larger volume of test liquor is taken and no milk of lime is added.

To determine the fixed ammonia, the residue from this last distillation may be diluted with water and redistilled after adding milk of lime; but in many cases it is sufficient to calculate the fixed ammonia from the difference between the total and that in unstable combination.

The amount of active substance (CaO) in the lime is ascertained by rubbing down an average sample, and placing a weighed quantity (70 grms.) in boiling distilled water. After stirring the mixture thoroughly and allowing the liquid to cool, the volume is made up to 1000 c.c., and an aliquot part (20 c.c.) of the well-shaken liquid is treated with two to three drops of phenolphthalein and titrated with normal sulphuric acid until the red coloration disappears. For the proportions given above, 1 c.c. of normal acid corresponds to 2 per cent of active lime.

TREATING THE GAS LIQUOR.

The gas liquor from the pit or tank contains 1-3 per cent of ammonia. As this quantity is too small to make the carriage of the crude liquor to a distance profitable, the liquor must be concentrated, no matter for what purpose it is intended. It is therefore customary in gasworks to concentrate the liquor to a strength of 10 per cent or 25 per cent of ammonia, or else to convert the whole of the ammonia into sulphate. In some large works, strong ammonia is produced, but in the majority of cases the concentrated liquor is sold to firms who make a special feature of treating this material.

The simplest way to concentrate the ammonia, and one which dispenses with distillation, is to convert it into sulphate of ammonia; but this process is mostly confined to small works, where the quantity of gas-liquor to be dealt with is not large. Commercial sulphuric acid (66° Bé. strength) or waste acid is diluted by running it through a siphon, as a thin stream into gas liquor in a wooden vat. This dilute acid is then added to the gas liquor in the pit until the mixture just turns blue litmus paper red. Since sulphuretted hydrogen is liberated in this operation, the work should be carried on out of doors, a cowl being placed over the pit, to carry off the poisonous fumes. The sulphate of ammonia liquor thus obtained is concentrated by means of the heat of the flue gases from the retort fires, a number of long iron pans, lined with lead, being placed in the flue and charged with the liquor, which evaporates until the salt crystallizes out. The sulphate crystals are separated from the mother liquor by means of a centrifugal separator ("whizzer"). The product is an inferior grade of sulphate of ammonia, though containing about 20 per cent of ammonia, the colour being a dirty dark grey from the presence of tarry matters derived from the gas liquor.

THE DISTILLATION OF GAS LIQUOR.

The process almost exclusively used for concentrating gas liquor is one of distillation. As already mentioned the liquor contains stable ammonium salts in addition to free ammonia and easily decomposable salts. The principle of the treatment is to distil the ammonia and unstable salts off first, by warming the liquor to the boiling point of water. When this has been done, the stable salts are decomposed with lime, and the ammonia set free is recovered by distillation. The reason for not adding the lime until this second stage is because, in this way, the lime is utilized to the best advantage for liberating ammonia from the more stable salts; whereas if it were added before the first distillation, a large proportion would be consumed in combining with the carbon dioxide—a considerable quantity of which is contained in the gas liquor and is expelled at the same time as the free ammonia—without producing any corresponding yield of ammonia.

At one time any old boiler was considered good enough for the first distillation of gas liquor. The boiler was charged with liquor and fired until all the volatile ammonia had been driven off, after which it was filled up again and the operation repeated, until the remaining liquor had become sufficiently concentrated in fixed salts. On this stage being reached, the lime was added, and the fixed ammonia distilled off.

This method was improved by arranging a number of boilers side by side, and utilizing the flue gases from the first one to heat the others. The distilled vapours passed through the whole series of boilers in succession and thus became enriched with ammonia. When all the readily decomposable ammonia had been expelled in this way, the whole of the residual liquor was pumped into the first boiler of the series, and there freed from the ammonia in the stable salts after addition of the calculated amount of lime needed for their decomposition.

This intermittent method is now practically discontinued in favour of continuous distillation. The apparatus constructed by Franke (Bremen) for this purpose consists of a still, divided into two compartments (approximate ratio 3 : 2) by a horizontal partition. From the lower compartment a pipe for carrying off the ammonia vapours ascends through the upper compartment, and leads thence to the condenser and concentrated liquor tank. Both compartments of the still are fitted with pressure gauges, safety valves and upcast pipes. The still is enclosed in a wrought-iron jacket traversed by the hot gases from the fireplace which is situated underneath the still.

In working the apparatus, the lower compartment of the still is charged with about 90 galls. of gas liquor, the ammonia vapours from which pass through the exhaust pipe to the condenser, furnishing a 10 per cent ammonia liquor which runs into the collecting tank. When the ammonia has been expelled, the cock leading to the condenser is turned off, and the hot liquor rises through an upcast pipe into the upper compartment of the still, its place being taken by a fresh charge of gas liquor, which is distilled as before, after opening the condenser cock again. While this fresh charge is being treated, the liquor in the upper compartment remains at boiling temperature; and when this compartment has been filled with the residual liquor from several such charges, its contents are drawn off, cooled, and used as washing liquor in the ammonia washer. In this way the gas liquor passes through a continuous cycle of operations, and gradually becomes enriched with fixed ammonia salts, whereupon it is treated with lime and distilled in one operation.

In works where the amount of gas liquor available is large, the distillation of the ammonia is now almost exclusively performed by the continuous process, the heat being utilized in a very complete manner, and the method enabling far larger quantities of liquor to be dealt with, per unit of time, than in the old method of distillation in boilers.

The plant is arranged in such a way that the lime is not added until all the volatile ammonia has been driven off. The steam used for heating the apparatus is derived either from the gas liquor itself or else from a steam boiler. It is employed, in the first place, for expelling the ammonia liberated by the lime treatment; then for mixing the lime charge with water; and finally for driving off the free ammonia in the gas liquor, after which, laden with the whole of the ammonia from the gas liquor, it passes to the condenser. The heat liberated during condensation serves for preheating fresh quantities of gas liquor, for which purpose the heat of the spent gas liquor—effluent—can also be utilized.

The continuous distillation of the ammonia liquor is based on the same principle which led Savalle to devise the column still for rectifying alcohol. The whole system of the distillation of gas liquor is based on three phases: expulsion of the volatile ammonia; addition of lime; expulsion of the ammonia combined as stable salts.

This subdivision of the working process necessarily implies a corresponding subdivision in the arrangement of the column still. The three parts of the apparatus are disposed in such a manner that the gas liquor from a high-level tank traverses them in succession. Both the upper and lower parts of the column are divided into a number of superimposed cells, whilst the middle portion is occupied by the lime mixer, which in the newest patterns consists of only a single cell. The gas liquor is led away through tubular connections which project a short distance above the floor of each cell, so that a certain depth of the liquor remains in each, whilst the surplus overflows into the cell next below. Each tube is long enough to dip below the level of the liquor in each case; and the tubes are arranged so that the liquor traverses the cells in a zig-zag course. The steam which carries off the ammonia vapour passes upward from one cell to another through perforations arranged in the cell bottoms and extending upward through same in the form of short trunco-conical tubes which are long enough to project above the level of the gas liquor and are surmounted by loose caps supported by tripods resting on the cell floor. These caps dip below the level of the gas liquor and are provided with notches. In passing from one cell to another the steam is compelled to make its way through the liquor in the upper cell, and as it does this by bubbling through each of the notches provided in the caps, it comes into intimate contact with the liquor and becomes enriched with ammonia. The steam enters the apparatus by the bottom cell and leaves it at the top one, whilst the warmed gas liquor travels in the opposite direction, and parts with the whole of its ammonia before issuing from the bottom cell. The counterflow principle is thus amply made use of in this arrangement, the hot fresh steam coming into contact with the warm liquor which is poor in ammonia, and taking up from the latter merely the fixed ammonia which has just been liberated by the lime, whilst the steam that is fully laden with ammonia comes in contact with the fresh gas liquor.

A few types of this kind of apparatus will now be described.

Fig. 2 represents a column still made by the Berlin-Anhalt Maschinenbau Aktiengesellschaft. It is built up of a number of flanged cast-iron rings, superimposed on a pan which is provided with a sloping bottom, the whole being surmounted by a cover. The steam and ammonia escape through A. The cell bottoms already mentioned are mounted on the internal flanges of the rings. The cells are provided with openings, for cleaning purposes, and the whole interior is accessible, so that the whole still can be cleaned out without having to be taken apart. The preheated gas liquor enters the top cell through a lateral feed pipe, B, and flows downwards from cell to cell, meeting a current of steam on its way. The course taken by the steam is indicated by the light-coloured arrows, and that of the gas liquor by the black ones. As the steam flows through the crude liquor at the loose caps it gradually raises the same to boiling, so that, in the upper part of the apparatus, the volatile ammonia and the other gases pass into the steam. The lime is added in the third cell from bottom, in which section the tubes and caps are made higher, so as to provide for the increased volume of liquor due to the addition of the milk of lime. The deeper immersion of the caps causes the liquor to be kept in active movement by the steam. The milk of lime, in slight excess, is introduced through a lateral pipe C, and mixed with the water. In the two bottom cells the fixed ammonia is extracted from the gas liquor. The effluent, which should contain only about 0·005 per cent of ammonia,

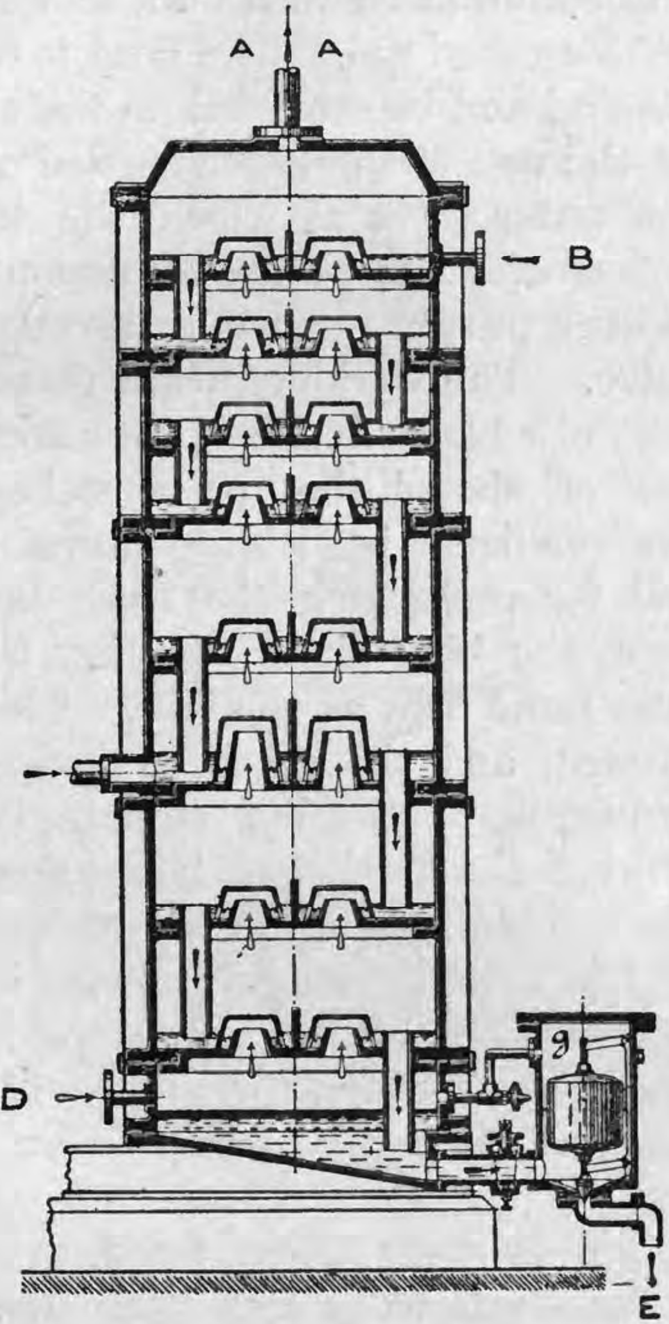

FIG. 2.—Column still. A—A = steam and ammonia gas; B = ammoniacal liquor; C = milk of lime; D = steam; E = to spent lime pit.

issues from the apparatus through a self-adjusting draw-off valve, *g*, which consists of a movable float made of sheet-iron, faced with lead, and carries the cone valve on an iron rod. The float is housed in a cast-iron casing and is subjected to the same steam pressure as the rest of the lower portion of the still, so that the water level at which the valve opens remains constant. The steam admission pipe D is provided with a pressure gauge, a throttle valve and a safety valve. The working steam pressure of the apparatus is only $1\frac{1}{2}$-$4\frac{1}{2}$ lb., and the safety valve is set to blow off should that pressure be exceeded. The effluent gas liquor has a temperature of 212° F., and is used for preheating the fresh liquor in an apparatus of the kind shown in Fig. 3, which is made by the same firm as the still. This is of the tubular pattern, and the tubes are traversed from above downwards, by the hot effluent liquor from the still, whilst the fresh gas liquor flows upward through the cylinder, and is thereby warmed to about 60-70° C. (140-158° F.) before entering the column still. The admission of the gas liquor is adjusted by a feed regulator ; whilst the supply of lime to the still is controlled by a hand-pump or an automatic steam pump.

The Koppers still differs from the one just described, both externally and internally. It consists of two portions ; and only the volatile ammonia is expelled, and the mixing of the lime and gas liquor effected, in the main column. The vessel for mixing the milk of lime consists of a single, funnel-shaped chamber. The gas liquor, deprived of its volatile ammonia, enters the mixing vessel, along with the milk of lime, at the lowest point ; and at a point about half way up the side of the vessel the mixture runs off through a pipe into an independent auxiliary column, in which the fixed ammonia is expelled. The escaping gases pass underneath the lowermost cell into the mixing vessel. The

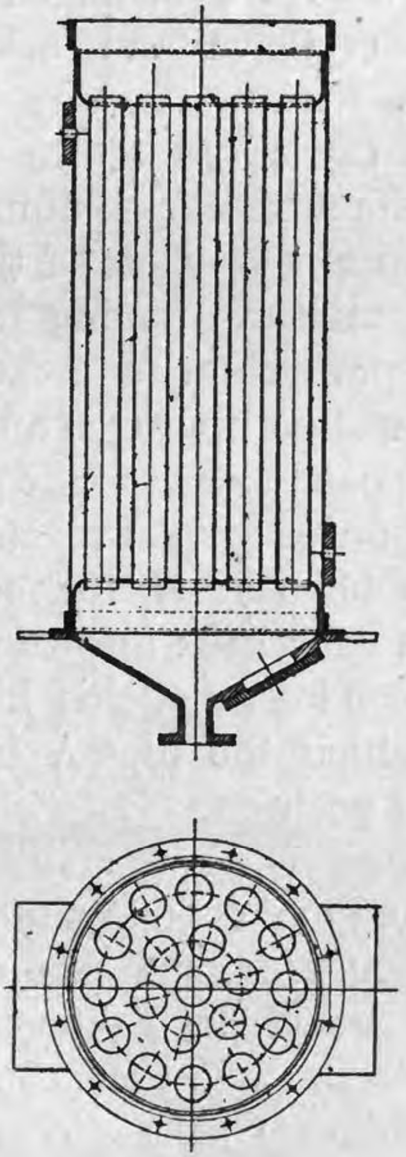

FIG. 3.—Tubular preheater.

openings in the cells, for the passage of the mixed steam and gases, consist of two long, narrow slits, with loose caps of corresponding shape; and those in the various cells are arranged crosswise with relation to those above and below. Distillation proceeds in the manner already described. The separation of the two stages of the process has the advantage that the auxiliary column can be cleaned without taking apart the whole of the apparatus.

The gaseous mixture issuing from the column contains a large proportion of steam, together with ammonia, sulphuretted hydrogen and carbon dioxide. A water-cooled condenser, for concentrating the ammonia, is mounted over the column. The gas liquor may also be utilized for condensing. The condensed steam runs back into the top cell of the still. A reflux condenser of this kind is illustrated in Fig. 4, in which the pipe A is shown at right angles to its real position.

The gas issuing from the still is mostly contaminated with carbon dioxide and sulphuretted hydrogen. If strong ammonia liquor were produced, the carbonates would be liable to deposit in the condenser and choke it, so that continuous working could only be obtained at the cost of very careful supervision. On leaving the apparatus, the gases are pumped to their further destination. Any obstruction in the condenser would set up increased pressure in the still, on the one hand, and on the other a vacuum would be produced between there and the pump. It follows therefore that any such

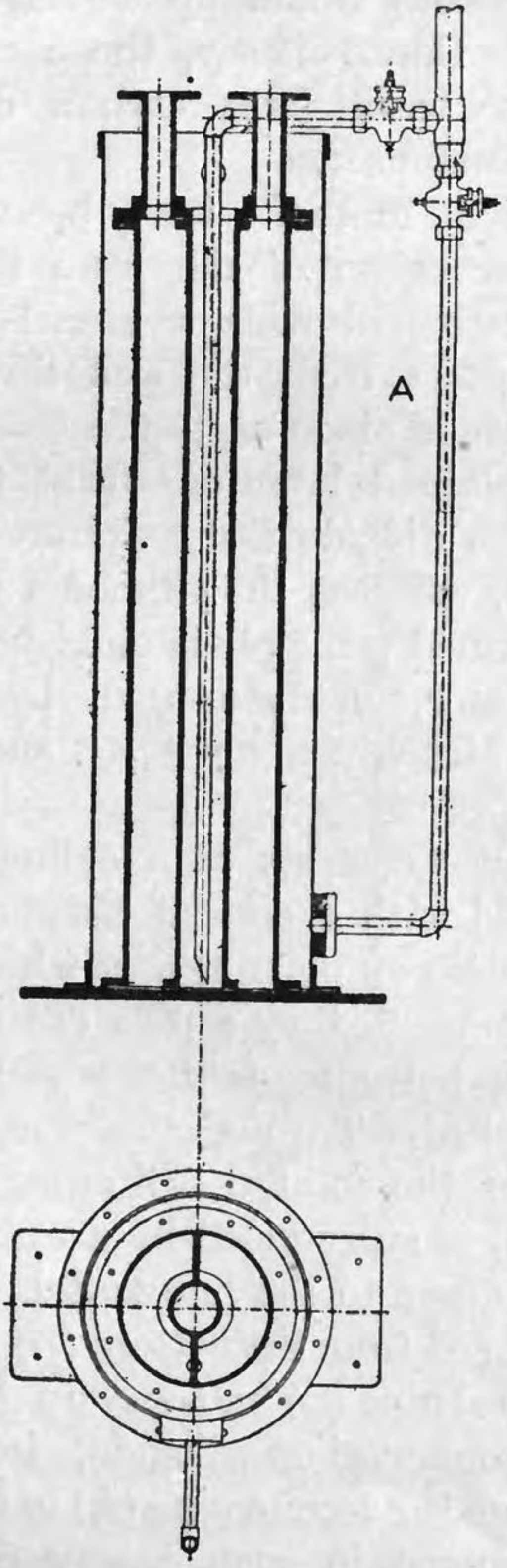

FIG. 4.—Reflux condenser. A = pipe turned at right angles.

deposition of salts would upset the whole series of operations. Consequently, the concentrated gas liquor must be freed from carbon dioxide before entering the condenser.

Two principal methods have been proposed for eliminating the carbon dioxide from the still gases. Either the carbon dioxide is absorbed by passing the effluent gases from the still through milk of lime, or else use is made of the fact—which will be more fully explained later on—that the gas liquor gives off carbon dioxide and sulphuretted hydrogen when warmed, whereas the ammonia is retained.

The first-named principle is embodied in a carbon-dioxide separator, manufactured by the Berlin-Anhaltischer Maschinenbau A. G. and illustrated in Fig. 5.

This separator consists of a cylindrical cast-iron vessel, provided with a conical bottom. The cover is provided with two openings, of which the one in the centre is traversed by a pipe (T) which extends nearly to the bottom of the vessel, where it is flared and notched. Through this pipe, at B, the effluent gases from the column still enter the separator. The pipe itself is surrounded by a number of plates sloping at an angle to the horizontal. The milk of lime is introduced from the bottom (D) and flows away through a lateral pipe (C) half-way up the vessel. The gas, freed from carbon dioxide, issues from the purifier through the second pipe (A) in the cover. The plates are arranged in such a way that the gas is compelled to describe a zig-zag course through the liquid. The milk of lime runs into the lime vessel of the column still, and is there freed from the ammonia it has absorbed, thereafter serving to liberate the fixed ammonia. The purified gas is then forwarded to the condenser.

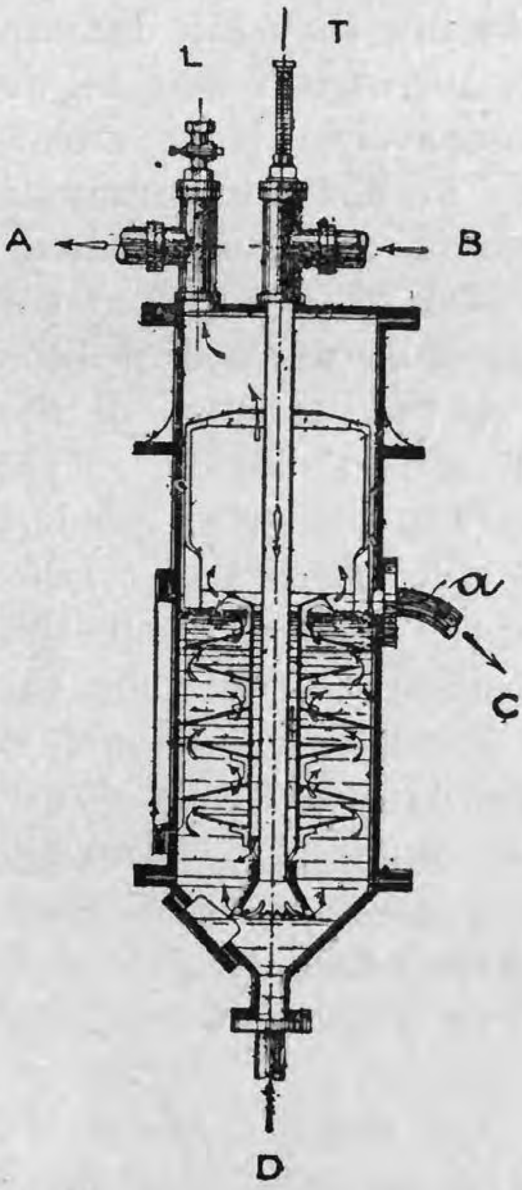

FIG. 5.—Carbon-dioxide separator. A = purified ammonia gas; B = ammonia gas and CO_2; C = to still; D = milk of lime.

The separation of the carbon dioxide by warming the gas liquor is based on the following considerations: Ammonium sulphide and ammonium carbonate belong to the most readily decomposable class of salts, that is to say they are decomposed by heat into ammonia and carbon dioxide, or sulphuretted hydrogen, respectively. Now, warm water has a greater capacity for absorbing ammonia than it has for carbon dioxide and sulphuretted hydrogen, so that if a solution of ammonium sulphide or ammonium carbonate be warmed, it becomes enriched in ammonia at the expense of the sulphuretted hydrogen and carbon dioxide. Experiments performed by Bertelsmann with gas liquor in a Feldmann column still showed that gas liquor ceases to absorb carbon dioxide when the temperature reaches 96° C. (205° F.)—see the subjoined Table, in which the content of ammonia, carbon dioxide and sulphuretted hydrogen is set down as 100. The column still was composed of eleven cells; and during the experiment, determinations were made of the temperature in each cell, and also of the amounts of ammonia, carbon dioxide and sulphuretted hydrogen in the liquid.

In the first five cells, in which the temperature rose to 93° C., the gas content in the water increases continually, the ascending vapour giving up a portion of the gases to the water again. In the sixth cell, in which the temperature attains 96° C., the percentage of carbon dioxide diminishes by one-half, and that of the sulphuretted falls by more than 50 per cent, whereas the water still contains 170 per cent of ammonia. Up to the ninth cell the temperature rises to 97° C., and whilst practically the whole of the carbon dioxide has been expelled, the ammonia content still amounts to 26 per cent.

Water Sample from Intake of	Temperature °C.	Gas Content of the Water in Percentages of Original Amount.		
		Ammonia.	Carbon Dioxide.	Sulphuretted Hydrogen.
Cell 1	55	142	144	144
„ 2	87	380	187	269
„ 3	90	377	168	165
„ 4	93	359	134	181
„ 5	93	307	109	126
„ 6	96	170	57	50
„ 7	96	89	39	4·3
„ 8	97	49	18	3·4
„ 9	97	26	0·3	1·9

Hence, if the crude gas liquor be kept at this temperature before it is admitted to the column still, a liquor very low in carbon dioxide will be obtained. The Feldmann-Pintsch separator is based on this principle, and consists of a cast-iron cylinder divided into two parts. The gas liquor, preheated by the effluent from the column still, is introduced into the lower part of the apparatus and is heated by a steam coil to 88-95° C., which causes it to give off carbon dioxide, sulphuretted hydrogen and also ammonia. The liberated gases pass into the upper part of the separator, where they come in contact with a current of cold gas liquor, which absorbs the ammonia completely, leaving the carbon dioxide and sulphuretted hydrogen to escape into the open air.

WORKING THE STILL.

Starting the apparatus for the continuous distillation of the gas liquor is a very simple operation, all that is necessary beforehand being to employ the usual precautions to see that none of the apparatus is leaky. Heating up should be effected slowly, and it is not until the entire contents of the still are properly warmed through that the fire should be quickened, to raise the liquid to boiling. When the contents are drawn off, the fire should be extinguished.

If milk of lime be used from the start, the liquid should be stirred up from time to time, to prevent the lime burning on to the metal, since, in addition to the loss of heat, this would give rise to the usual dangers of boiler incrustation.

The continuous column stills are heated by direct steam. Before starting, the still should be warmed up in the dry state, the water of condensation from the heating steam collecting in the bottom of the cells. The admission of steam is gradually increased, and at the end of about two hours, the pressure should attain $1\frac{1}{2}$-3 lb. per square inch. The gas liquor is then admitted, and the pressure is maintained by controlling the supply of steam. As soon as the effluent water begins to drain off, the milk of lime is added; and the temperature is raised, by admitting more steam, until no more volatile ammonia can be detected in the cell above the lime-mixing vessel. The inflow of milk of lime is then regulated in such a manner that the effluent water is free from combined ammonia as well. This condition can be ascertained by testing a sample of the effluent with a little fresh lime, under which conditions no smell of ammonia should be noticeable. After the admission of the steam, gas liquor and milk of lime has been properly adjusted, care must be taken to see that the supply of each remains constant throughout the whole of the distillation process, the effluent liquor being tested from time to time to make sure that everything is in order. If the steam pressure be too high, the gas liquor is liable to be forced into the gas delivery pipe. To test whether this is the case, a hole is bored in the ammonia pipe, and if the steam which then escapes contains moisture—which may be ascertained by holding the hand in the escaping current, whereupon any moisture present will make the hand wet—the supply of steam must be reduced.

In the course of distillation the temperature will fall unless the supply of steam be increased, owing to the walls and bottom of the cells becoming incrusted with lime. For this reason the column should be cleaned out, by means of the manholes, at the end of every month or two.

One of the most troublesome obstructions to the working of the still is caused by tar passing into the column; but this drawback can be prevented by careful supervision of the pumps and the ammonia liquor pits. If, notwithstanding, any considerable quantity of tar finds its way in, about the only thing that can be done is to dismount the apparatus entirely and clean it out.

The consumption of fuel depends on the nature of the fuel and the construction of the still. With the Feldmann-Pintsch apparatus, 4 cwt. of steam will be required for the distillation of 220 gals. of gas liquor, so that, given an evaporative power of 7:1, 43 tons of coal will be needed in treating 330,000 gals. of gas liquor.

PREPARATION OF CONCENTRATED GAS LIQUOR.

Although a method of obtaining 10 per cent gas liquor has long been known, a higher concentration is generally desired, and for this purpose a continuous process is exclusively employed.

As a rule, two grades of concentrated liquor are produced: a weak liquor containing 16-20 per cent of ammonia, and a stronger liquor with 18-25 per cent.

The weaker liquor has a density of 15-18° Bé., and contains a large proportion of ammonia in combination, chiefly as carbonate. It is prepared without the employment of a carbon-dioxide separator. The manufacturing process may be illustrated by reference to the plant made for this purpose by the Julius Pintsch A. G. (Ger. Pat. 179,080) and illustrated in Fig. 6.

The crude liquor runs from a high-level tank to the ball-cock tank *b*, which serves to keep the gas liquor at a constant level and ensure uniform feed. From this tank the liquor flows through the cock *c* to the condenser *n*, which it enters from below and in which it plays the part of condensing agent. The gases from the still enter the top of this condenser and are cooled down, the crude liquor being preheated at the same time. The condenser is composed of several members united together to form a double worm, the cooling agent, the crude gas liquor, flowing upward through the one coil, whilst the hot gases pass down inside the other and are condensed. To ensure complete condensation, the condenser is divided into two parts, cooling water being used in the smaller, upper compartment. The preheated crude liquor next enters the top cell of the column still, *d*. In the upper part, *h*, the volatile ammonia is expelled, whilst the crude liquor runs off into the lime mixer, *g*. Here it is mixed with milk of lime, which is admitted, either at stated intervals by means of a hand pump, or else continuously by means of a steam pump, *k*, the delivery of which can be carefully adjusted. The intimate mixture of the lime and gas liquor is effected by means of a steam spider. The resulting mixture is then run into the auxiliary column still, *f*, and thence to the bottom chamber, *e*, where the final traces of the combined ammonia are driven off. From this chamber the spent mixture is discharged, as effluent, to the settling tank, through a cock, *l*, which may be either operated by hand, or else self-acting.

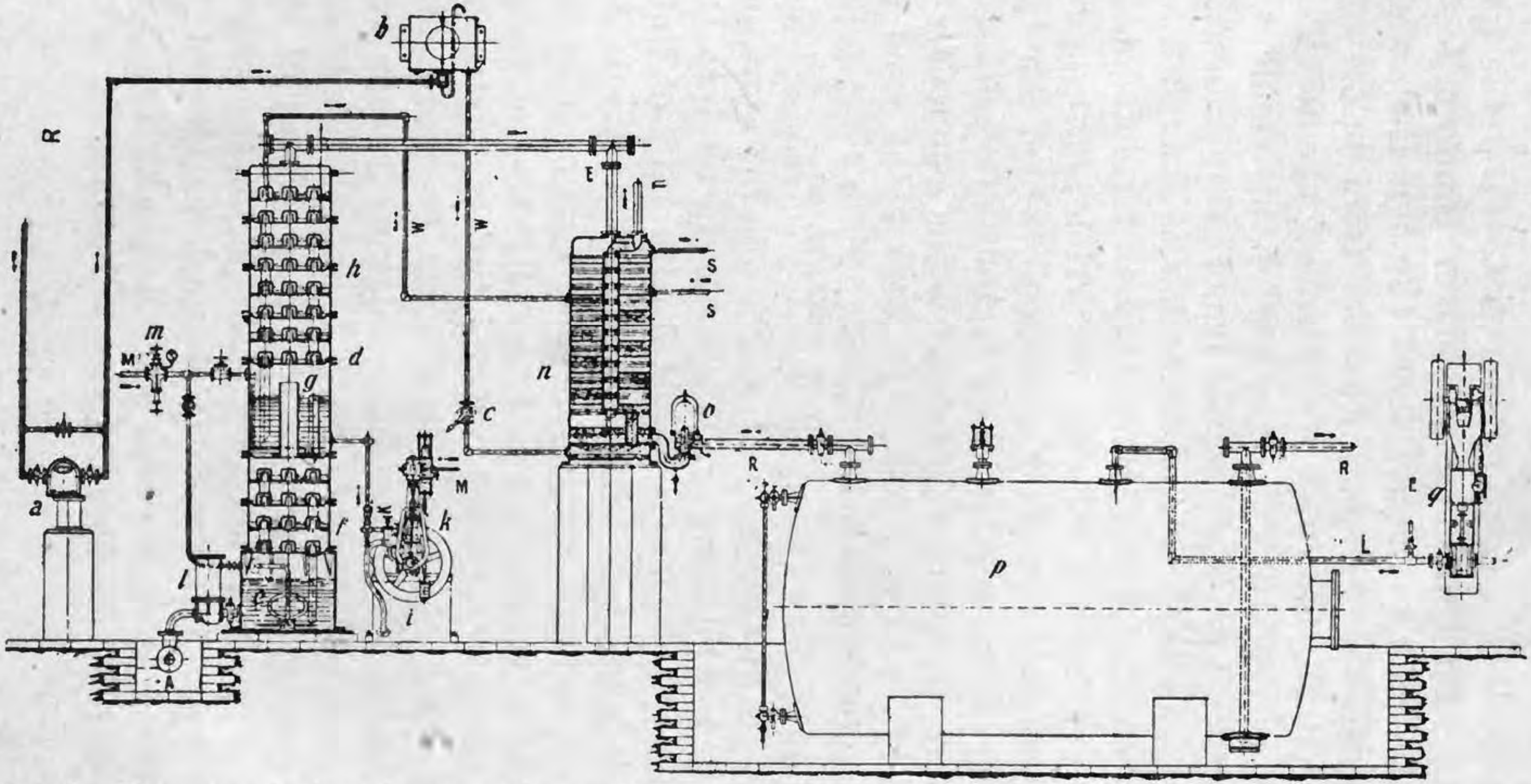

FIG. 6.—Diagram of plant for preparing weak ammonia liquor. A = effluent water; E = ammonia vapour; K = milk of lime; L = compressed air; M = steam; R = concentrated ammonia liquor; S = cooling water; T = vent; V = gas liquor from high level tank; W = gas liquor.

The steam enters the lower chamber, *e*, flows through the cap-covered openings in the bottom of the several cells, and becomes saturated with ammonia, ammonium carbonate and small quantities of ammonium sulphide. The ammoniacal vapours are condensed in a condenser, *m*, and are delivered to the storage vessel, *p*. This vessel is emptied by compressed air, furnished by the compressor, *q*.

This plant will produce a liquor containing up to 18 per cent of ammonia, assuming the crude liquor to have an average content of 20 per cent of combined ammonia.

In order to obtain the stronger grade of ammoniacal liquor (up to 6° Bé. strength), it is necessary to free the gas liquor from carbon dioxide. As has already been seen, this elimination of carbon dioxide can be effected in two principal ways. One of these —the warming of the gas liquor—forms the basis of the apparatus illustrated in Fig. 7 and embodying the Feldmann-Pintsch system. It differs from the apparatus just described, for the production of weak ammonia liquor, by containing a carbon-dioxide separator, *t*, and a reflux condenser, *x*, mounted on the column still. Clarified water alone is used for condensing the waste bases in *s*.

The crude liquor flows from the ball-cock tank into the ammonia absorber, *r*, of the carbon dioxide separator, *t*, whence it is passed through the preheater, *v*, to be warmed by the effluent water from the column still. The preheated liquor is next heated to 88-95° C. in the heating chamber, *s*, of the

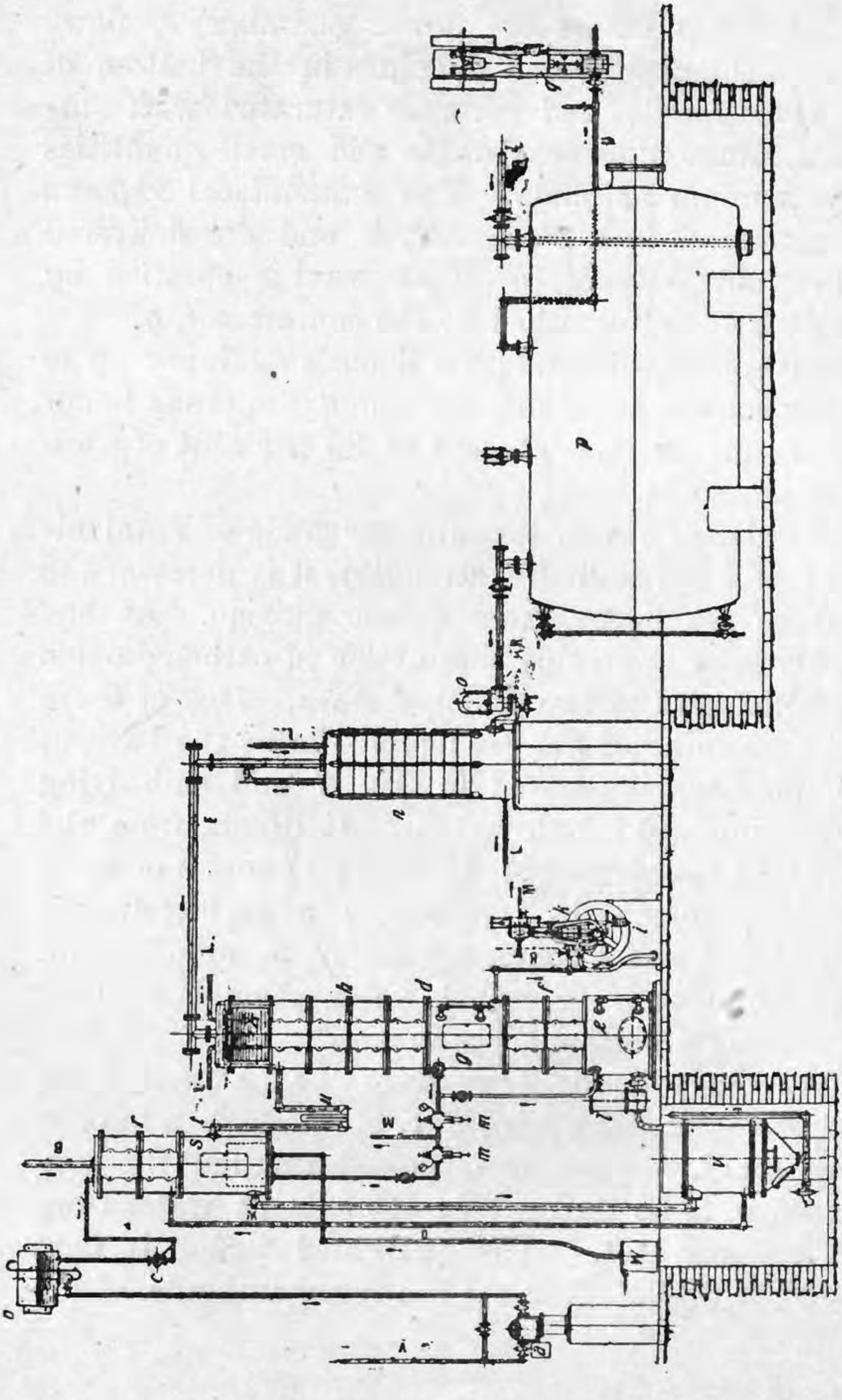

FIG. 7.—Diagram of plant for preparing strong ammonia liquor. B = waste gas; E = ammonia vapour; G = vent; L = cooling water; O = condensed water; V = compressed air; W = gas liquor.

separator, *t*, by a steam coil, and parts with its carbon dioxide. Any ammonia carried off at the same time is reabsorbed by the crude liquor in *r*. The liquor freed from carbon dioxide is distilled in the column still, *d*. In order to concentrate the ammoniacal vapours, a portion of the steam is condensed in the reflux condenser, *x*, mounted on the still. The further course of the process is identical with that given in connection with the preparation of the weaker grade of liquor.

To prepare concentrated ammonia liquor by removing the carbon dioxide with lime, the separator illustrated in Fig. 5 is employed. The gas liquor flows from the high-level tank through a cellular condenser of the kind shown in Fig. 8, where it is preheated, and at the same time the still gases are condensed. The preheated liquor is distilled in the column still, and the gases from the latter are freed from steam by the reflux condenser, from which they pass into the carbon dioxide separator, in which both the carbon-dioxide and the sulphuretted hydrogen are absorbed. The outflowing gases are condensed in the cellular condenser and conveyed to the storage vessel. The milk of lime used for purifying the gases is run into the lime mixer of the still, and there serves to expel the combined ammonia.

The concentrated ammonia liquor resembles the crude gas liquor in appearance, and, like the latter, darkens in colour on standing. Its value is ascertained by a simple titration, 10 c.c. being diluted to

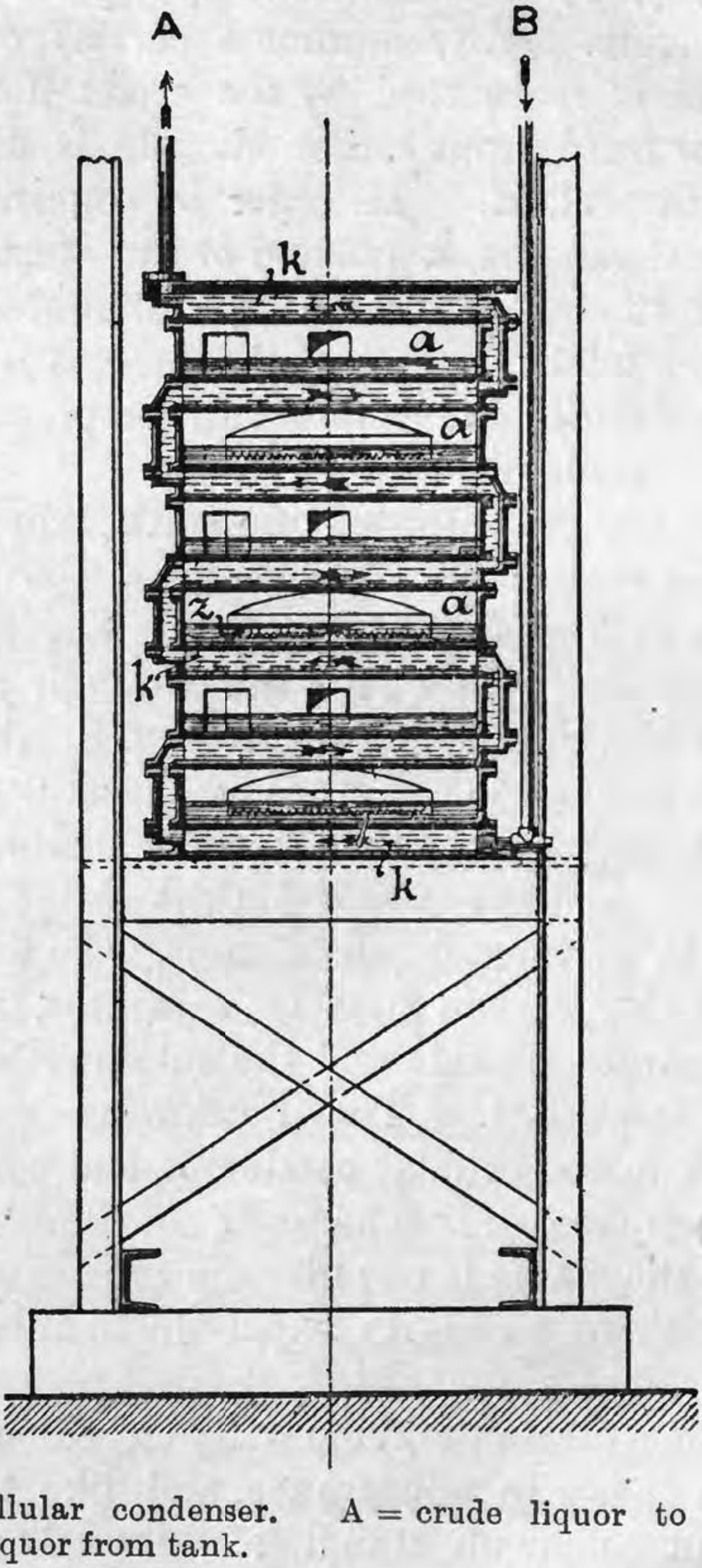

FIG. 8.—Cellular condenser. A = crude liquor to still; B = crude liquor from tank.

1000 c.c. and an aliquot part being treated with an excess of normal sulphuric acid. After boiling for a short time the excess of sulphuric acid is titrated back with normal caustic soda, methyl orange being used as indicator.

The concentrated liquor is not, in itself, a commercial article, but forms the raw material for the manufacture of ammonia preparations, and is therefore a semi-manufactured product.

PREPARATION OF AMMONIA.

The most valuable products recoverable from gas liquor are aqueous ammonia and liquefied ammonia, the former being a chemically pure product obtained by absorbing ammonia in distilled water. It is recovered direct from the gas liquor, without the assistance of any other chemical agents, such as acids or salts, and differs from the crude gas liquor in being free from any contamination with carbon dioxide, sulphuretted hydrogen or organic (empyreumatic) substances. In connection with the preparation of aqueous ammonia, Pfeiffer of Magdeburg has rendered valuable service. It is prepared, either by the intermittent process in boiling pans, or by the continuous process in column stills. The gases from the pans or stills are freed from contained acids by milk of lime and are then dried, the dried gases being filtered through wood charcoal (and also through vaseline oil if necessary) to eliminate organic substances, chemically pure gaseous ammonia being finally left. The further treatment of this gas can be carried out in two ways. For the production of aqueous ammonia it is passed into distilled water, whilst for making liquefied ammonia it is put through a compressor.

The intermittent process of preparing aqueous ammonia is carried on in the following manner:—

The still is charged half full with the crude liquor and slowly heated, the gases liberated during this stage being returned to the crude liquor tank. When the liquor has reached distillation temperature (100° C.), a calculated quantity of milk of lime is added at once. The gases disengaged are passed into a high reflux condenser, two cells, provided with loose caps, being interposed between the still and condenser, in order to prevent any lime from being carried off with the gases. The addition of the milk of lime before distillation causes practically the whole of the carbon dioxide and sulphuretted hydrogen to be retained in the still. The high reflux condenser condenses the whole of the steam, which then flows back into the still, carrying with it a portion of the ammonia and the final traces of carbon dioxide and sulphuretted hydrogen. The gas, dried in this way, is next passed through several cylinders charged with wood charcoal, in which the empyreumatic substances are absorbed. The final traces of carbon dioxide and sulphuretted hydrogen are extracted with caustic soda, leaving the gaseous ammonia chemically pure. To prepare aqueous ammonia, this gas is introduced into a cylinder containing distilled water, the absorption being effected by the acid, on the counterflow system. The absorption of ammonia by water is based on a chemical reaction accompanied by the disengagement of heat:—

$$NH_3 + H_2O = NH_4HO + 8435 \text{ cal.}$$

In order to enable the water to take up as much ammonia as possible it must be cooled, preferably by immersing a cooling worm in the liquid. The absorption vessel is composed of several cells, communicating by means of syphons. The pure ammonia gas enters the liquid in the lowest cell first, where the bulk of the absorption takes place. The unabsorbed gas traverses the superimposed cells in succession, so that the water which is poorest in ammonia has only to absorb the final traces of the gas. When the water in the lowest cell is completely saturated with ammonia it is drawn off into carboys or drums. The liquid charge in each of the higher cells is transferred to the one next below, and the top cell is recharged with fresh water. With a plant of this kind a solution containing 25-28 per cent of ammonia can be prepared. The still is heated by steam, the exposure of the still directly to fire heat necessitating careful supervision on account of the addition of lime. The charcoal filters must be renewed every five or six weeks; and the charcoal can be regenerated, for which purpose steam is blown through the filter before the latter is emptied, the steamed charcoal being then heated to incandescence out of contact with air, whereupon it is ready for use again. The process of making aqueous ammonia requires to be carefully controlled, the gases being subjected to constant examination, for the presence of sulphuretted hydrogen, after the washing with caustic soda.

It is only of late years that the preparation of aqueous ammonia by the continuous process has been carried on with success. The Berlin-Anhaltische Maschinenbau A. G., in collaboration with Grüneberg, Tieftrunk and Buhe, was the first to devise a process of this kind on the large scale, with which it was found practicable, in an Upper Silesian works, to treat nearly 1800 galls. of gas liquor in twenty-four hours.

From that time onwards, the continuous process has developed progressively. The plant now supplied by the above firm is based mainly on the patented carbon-dioxide separator and the grouping of the apparatus in such a way that, throughout the process, the milk of lime flows in the opposite direction to that taken by the ammoniacal gases.

The working of the process is checked by testing the effluent ; and so long as the latter contains an excess of lime, it is evident that such excess is also present throughout the process. The ammoniacal gases issuing from the still are passed through a reflux condenser which eliminates all but a slight trace of steam from the gas. The latter still contains carbon dioxide, sulphuretted hydrogen and empyreumatic substances, the first two of which are completely removed by passing the gas through a series of three milk-of-lime vessels (Fig. 9), such as are used in concentrating the crude gas liquor, and in which the milk of lime flows in the opposite direction to that of the gas and runs off into the still. The gas passes through two condensers and a coke filter,

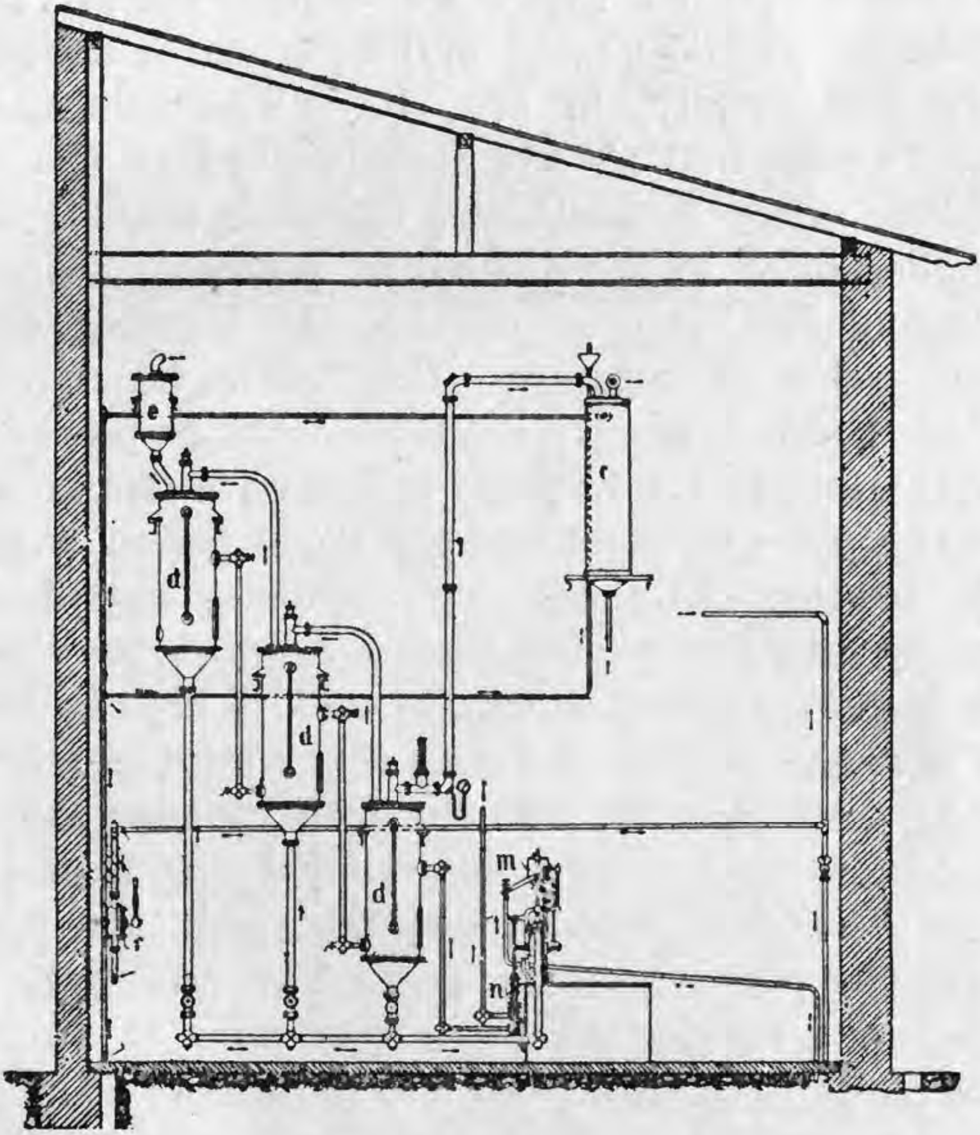

FIG. 9.—Lime washer.

after which the bulk of the chief organic impurities is removed by an oil washer, and the remaining impurities of all kinds by charcoal filters. The gas issuing from the last named is pure ammonia, and is passed into distilled water in a cooling apparatus which enables aqueous ammonia of any desired concentration to be obtained.

The carbon dioxide and sulphuretted hydrogen can also be eliminated by the application of heat; and a Feldmann-Pintsch plant for this purpose is illustrated, diagrammatically, in Fig. 10. The column still differs from that already described in that the milk-of-lime mixer is abolished, the lime reagent being applied prior to the distillation process. Up to the stage of issuing from the heating chamber of the carbon-dioxide separator, the course taken by the crude liquor is exactly the same as in the preparation of concentrated gas liquor; and there is also no need, in this case, to warm the gas liquor before it enters the heating chamber. The liquor is passed alternately into two mixing vessels, *f*, which are charged with the necessary amount of milk of lime by means of a steam syphon, it being the intention that the lime shall combine with the acids of both the fixed and more volatile ammonia salts, the latter of which are present in smaller quantity, and thus furnish perfectly pure ammonia gas. The arrangement of the plant enables the mixture of milk of lime and gas liquor to be introduced into the still whilst still hot. The preliminary elimination of the carbon dioxide and sulphuretted hydrogen by heat enables up to 90 per cent of the consumption of quicklime to be saved, if the operations be accurately performed. By means of the steam pump, *g* (shown in the Figure as situated between the two mixers, *f*), the power of

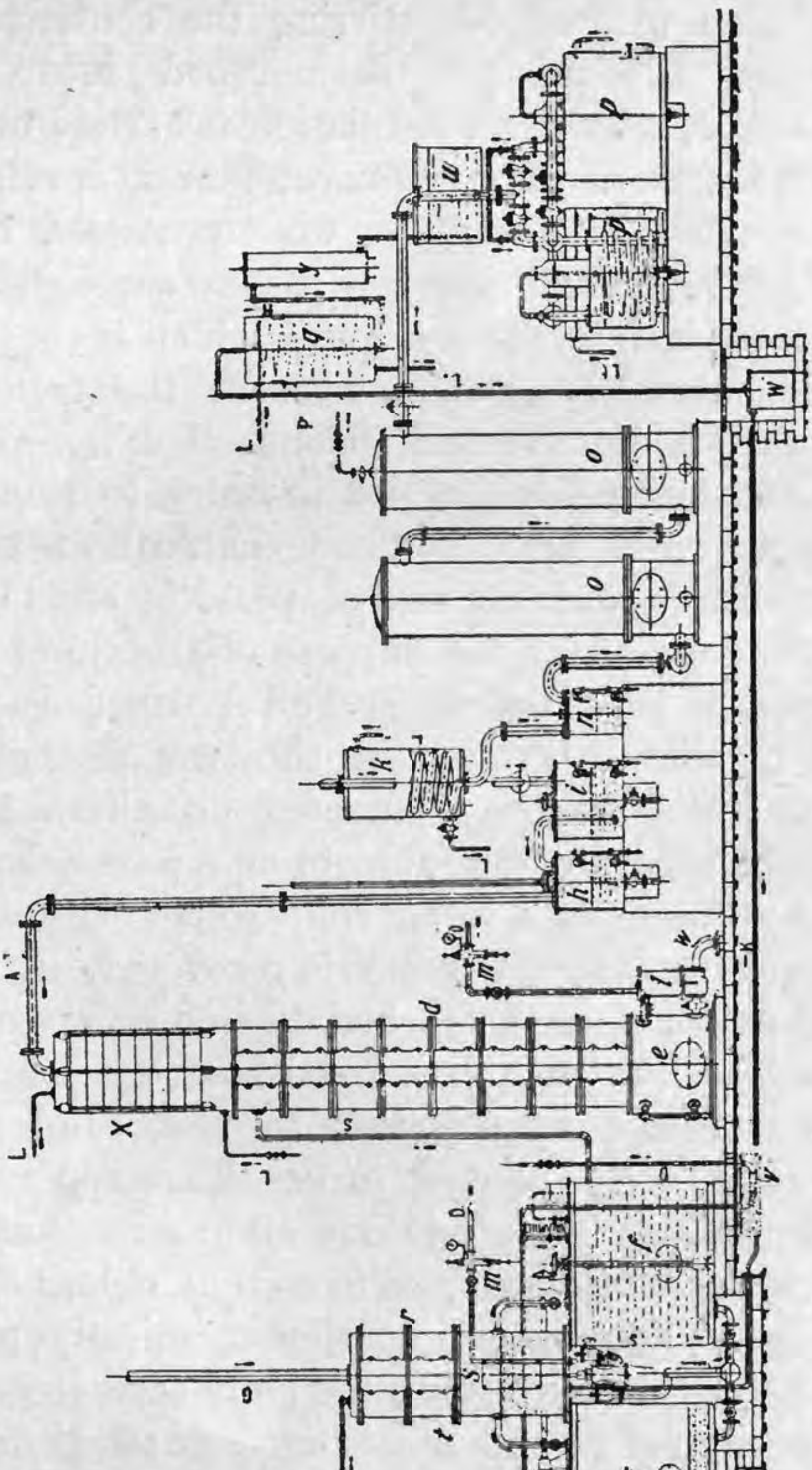

FIG. 10.—Diagram of plant for preparing aqueous ammonia. A = dry ammonia gas; D = steam; G = waste gas; H = gas liquor from high level tank; K = condensed water; L = cooling water; M = milk of lime; P = steam for evaporating; R = distilled water; S = mixture of gas liquor and milk of lime; W = effluent water.

which is also utilized for stirring the contents of the mixers, the mixture is pumped into the column still, *d*, where the distillation is carried on in the known manner. The reflux condenser, *x*, retains nearly the whole of the water vapour carried over with the gases. The dried gas passes through the safety device, *h*, into the washer, *i*, which is charged with caustic-soda lye, which absorbs the residual traces of carbon dioxide and sulphuretted hydrogen present. In *k* the gas is cooled in order to remove the heat acquired in *i*. Wood charcoal or bone black, in lumps about the size of peas, is employed in two cylinders, *o*, for the purpose of absorbing the empyreumatic constituents. The purified gas is absorbed by distilled water in the two absorption vessels, *p*, which can be connected up alternately, the heat liberated by the absorption process being removed by means of a water coil.

The requisite distilled water is recovered, in the heating chamber *s*, of the carbon-dioxide separator *t*, this water being distilled in *q*, freed from mechanical admixtures of iron by filtration through sand and charcoal in *y*, and collected in *u*. This apparatus enables technically pure aqueous ammonia, that is to say, a water-white product free from chlorine, to be obtained. For preparing the chemically pure article, the absorption vessels must be of earthenware, and the purifying agents must be renewed at more frequent intervals.

Liquefied Ammonia.

The highest-grade product obtainable from gas liquor is liquefied ammonia. It is prepared in exactly the same way as chemically pure aqueous ammonia, up to the absorption stage, this latter operation being replaced by compressing the gas into the liquid condition, after having passed it over quicklime in order to make certain that the gas is perfectly dry. For the purpose of compensating the fluctuations in pressure between the still and the compressor, the gas is usually stored in a gasholder provided with an oil seal. According to the practice recently adopted by the Pintsch Company, the gas is conveyed direct from the still to the compressor, and any considerable fluctuations in the pressure are avoided by means of several closed storage vessels, provided with suitable pressure gauges.

The dried gas still always contains impurities, such as pyridin, methyl alcohol, benzol and organic substances. These are removed by repeated compression and re-evaporation of the ammonia, the impurities remaining behind in the liquid condition.

There is nothing essentially different between the manufacture of liquefied ammonia and that of liquefied gases; and therefore there is no need to go into detail on the subject. The liquefication is entirely on a par with that of carbon dioxide and sulphur dioxide. At 10° C., the vapour tension of ammonia is about $6\frac{1}{2}$ atmospheres; and any pressure exceeding this value liquefies the gas, at said temperature. In the compressor, the thoroughly cooled gas is subjected to a pressure of 8 atmospheres. The nearly colourless liquid is forced by the pressure in the compressor through an oil separator and a steel cooling coil, into the usual steel flasks met with in commerce. In charging these flasks, an allowance of about 58 cub. inches should be made for each 1 lb. of ammonia, under which conditions the filled flasks may be exposed to any temperature up to 65° C. (149° F.) without exceeding the pressure they have been tested to stand (1420 lb. per sq. inch).

The chief use of liquefied ammonia is in refrigerating machines (Linde ice machines). In consequence of the handy nature of the steel flasks, and the fact that the ammonia is 99-100 per cent pure, liquefied ammonia is now used instead of aqueous ammonia. It forms a water-white aqueous liquid, having a high refractive index, and has the sp. gr. 0·6362 at zero C., the boiling-point under normal pressure being 33·7° C.

SULPHATE OF AMMONIA.

Sulphate of ammonia is the product most usually obtained from gas liquor, because, in contrast to concentrated gas liquor, it is an article of direct commercial value, and is also more convenient to store. It is prepared by passing the gases from the column still into dilute sulphuric acid, ammonium bisulphate, which is readily soluble in water, being formed at first. On continuing the introduction of ammonia until the whole of the acid is neutralized, the neutral sulphate of ammonia, which is only sparingly soluble in water, is obtained. These reactions are accompanied by the disengagement of heat (100 calories per lb. of salt). The liquid becomes heated, so that not only is the condensation of the water vapour coming over from the still prevented, but even more water is evaporated. Consequently, the cooling of the gases from the still can be dispensed with. Moreover, the gases need not be freed from sulphuretted hydrogen or carbon dioxide, since these substances are not absorbed by the acid solution. Hence, in the manufacture of sulphate of ammonia, carbon dioxide, sulphuretted hydrogen and hydrocyanic acid escape from the absorption apparatus, a point which must be remembered, and precautions taken to render these gases innocuous. The most primitive method of obtaining sulphate of ammonia has already been mentioned in dealing with the treatment of gas liquor. The absorption of the ammonia is generally effected in rectangular wooden vats, lined with sheet lead and charged with sulphuric acid. The gases from the column still are conveyed to the vats through iron pipes, the last length of piping, however, being of lead and extending nearly to the bottom of the vat, being notched at the lower end. This pipe is surrounded by a bell cover, which dips into the acid and is provided with an outlet pipe for the residual gases, which, since they still contain small quantities of ammonia, are passed through a lead-lined separator, in which parallel surfaces are arranged in such a manner as to compel the gases to traverse a zig-zag course. If necessary, the effluent gases are re-washed with sulphuric acid.

This type of plant enables sulphate of ammonia to be produced by the intermittent process, at least two absorption vats being provided, so that when the charge in one is saturated, the other can be connected up, and vice versa, without interrupting the distillation of the ammonia.

A Pintsch plant for the intermittent production of sulphate of ammonia is illustrated in Fig. 11. The arrangement for distilling the gas liquor is similar to that used in making concentrated gas liquor, except that, whereas in that case the crude liquor is warmed up by the gases escaping from the column still, the same effect is produced here by the spent gases from the absorption vats (saturators) *p*, in *o*. The gases from the still are admitted, under a leaden bell, into the saturator. The small amount of ammonia not taken up by the sulphuric acid in the saturators passes, along with steam, carbon dioxide and sulphuretted hydrogen, into the acid receiver, *q*, to retain the ammonia, which comes over more particularly toward the end of the saturation process in *p*. The acid receiver, *q* (see Fig. 12) —Pintsch's Ger. Pat. 134,967—consists of a closed vessel, lined throughout with lead, and provided with an internal vertical partition. The second or discharge chamber contains a number of sloping baffles, which prevent any of the sulphuric acid

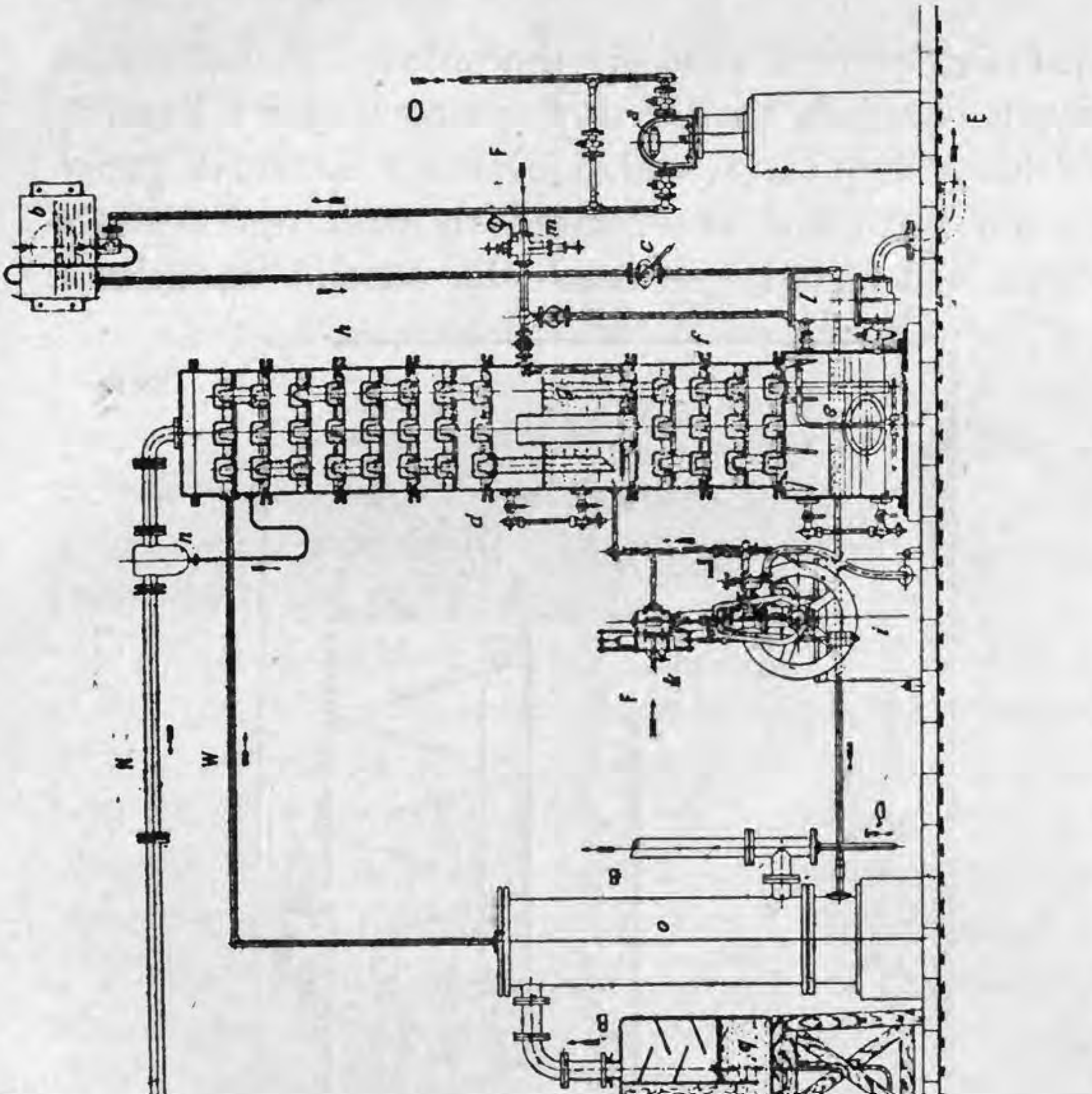

FIG. 11.—Diagram of sulphate of ammonia plant. A = lye; B = waste gas; D = condensed water; E = effluent water; F = steam; L = milk of lime; N = ammonia vapour; O = gas liquor from high level tank; S = sulphuric acid; W = gas liquor.

from being carried away by the effluent gases. The receiver is filled, to about a quarter of its height, with dilute sulphuric acid. The ammoniacal gases from the saturator are obliged to pass underneath the partition in order to reach the second chamber; and in this way the whole of their ammonia is combined by the acid. When the charge in the one saturator has been neutralized by the ammonia in the gases, the latter coming from the still are diverted into the second saturator. The sulphate of

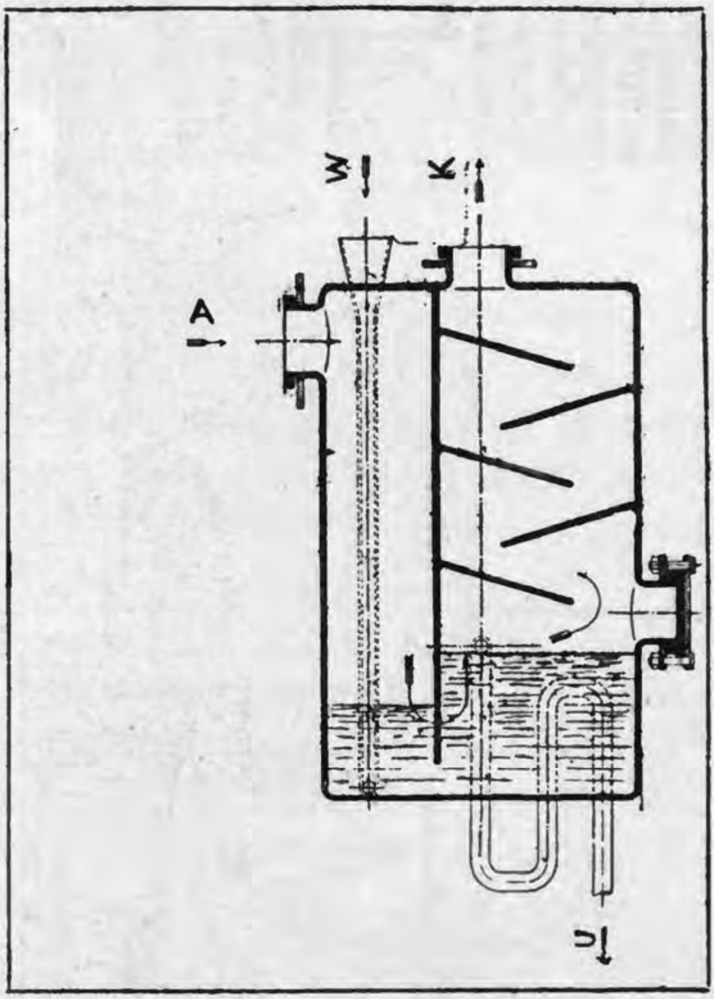

FIG. 12.—Acid receiver for sulphate of ammonia plant. A = waste gas containing ammonia; K = waste gas free from ammonia; U = lye; W = sulphuric acid.

ammonia which precipitates in the saturator—especially towards the end of the saturation process—is taken out and placed on the drainer, *r*, where the bulk of the adherent liquor runs away. The salt is then purified by whizzing it in a centrifugal machine, and washing it until almost entirely free from acid.

The spent gases from the receiver, *q*, pass into the crude liquor preheater, *o*, and are then led into a purifier, charged with ferric hydroxide, for the recovery of the sulphur, or else are allowed to escape direct into the chimney stack.

Towards the close of the reaction, the absorption of ammonia in the saturators proceeds very slowly, so that a thorough washing of the effluent gases is essential for preventing loss of ammonia. On this account, various proposals have been made of late for ensuring complete absorption of the ammonia.

Zimpel washes the gases at once in the bell, for which purpose he provides a second bell, *e* (Fig. 13), of the same construction as the bell G. The acid is introduced at *r*, filling the vessel sufficiently to cover the notches in the bell, *e*. Consequently, the gases coming from G are rewashed in exactly the same way, before passing off into the trap by way of *d*. When the washing acid is renewed, the previous charge is run off, through *f*, into the saturators.

The counterflow principle is employed in the absorption apparatus of Rosenkranz, in which two saturators are used. So long as the ammonia is absorbed in the form of an acid salt in the saturator, the absorption is complete; and it is only during the second stage of the reaction that any ammonia escapes with the waste gases. On this account, therefore, Rosenkranz allows the exhaust gases to escape during the first stage, but when the second stage is reached, diverts these gases into a fresh saturator which is charged with fresh acid. As soon as saturation in the first saturator is complete, it is disconnected and replaced by the second one.

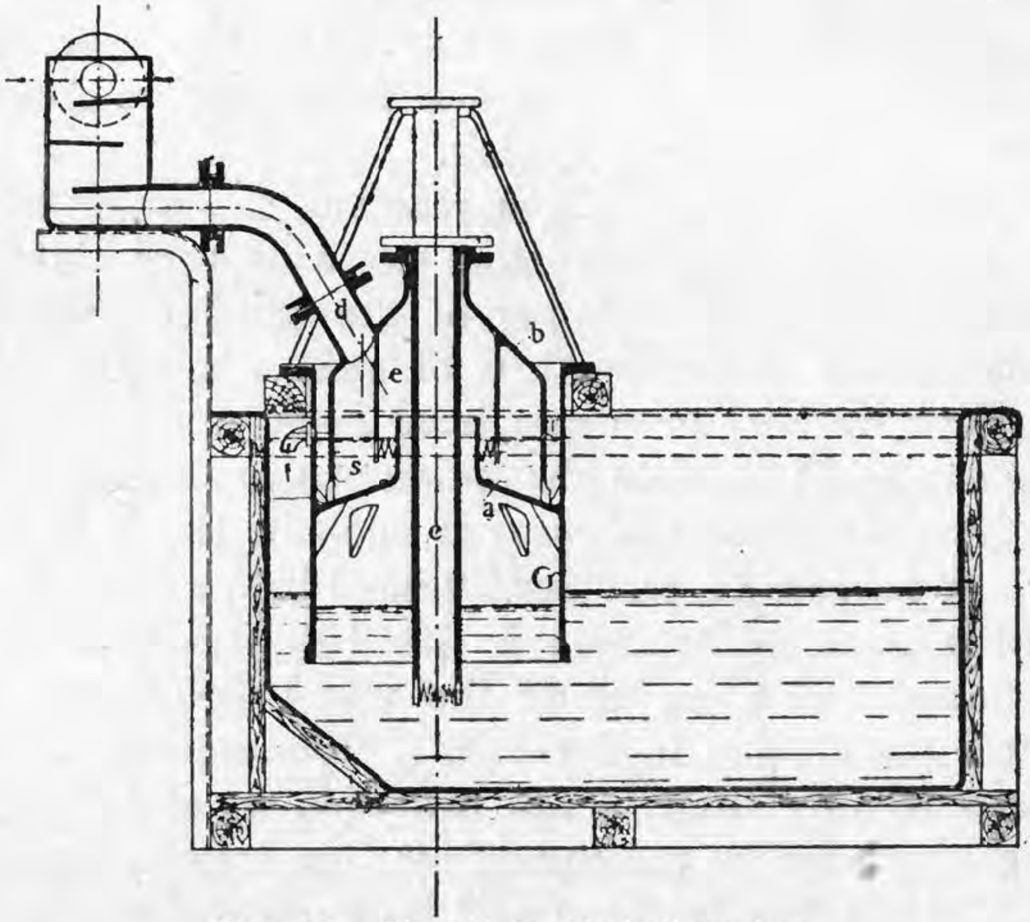

Fig. 13.—Zimpel double bell washer.

The salt in the first saturator is taken out, and the apparatus is recharged with fresh acid, to be ready for the exhaust gases from the other saturator to be passed through it when the proper moment arrives.

The acid charge of the saturators should have a density of about 42° Bé., under which conditions the sulphate of ammonia is deposited as large crystals when the saturation stage is reached; and the resulting product is of a high degree of purity. It has mostly a greyish or yellowish tinge, which, however, is not objected to in commerce, whereas if the salt is of a blue shade, it must be sold at a loss, although the blue colour—which is due to Prussian blue from the cyanogen impurities—is quite harmless when the salt is used as a fertilizer. A blue tinge also appears when local supersaturation of the acid has occurred; and for some unexplained reason, the salt obtained from imperfectly saturated liquor turns blue in draining. Sulphate of ammonia is sold on the basis of its ammonia content only, this amounting as a rule to 24·5 per cent. The following Table gives the solubility of sulphate of ammonia per 100 parts of water, at various temperatures:—

at 0° C.	71·00 parts	at 60° C.	86·90 parts
,, 10° ,,	73·65 ,,	,, 70° ,,	89·55 ,,
,, 20° ,,	76·30 ,,	,, 80° ,,	92·20 ,,
,, 30° ,,	78·95 ,,	,, 90° ,,	94·85 ,,
,, 40° ,,	81·60 ,,	,, 100° ,,	97·50 ,,
,, 50° ,,	84·25 ,,		

The manufacture of sulphate of ammonia in saturators, as described above, entails stoppages for the purpose of emptying the apparatus and recharging it with fresh acid; but the process may be carried on in a continuous manner by means of the same plant, by introducing both the mother liquor and acid in the form of continuous thin streams. The acid, however, must not be so strong as in the intermittent process, the strength employed being

32° Bé. The crystallized salt is scraped out at intervals, or else is transported, by mechanical means, along with the mother liquor, to a centrifugal machine, where the two are separated, the mother liquor being run back into the saturators.

Latterly, a number of gasworks have taken up the manufacture of by-products; and, so far as the manufacture of sulphate of ammonia is concerned, the problem may be regarded as solved.

The two methods of Burkheiser and Feld enable sulphate of ammonia to be produced simultaneously with the purification of the gas, thus rendering the operation independent of the sulphuric acid manufacturer.

The idea of combining the sulphuretted hydrogen and ammonia in such a manner as to form sulphate of ammonia, dates back as far as the fifties of the last century, though no practical solution of the problem was effected. The attempts were all wrecked in the endeavour to convert the sulphite into sulphate, and consequently trials were made for utilizing the sulphite as a fertilizer. This step was rightly characterized by Feld as merely an emergency remedy.

The Burkheiser process is described in German Patents 212,209/07, 215,907/08 and 217,315/08. This inventor oxidizes the iron sulphide of the gas-purifying agent to sulphurous acid by a current of air, and absorbs the product in a neutral solution of ammonium sulphite, ammonium bisulphite being formed. The ammonia of the gas liquor is distilled in a column still, and is returned, in a dried state, to the crude coal gas before the sulphuretted hydrogen absorption stage is reached. After the removal of the sulphuretted hydrogen, the gas parts with its ammonia to the ammonium bisulphite liquor and, thus purified, is passed on to the gasholder. The sulphite of ammonia deposited from the liquor, and already containing 10 per cent of sulphate of ammonia, is completely oxidized by the oxygen of the air.

The method of operating may be explained by reference to the accompanying diagram. The gas liquor is distilled in a column still, and the dried ammonia is returned to the crude gas before the sulphuretted hydrogen is absorbed, so that the gas contains the same quantity of ammonia as it did before the ammonia absorption stage.

In absorbing the sulphuretted hydrogen, the gas purifying agent in the No. I H_2S purifier is heated above 100° C., in contrast to the ordinary procedure. The gas, freed from H_2S, next passes to the saturators, which will be mentioned again later. Here it is freed from the bulk of the ammonia, and passed on to the No. I scrubber, where it comes in contact with a flow of acid ammonium sulphide liquor, produced in No. II scrubber. While the purifier I is absorbing sulphuretted hydrogen from the crude gas, the purifier II is being regenerated by a blast of air. The heat generated by the oxidation of the iron sulphide to ferric oxide and sulphur dioxide is partly nullified and partly serves to keep the purifier I heated to above 100° C. during the absorption of the sulphuretted hydrogen. The mixture of sulphur dioxide and air is passed through scrubber II, where it encounters a flow of ammonium sulphite liquor, which absorbs the

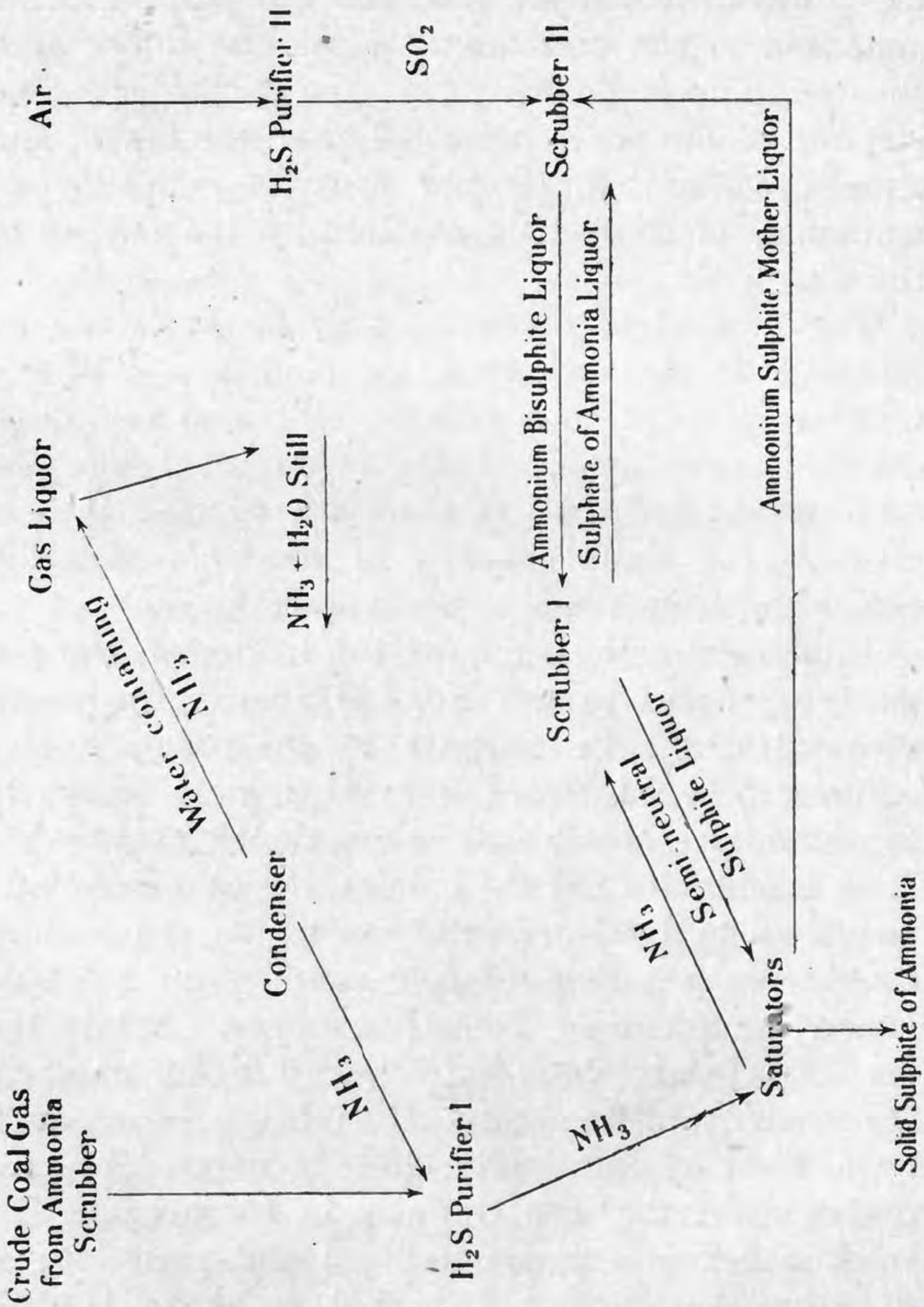

Diagram.

dioxide and becomes bisulphite, in which condition it is run through scrubber I and arrests the residual ammonia in the coal gas. The resulting semi-neutral liquor passes to the saturators, where the bulk of the ammonia of the coal gas is absorbed, neutral sulphite of ammonia being formed. This salt, being very sparingly soluble, is deposited for the most part, and the residual neutral mother liquor is used again for absorbing sulphur dioxide in scrubber II. The deposited salt, about 60 per cent of which is already oxidized into sulphate of ammonia, is centrifugalized, dried and completely oxidized in a conveyor stove.

This stove consists chiefly of a horizontal drum, provided at one side with a charging hopper for the admission of the mixture of sulphite and sulphate, another opening, for the discharge of the completely oxidized salt, being provided at the other side. Inside the drum is a worm conveyor which transports the salt from the charging end to the delivery end, whilst a current of air traverses the drum in the opposite direction. For half its length, measured from the charging end, the drum is cooled, whilst the other half is heated. When the mixed salt enters the heated end of the drum, the sulphite of ammonia is decomposed into ammonia and sulphur dioxide, and is carried back by the current of air—which partially oxidizes it at the same time—into the cooled end of the drum, where it recondenses and is moved onward again, together with the mixed salt, into the heated end of the drum, and so on. The salt discharged from the drum is perfectly free from sulphite.

Of course, the whole purifying plant is arranged in such a way that the H_2S purifiers can be connected and disconnected, according as they are regenerated or exhausted. A small amount of sulphur trioxide is formed along with the dioxide in the purifiers and combines with the ferric oxide to form sulphate. As soon as any considerable accumulation of this sulphate collects in the purifying agent it is extracted by lixiviation.

The oxidation in the conveyor stove seems, however, to be not quite complete, or else a considerable amount of sulphur dioxide is carried away by the current of air and lost, for, according to a more recent process (Ger. Pat. 223,713/09) Burkheiser does away with the supplementary oxidation process, and converts the sulphur dioxide into trioxide direct, by interposing between the purifier and scrubber a contact mass of platinum or ferric oxide, as in sulphuric acid making. In other respects the procedure is the same, except that sulphate liquors replace the sulphite liquors.

The Burkheiser process has emerged beyond the experimental stage and is already in use at the Tegel gasworks, Berlin, and at several other gasworks and by-product cokeries in Germany, etc. (Aachen, Hamburg and Liége).

Whereas, in the Burkheiser process, the transformation into sulphate is effected directly, by the aid of atmospheric oxygen, Feld employs polythionates as the carriers of oxygen, these being decomposed again into sulphate and sulphur. The Feld process passed through a series of experimental stages before a practically usable method was obtained. These experiments afforded, at the same time, an opportunity for elucidating the reactions of the complex polythionates.

Of the four stages of development of the process, namely the tar-oil absorption process, zinc thionate process, iron thionate process and polythionate process, only the two last named have found application in practice. The iron thionate process is used at the East Hull gasworks, but is found to be attended by certain defects, the absorption not being always complete and proving nearly an entire failure in presence of an excess of ammonia. Rises in temperature decompose the ferric thiosulphate into ferric sulphate, sulphur dioxide and sulphur, in consequence of which the absorption of the sulphuretted hydrogen (but not that of the ammonia) is impaired.

The polythionate process (Eng. Pat. 5838/11) is employed at the Königsberg gasworks, and is free from the above-named defects. The principle is as follows: When led into even a moderately concentrated solution of ammonium thiosulphate, sulphur dioxide is absorbed, quantitatively, with formation of ammonium tetrathionate and trithionate:

(*a*) $2(NH_4)_2S_2O_3 + 3SO_2 = (NH_4)_2S_4O_6 + (NH_4)_2S_3O_6$.

The resulting solution serves as absorbent for the ammonia and sulphuretted hydrogen in coal gas, sulphate of ammonia and sulphur being formed, together with some ammonium thiosulphate. The deposited sulphur is burned off as sulphur dioxide and serves for regenerating the absorbent liquid from the thiosulphate (reaction *a*) :—

(*b*) $(NH_4)_2S_4O_6 + 2NH_3 + H_2O = (NH_4)_2SO_4 +$
$(NH_4)_2S_2O_3 + S.$

(*c*) $(NH_4)_2S_4O_6 + 3H_2S = 3H_2O + (NH_4)_2S_2O_3 + 5S.$

(*d*) $(NH_4)_2S_4O_6 + (NH_4)_2S = 2(NH_4)_2S_2O_3 + S.$

When the liquor is sufficiently enriched with sulphate of ammonia, a portion of it is worked up for the recovery of sulphate, by treating it with sulphur dioxide and heat, thus converting the polythionate into sulphate, accompanied with deposition of granular sulphur :—

$$(NH_4)_2S_4O_6 \text{ (hot)} = (NH_4)_2SO_4 + SO_2 + 2S.$$

The sulphur is separated from the liquor, which is then concentrated to allow the sulphate of ammonia to crystallize out. The mother liquor, sulphur dioxide and sulphur are used over again in the manufacturing process.

The only direct oxidation occurring throughout the whole process is the combustion of the sulphur to sulphur dioxide, the further oxidation of the thiosulphate to sulphate being based on a reaction of displacement between the thiosulphate and sulphur dioxide, accompanied by the deposition of sulphur.

The Feld process has enabled a wet purification for washing out the sulphuretted hydrogen to be introduced in addition to purifying the coal gas and producing sulphate of ammonia.

CHAPTER VI.

THE TREATMENT OF THE GAS-PURIFYING AGENTS.

THE spent purifying agents contain, as valuable constituents: ammonia, cyanogen, sulphur, sulphuric acid and thiocyanogen, the cyanogen being perhaps the most valuable at all. This substance is present in the spent mass in the form of compounds of still unknown composition. The percentage of cyanogen varies considerably according to the origin of the mass, and it is therefore important, in connection with the sale of spent gas purifying agents, to have a good method for the determination of the cyanogen. Consequently, the divergent character and chemical composition of the purifying agents have led to the elaboration of a whole series of methods of determination, the most customary of which will now be briefly described. In valuing the article it is important that both buyer and seller should agree on the method of determination to be employed, since otherwise it will be difficult for concordant results to be obtained.

One of the oldest methods for the determination of ferrocyanogen is that introduced by Zulkowsky in 1883 (Dingler, No. 249, p. 168). It was originally intended for application to ferrocyanide melts, but was afterwards used also for determining cyanogen in gas-purifying agents.

The mass is extracted with caustic potash, the filtrate being then acidified with sulphuric acid, and the cyanogen determined by titration with zinc sulphate solution of known strength. The end point of the titration is ascertained with ferric chloride solution as indicator.

Leybold and Moldenhauer ("Journal für Gasbeleuchtung," 1899, p. 155) ascertain the percentage of ferrocyanogen by determining the combined iron volumetrically. The mass is treated with caustic potash in the warm, and is then made up to a definite volume. An aliquot part of the filtrate is concentrated, and is evaporated with sulphuric acid and calcined, to eliminate the cyanogen. The residue is taken up with a little sulphuric acid in water, and the iron is determined in the solution, with potassium permanganate, in known manner, after reduction with zinc.

De Koningh ("Zeitschrift für angewandte Chemie," 1898, p. 463) evaporates the alkaline extract to dryness and eliminates the cyanogen by fusion with sodium carbonate and saltpetre, the iron being determined, gravimetrically, in the melt. The determination of the cyanogen in gas-purifying agents by estimating the iron in the alkaline extract has also been proposed by others; but since this extract contains other iron in addition to that in combination with cyanogen, the ferrocyanogen content comes out higher than the truth; and seeing that the cyanogen content in the mass is always small, even slight sources of error are sufficient to produce a considerable percentage difference.

A method which is based on the technical process of treatment has been elaborated by Dr. Knublauch ("Chemiker Zeitung," 1902, p. 1039), and as this is largely employed in practice, it may be described in a somewhat fuller manner. According to Knublauch, the ferrocyanogen is determined as Prussian blue, in the alkaline extract, by means of copper-sulphate solution.

Two hundred to two hundred and fifty grms. of a good average sample of the spent purifying material under examination are dried on a weighed sieve, covered with paper, for five to six hours at 50°-60° C. The mass it then left exposed to the air for four hours until of constant weight, the hygroscopic moisture being ascertained from the difference in weight. The sample is next crushed to powder and passed through a sieve with 360 meshes per square centimetre, the residual fragments of wood being cut up with a knife so that they too pass through the screen. Ten grms. of this air-dry powder are suffused with 250 c.c. of 10 per cent caustic potash in a 250-c.c. flask, and left to stand for about sixteen hours at room temperature, the liquid being shaken up repeatedly at first and towards the end. In order to prevent the formation of lumps or nodules, the extraction may also be effected in a porcelain mortar, the liquid being stirred, at the prescribed times, with the pestle. At the end of the sixteen hours, the thoroughly triturated mixture is rinsed into a 250-c.c. flask, which is then filled up with distilled water, to 5 c.c. above the mark (to allow for the space occupied by the solids). The flask is then shaken up well, and the contents passed through a dry filter. Owing to the presence of impurities, mainly of an organic character, the potassium ferrocyanide cannot be determined direct by titrating the filtrate, but the extract must first be re-purified by precipitating the cyanogen as Prussian blue. The ferric chloride solution used for this precipitation contains 60 grms. of Fe_2Cl_6 per litre, along with 200 c.c. of concentrated hydrochloric acid. One hundred c.c. of the alkaline extract are run (with stirring) into 25 c.c. of the ferric solution, which has been warmed to 80° C. The ferrocyanide is thrown down as Prussian blue, which is filtered through a folded filter in a hot-water funnel, this latter being kept covered up and the solution warmed before each portion is poured in. The precipitate is washed two or three times with hot water, and is then stirred up well, in a glass beaker, along with 20 c.c. of 10 per cent caustic potash, in order to decompose all the Prussian blue, this process being assisted by a careful, gentle warming. When all the blue is decomposed, the contents of the beaker are rinsed into a 250-c.c. flask, which is then filled up to the mark Any sulphuretted hydrogen present is precipitated by the addition of 1 grm. of freshly prepared lead carbonate. After a thorough shaking, the liquid is passed through a folded filter, and an aliquot part of same, in acid solution, is titrated with copper sulphate, ferric chloride being used as indicator.

The copper reagent is prepared as follows: 12-13 grms. of pure copper sulphate are dissolved in 1 litre of water, and the solution is standardized with a 0·4 per cent solution of pure potassium ferrocyanide. With this object, 50 c.c. of this latter solution are treated, in a beaker, with 5 c.c. of dilute sulphuric acid (1 : 5). Copper sulphate solution is next allowed to run in from a burette until the application of a strip of test paper no longer reveals the formation of Prussian blue. This test paper is prepared by allowing one drop of the test liquid to fall on to a strip of absorbent paper (free from iron), and then letting one drop of ferric chloride fall on the paper so that the edges of the two liquids coalesce. In presence of potassium ferrocyanide, a blue coloration is produced at the plane of contact. Since copper ferrocyanide also reacts with ferric chloride, care must be taken to see that the ferric chloride solution comes in contact with the test liquid only.

Another method of ascertaining the end point of the reaction consists in filtering off 1 c.c. of the test liquid, after each application of the copper solution, and adding ferric chloride solution to the filtrate. If no blue coloration appears after the solution has been observed on white paper for half a minute, then the reaction is complete.

A sharp distinction must be made between these two methods of determining the end point, the resulting values not being identical. In both cases it is desirable to repeat the titration, adding, in a single dose, a slightly smaller quantity of the copper solution than was consumed in the first test, and ascertaining the end point in the same way as before. In these circumstances the difference between the two methods is reduced; but in any event the filtration method gives higher values than the other. The standardized copper-sulphate solution, prepared as above, corresponds to 0·004 grm. of

$$K_4Fe(CN)_6 + 3H_2O.$$

In order to calculate the results to cyanogen compounds other than potassium ferrocyanide, the values obtained must be multiplied by the following factors:—

For Cyanogen $CN = 0·3696$
Hydrocyanic acid, $HCN = 0·3839$
Hydroferrocyanic acid, $H_4Fe(CN)_6 = 0·5118$
Prussian blue, $Fe_7 (CN)_{18} = 0·6792$.

Dreschmidt found that the unfavourable influence exerted on the titration by the re-solution of the Prussian blue cannot be avoided entirely; and he therefore proposes to determine the ferrocyanide in the spent purifying agent by means of mercuric oxide. When cyanogen compounds are boiled along with mercuric oxide, soluble mercuric cyanide is formed; but since the purifying agent also contains thiocyanogen, which likewise enters into soluble combination with mercuric oxide, this reaction must be prevented by the addition of a reducing agent to transform the product into insoluble mercurous thiocyanate. By reduction with zinc dust, the mercuric cyanide is transformed into ammonium cyanide, which can be determined, volumetrically, by the Volhard method.

For the determination of cyanogen in gas purifying agents by the Dreschmidt method, 10 grms. of the thoroughly pulverized, air-dry average sample (as already described) are mixed with 150 c.c. of water in a 500-c.c. flask, and treated with 1 grm. of ammonium sulphate and 15 grms. of mercuric oxide, the former reagent being added to obviate the disturbing influence of the fixed alkali on the decomposition. The mixture is kept boiling for fifteen minutes and, when cooled, is treated with about 1 c.c. of a saturated solution of mercurous nitrate until all the mercuric thiocyanate has been thrown down as the corresponding mercurous salt. The flask is then filled with distilled water up to about 6-8 c.c. above the mark (to allow for the space occupied by the solids), and well shaken. Two hundred c.c. of the solution, passed through a dry filter, are treated, in a 400-c.c. flask, with 6 c.c. of ammonia solution (0·910) and 7 grms. of zinc dust (free from chlorine). The whole is shaken up well for a short time, and then treated with 2 c.c. of a 30 per cent solution of caustic potash. The flask is filled up again with water to 1 c.c. above the mark, and after being well mixed, the liquid is filtered through a dry filter. Of the filtrate, 100 c.c. are run into a 400-c.c. flask containing 40 c.c. of decinormal silver solution and 30 c.c. of a 10 per cent solution of nitric acid (free from chlorine). The cyanogen, thrown down as silver cyanide, is collected together by shaking, and the flask is filled up to the mark. The contents are next filtered again through a dry filter, and the excess of silver nitrate in 200 c.c. of the filtrate is titrated back with 1/20-normal thiocyanate solution, by the Volhard method, in presence of ferric sulphate as indicator. The difference between the number of c.c. of thiocyanate solution consumed and the 40 c.c. of silver nitrate solution taken gives the consumption of decinormal silver solution per 1 grm. of air-dry purifying material.

One c.c. of decinormal silver solution corresponds to:—

0·002598 grm. of CN,
0·007042 grm. of $K_4Fe(CN)_6 + 3H_2O$,
0·004782 grm. of $Fe_7(CN)_{18}$.

A quick method which gives values only slightly higher than those of Knublauch and Dreschmidt has been worked out by Witzeck, in consequence of an exhaustive examination of Feld's method of determining cyanogen. According to his proposal, 2 grms. of the gas-purifying materials are triturated for about five minutes in a porcelain mortar with 1 c.c. of a solution of ferrous sulphate (containing 278 grms. of ferrous sulphate per litre) and 5 c.c. of caustic soda (3·20 grms. per litre). Into this mixture, 30 c.c.

of magnesium chloride solution (600 grms. of $MgCl_2$ per litre) are run by degrees with continued stirring, the whole being swilled with a large volume of hot water into a 200 c.c. retort. In presence of 30 c.c. of sulphuric acid (of four times the normal strength), the liberated hydrocyanic acid is distilled over, the distillate being collected in 2-normal caustic soda and titrated with decinormal silver nitrate solution in presence of 5 c.c. of $\frac{1}{4}$-normal potassium iodide solution. One c.c. of decinormal silver solution corresponds to 0·00956 grm. of Prussian blue.

The selling value of the spent purifying material depends on its cyanogen content, though the amount of the other utilizable substances present must also be determined, for manufacturing reasons. The determination of the sulphur, sulphuric acid, thiocyanogen and ammonia does not differ essentially from the methods generally used for these substances, and therefore need not be gone into in detail here.

In determining the sulphur by extracting the air-dry material with carbon disulphide in the Soxhlet apparatus, the sulphur content can be ascertained direct, from the loss in weight of the flask after the expulsion of the solvent. Gas purifying materials, however, always contain small quantities of organic substances, which pass into solution during the extraction process. Unless very accurate results are required, it will be sufficient to suffuse the residue with ether, and to pour off the organic substances thus dissolved along with those from the sulphur. For accurate determinations, the sulphur must be converted into sulphuric acid, by oxidation with potassium chlorate or fuming. nitric acid, and determined as barium sulphate.

The products recovered from the spent purifying material are: cyanogen compounds, thiocyanogen compounds, ammonia and sulphur, or sulphuric acid. The ammonia is almost entirely in a state of combination.

The preparation of cyanogen compounds from the spent purifying materials is not altogether among the simplest of operations. The large content of sulphur, which, on account of its low market value, cannot be extracted at a profit, has to be carried through the whole process as ballast, and, in the basic dissociation of the materials, favours the formation of thiocyanogen—of course at the expense of the cyanogen. In spite, however, of the fact that the extraction of sulphur is prescribed in many processes, it is seldom carried out in practice.

A large number of methods have been proposed for the recovery of the cyanogen compounds, only a few of which, however, have been adopted into practice. The most important and the one almost exclusively in use at present is that described in Kunheim and Zimmermann's German Patent 26,884/83. The spent purifying material is first lixiviated with water, to extract the soluble ammonia salts, and is then dried in the air. The sulphur is recovered by extraction with carbon disulphide, and the residual mass is intimately mixed with ground caustic lime and warmed to 40-100° C.

(104-212° F.) in a closed vessel provided with stirrers. The dissociated mass is placed in filter boxes and leached systematically with water, an ammoniacal solution of calcium ferrocyanide being obtained, which, on concentration, deposits the sparingly soluble double salt $Ca(NH_4)_2Fe(CN)_6$. This is filtered off, and transformed into calcium ferrocyanide by boiling the calcium hydroxide, this compound being, in turn, transformed, by the aid of potassium chloride, into the sparingly soluble potassium-calcium ferrocyanide, $K_2CaFe(CN)_6$, from which potassium ferrocyanide is finally obtained by treatment with potassium carbonate.

Valentine (Eng. Pat. 3908/74) proposed to dissociate the lixiviated purifying material with calcium and magnesium carbonates at boiling temperature, recovering the corresponding ferrocyanide compounds from the clear solution, and transforming them into Prussian blue for the production of potassium ferrocyanide. The dissociation is, however, very imperfect and takes a long time to effect.

Proposals have been made by O'Neill and Johnson, and also by Grüneberg, to use caustic soda as the dissociating agent; but the high cost of the reagent and the risk of producing thiocyanogen render the process unprofitable.

More recently, it has been proposed to extract the Prussian blue by means of acids. Donat and Ornstein (Ger. Pat. 110,097), after eliminating the soluble salts and sulphur, treat the residue with dilute hydrochloric acid (1 : 3), and thus get rid of all the ferric hydroxide. The Prussian blue is then extracted with concentrated hydrochloric acid and is thrown down, in a pure state, on dilution with water.

Another possible method of treating spent purifying materials consists in converting the cyanogen compounds into thiocyanogen compounds, with quick lime (Marrasses, Ger. Pat. 28,137), or with baryta or barium sulphide (Hölbling), under pressure. Since, however, the demand for thiocyanogen compounds is far smaller than that for cyanogen compounds, and can, in fact, be met by the compounds already present in the spent purifying materials, there is no need to go into the details of these processes.

For the treatment of spent purifying materials there is a choice of three systems:—

1. Extracting the sulphur with carbon disulphide. and then treating the material further as under 2 and 3.

2. The material is first freed from the soluble ammonium thiocyanate and sulphate by lixiviation, and the residue is dissociated with lime or alkalis.

3. The material is treated direct with lime or alkalis, so as to obtain cyanogen, thiocyanogen, and sulphuric acid in the same extract.

In 2 and 3, the sulphur content (about 30-40 per cent) of the material is carried, as ballast, right through the process. It would, therefore, from the ideal standpoint, be preferable to extract the sulphur first; but in spite of the attractiveness of the idea, the preliminary extraction of the sulphur is rarely carried out, the operation requiring very careful supervision, owing to the high fire risk and injurious action of the solvent (carbon dioxide) on the human organism.

ELIMINATING THE SULPHUR BY EXTRACTION.

The air-dry spent purifying material is first ground in a disintegrator, so as to pass through a 4-m.m. sieve. The apparatus used for extracting the sulphur consists of the extractor, the condenser, a still, a tank for the solvent and a trap for the separation of water. The cylindrical extractor is provided with a perforated false bottom covered with a filter cloth, on which the purifying material is spread so as to fill the vessel, being introduced through a manhole for this purpose. The material is then covered over with another filter cloth and the manhole is closed. The carbon disulphide in the still is vaporized by means of a steam coil and admitted into the charged extractor, where most of it condenses, draining down through the charge and extracting the sulphur, after which it is run through a second pipe back to the still. The uncondensed carbon disulphide passes away to the condenser, where it condenses in a water-cooled worm and collects in a receiver, whence it can be led off to the still as required. All the connections are provided with valves. In conducting the distillation, a quantity of solvent equal to the amount condensed in the condenser is run from the storage tank into the still. The extraction is continued until a sample of the carbon disulphide, taken from between the extractor and the still, no longer leaves any sulphur behind on evaporation. After all the sulphur has been extracted, the valves are set so that all the carbon disulphide vapour coming from the still passes into the condenser, whilst at the same time the supply from the storage tank to the still is cut off. In this way the sulphur is freed from the solvent, and is drawn off when melted. Steam is then blown through the extraction residue, in order to expel the carbon disulphide completely.

The residual material is treated, for the extraction of the ammonium salts, in exactly the same way as when the sulphur is left in.

LIXIVIATING THE PURIFYING MATERIAL.

In the course of treatment for recovering the cyanogen compounds, the usual practice now is to extract the material with water first, the method of extraction in an apparatus fitted with stirrers, for the purpose of obtaining a concentrated liquor which can be worked up for thiocyanogen compounds, having been entirely abandoned in favour of filter boxes in which the material is lixiviated systematically. The usual dimensions of the filter boxes are 7 feet by 6 feet by 3 feet, and the holding capacity is about 3 tons. The boxes are of iron, or preferably wood, the bottom being of six to seven baulks, arranged at uniform intervals and provided on the upper face with V-shaped grooves, 2 inches deep and 6 inches apart, to allow the liquid to drain away unimpeded. On the bottom, and at right angles to the timbers, is a grating of laths (about 1½ inches in width), covered by a filtering layer of twigs or straw, the whole being topped by a filter cloth of loosely woven cotton or jute fabric. In one part of the box a pipe extends down through the filtering material to the bottom timbers; and in this place the filter cloth is preferably provided with a double iron ring, fitted with an internal thread in which the pipe is screwed to hold it in position. The object of this pipe is, first of all, to allow free outlet to any imprisoned air when the water is poured on to the charge, and, secondly, to prevent suction, which would compress the charge and hinder filtration when the water is being run off. At one side of the box, and below the level of the grating, is an earthenware cock for drawing off the liquor. The box is charged with spent gas-purifying material, nearly up to the rim, the charge being merely shovelled in and not stamped down. Water is next admitted through a hose. The air escapes through the upcast pipe, and the material is uniformly penetrated by the water, which is allowed to fill the box until the level is a little above the surface of the charge. The box is left for fifteen to twenty hours, during which time the soluble salts are taken up by the water, whereupon the liquor is drawn off through the cock. Since a single extraction is not sufficient to remove all the soluble salts, the operation must be repeated several times; but since these repeated extractions in the same box would give very dilute liquors, several boxes are connected up in series to form a battery, and the lixiviation is performed on the counterflow principle. After leaching the contents of the first box, the liquid passes into the second and there becomes enriched by extracting further quantities of soluble salts, and so on until the end box is reached. In this way the box containing the most exhausted material receives the fresh water, whilst the freshly charged box is first extracted with the most concentrated liquor, the succeeding extractions being effected with progressively weaker liquors, until, finally, fresh water comes into action on the nearly spent charge. As a rule, eight boxes are connected together to form a battery, so that the material in each is extracted eight times.

Assuming, in the first place, that all the boxes are charged with fresh spent material. Fresh water is admitted into box No. 1, and left to stand for about twenty hours, the liquor being then run off into a collecting basin, and transferred thence to box No. 2 by a pump or injector. Owing to the fact that a certain quantity of water is retained by the material in the first box, a corresponding amount of fresh water must be supplied to No. 2. Box No. 1 is recharged with fresh water. At the end of twenty hours the liquor from box 2 is run off into a collecting basin, and at the same time that from No. 1 is discharged into another basin. The two liquids are transferred to boxes Nos. 3 and 2 respectively, and No. 1 is recharged with fresh water. These operations are repeated until the first liquor is discharged from the eighth box. No. 1 box is now disconnected and receives a fresh charge of spent purifying material, the liquor from box 8 is admitted into box 1, and all the other liquors are advanced a stage to correspond. The liquor discharged from box 1 after a further sojourn of twenty hours therein is almost completely saturated with soluble salts. It has a density of 12-14° Bé., and is run off into a collecting tank for further treatment, whilst box No. 2 now receives a charge of fresh water. By proceeding in this way a charge of liquor can be drawn off into the collecting tank each day, and one unit of the battery must be recharged. With a battery of this kind, 24 tons of spent purifying material can be leached in a week.

TREATING THE LIQUOR.

The valuable contents of the liquor from the lixiviation of the spent purifying material consist of ammonium thiocyanate and sulphate. The liquor can be treated direct in a column still of the kind already described, thus recovering the bulk of the ammonia contained in the spent purifying material. If, however, it be desired to prepare thiocyanates from the liquor, this latter is concentrated in evaporating pans, and the two salts are separated by fractional crystallization. The sulphate of ammonia is deposited first, and the bulk of the thiocyanate is afterwards recovered by further concentration and crystallization. Neither of the salts is as yet in a marketable condition. The sulphate is freed from ammonia in a column still and is then obtained in a pure state, whilst the thiocyanate is purified by recrystallization. The thiocyanate can also be recovered from the mother liquor of the sulphate of ammonia, as cuprous thiocyanate, by treatment with copper sulphate and sulphurous acid, and is squeezed in the filter press. Further particulars on the treatment of the crude salt and the copper salt will be given later.

TREATING THE EXTRACTED MATERIAL.

The lixiviated purifying material is next subjected to further treatment for the recovery of cyanogen, which is present in the form of insoluble ferrocyanide. Treatment with alkalis or lime converts it into the soluble alkali- or calcium ferrocyanide compound. The transformation takes place in the cold, but is accelerated and rendered more complete by warming. In practice, of course, lime alone—or perhaps soda—is used as the dissociating agent, the other alkalis being too expensive. The process is carried on either in vessels provided with mechanical stirrers or in filter boxes.

At the first glance, the former method would seem the more suitable, the object being attained more quickly by constant stirring, whilst at the same time a smaller excess of reagent is sufficient. This treatment, however, results in a portion of the material being converted into a fine sludge, which cannot be separated into liquor and residue, either by settling or by suction filters, filter presses being necessary. Moreover, the homogeneity of the material is destroyed, nearly $\frac{1}{4}$-$\frac{1}{3}$ being still in the condition of coarse granules; and in these circumstances the filter press is very liable to be choked up. To prevent this, the material has to be diluted with the drainings from previous pressings, and the coarser ingredients must be allowed to settle down. Before washing, the press cakes still contain about 4 per cent of potassium ferrocyanide and about 35 per cent of water. Since the spent purifying mass originally contains from 7 to 14 per cent of cyanogen, it follows that nearly one half this has to be recovered from the press cakes by washing. The chief drawback of the stirring process therefore consists in the very weak liquors obtained; and for this reason the method has, in most works, been superseded by the filter-box process.

The apparatus used for the stirring process consists chiefly of a closed iron cylinder, the bottom of which slopes toward the periphery. The cover is provided with a stuffing box for the rotary shaft, and with a manhole for charging and emptying, a pipe connection being arranged for carrying off any gases that may be liberated; whilst a draw-off cock is fitted in the bottom. For treating 3-ton charges of spent purifying material, the cylinder should have a capacity of about 230 cub. feet, of which the material occupies about 53 cub. feet; so that, to fill the cylinder about three-quarters full, there is room for about 550 galls. of liquor. The cylinder is traversed by a pinion-driven vertical shaft, carrying, at the bottom end, a set of rakes adapted to the shape of the cylinder bottom, whilst a number of horizontal vanes are arranged at certain intervals on the shaft, in order to keep the upper layers of material in motion.

To start the apparatus, the cylinder is charged with a corresponding quantity of weak liquor, and the stirrers are set in motion, the material to be treated being then introduced through the manhole, and the steam turned on. The dissociation takes two to three hours, according to the quantity treated. At this stage the mass is diluted with weak liquor, the stirrers are stopped, and the whole is left at rest for about half an hour, to allow the coarser material to settle down. The sludge is next drawn off into a filter press by a siphon, which extends down to the level of the coarse material; and in this press the material is washed until the washings no longer exhibit any traces of cyanogen. A sufficient quantity of the weak liquor to dissociate a fresh charge is introduced into the cylinder, and a fresh quantity of spent purifying material is treated. When, in this way, a sufficient amount of coarse material has accumulated in the cylinder it is drawn off through the cock and completely extracted in the filter press. The various liquors are collected in a tank. According to the dissociating agent used, they contain sodium ferrocyanide or calcium ferrocyanide.

Bössner, in his work on the utilization of spent gas purifying materials, reports on a number of experiments made in the dissociation of the material with lime and soda, the method adopted being similar to that described above. The lime was used in the form of slaked lime containing about 50 per cent of CaO, 11 parts of CaO being added to every 100 parts of material in order to provide for the insoluble sulphates in the lixiviated mass. The actual consumption of lime ranged from one and a half to three times the theoretical quantity. At the ordinary temperature, although a threefold quantity of lime was used, the dissociation amounted to only 66 per cent, corresponding to the formula $K_4Fe(CN)_6 . 3H_2O$; but was increased to 80 per cent on raising the temperature to 55° C. (131° F.). Further rises in temperature greatly facilitated the formation of thiocyanogen compounds, all the requisite components of which (lime, cyanogen and sulphur) are present in the material. To increase the dissociation at the temperature mentioned, a mixture of lime and soda was added towards the end of the operation, the addition of lime being naturally reduced accordingly; and in this way the dissociation was increased to 96 per cent. The addition of soda converts the calcium ferrocyanide into $Na_2CaFe(CN)_6$; but a sufficient amount of soda must be used to dissociate the ferrocyanogen as well. A very important factor influencing the success of the treatment is not to work with very large charges.

As already mentioned, the stirring process has now been superseded by the filter-box method, because it enables a dissociation of 87 per cent to be obtained with lime alone, without the use of complicated apparatus. The filter boxes are of exactly the same pattern as those used for lixiviating the spent purifying material; and the process is carried out in just the same way. After the operation, the material is left to drain for several days in the boxes, and is then spread out to dry on a cement or asphalted floor and turned over frequently with a shovel. As soon as it no longer "balls" when squeezed, it is air-dry, whereupon a definite quantity of powdered lime is strewn over it, and the two are thoroughly mixed with the shovel. The amount of lime thus added is equal to the quantity of potassium ferrocyanide present. The mixture is screened in a 4 mm. sieve, and the residual lumps are also crushed and screened. This mixture is again placed in the filter boxes, sufficient water being added to cover the mass. The leaching process is precisely the same as in the original lixiviation in the filter-box battery. The resulting liquor has a density of 12-14° Bé. and contains 120 grms. of $K_4Fe(CN)_6 . 3H_2O$ per litre. Irrespective of the original content of potassium ferrocyanide, 0·8-1·5 per cent of that salt is left behind in the residue, the percentage referring to the mass in the condition in which it was, as regards moisture, previous to the addition of the lime. With the filter-box method the cyanogen obtained in the liquor is in the form of calcium ferrocyanide exclusively. The further treatment of the liquor will be described later, in connection with that of the liquor obtained from the cyanogen sludge.

The third system of treatment, by dissociation without previous lixiviation, is applied when the spent purifying material is very low in soluble ammonium salts; and the operation is carried on in closed filter boxes, in order to prevent inconvenience from the fumes of ammonia. When sufficiently rich in ammonia, the liquor is treated in a column still and then concentrated, the potassium ferrocyanide being precipitated direct with potassium chloride.

CHAPTER VII.

TREATING THE CYANOGEN SLUDGE.

THIS operation is comparatively simple, since one has only to deal with substances of known composition, and the work is rendered easier by the absence of sulphur.

Up to the present, only the methods of Foulis and Buëb have to be considered in the absorption of cyanogen by the wet process in the course of gas purification.

According to the Foulis method, the washing liquor contains Prussian blue, potassium ferroferricyanide and ammonium ferroferricyanide, together with soluble cyanogen compounds. The sludge is squeezed in the filter press, and the ammonia in the clear filtrate is expelled in a column still. The residual liquor from the latter contains calcium ferrocyanide in solution. The residue from the filter is dissociated with caustic lime in an apparatus fitted with stirrers, and the resulting clear liquor is united with that from the column still, to be treated for recovering ferrocyanide salts. According to the Buëb method, the soluble portion of the sludge contains ammonium ferrocyanide, whilst the insoluble portion corresponds to the formula

$$2NH_4(CN) : Fe(CN)_2 \text{ (Hand)},$$
$$\text{or } (NH_4)_2Fe_2(CN_6)_2 \text{ (Feld)}.$$

The cyanogen of the soluble ammonium ferrocyanide is converted into the insoluble form by boiling the sludge in closed iron vessels, fitted with condensing apparatus. In this process all the free ammonia is liberated, and is worked up in the manner already described. The sludge is next squeezed in filter presses, and the sulphate of ammonia contained in the filtrate is worked up as such, whilst the press cakes are dissociated with lime in a stirrer apparatus, the resulting calcium ferrocyanide liquor being subjected to further treatment.

CHAPTER VIII.

TREATING THE CRUDE LIQUORS.

THE crude liquors from the dissociation process contain a variable mixture of saline matters, according to the previous treatment of the material. When the preliminary lixiviation has been omitted, the material will contain calcium thiocyanate and gypsum, in addition to the cyanogen compounds, whereas if dissociated with caustic soda and lime, the hydroferrocyanic acid will be in combination with calcium, sodium, and sometimes ammonium as well. Irrespective of the preliminary treatment, this acid must be separated from the other constituents of the liquor, by precipitation or crystallization, three systems being available:—

1. Precipitation with iron salts, as a blue precipitate which varies in composition and is commonly termed "blue".

2. Precipitation, as a double calcium-ammonium salt, by means of ammonium salts.

3. Precipitation, with potassium chloride, as a double, calcium-potassium salt.

1. PRECIPITATION WITH IRON SALTS.

The crude liquor is slightly acidified, with hydrochloric acid, in wooden or lead-lined vats, the sulphur resulting from the dissociation of the sulphides being thrown down. This will subside to the bottom of the vat inside twenty-four hours, and the clear liquor can then be drawn off. The liquor is next treated with ferrous chloride or ferric sulphate—which latter salt should not be used when the dissociation has been effected with lime, since otherwise gypsum would be formed—until a sample, taken from the filtrate, no longer gives a precipitate with the iron salt. In such case the amount of iron is not sufficient to convert the whole of the ferrocyanogen salt into Prussian blue, the white precipitate obtained containing in addition substances corresponding to the formula $Na_2FeFe(CN)_6$. The reaction is expressed by the equations :—

$$K_4Fe(CN)_6 + 2FeCl_2 = Fe_2Fe(CN)_6 + 4KCl:$$
$$Na_4Fe(CN)_6 + FeCl_2 = Na_2FeFe(CN)_6 + 2NaCl.$$

The white precipitate, however, contains compounds of a more complex nature, since calcium (and also ammonium) is present, in addition to sodium, in the crude liquor.

The precipitate is left to settle for twenty-four hours, and, after the clear liquor has been siphoned off, is squeezed in filter presses. Owing to the slimy character of the precipitate, the pressing is accompanied with difficulties. On account of the acidity of the liquor, diaphragm pumps have to be used, and the resulting pulsating action of the pump is liable to tear the filter cloths, so that the use of a pressure vessel is preferable. The washing, too, is a protracted operation and is always attended with loss. The resulting press cakes, which contain about 30 per cent of $K_4Fe(CN)_6 . 3H_2O$ are decomposed with caustic potash or soda, in a stirrer apparatus, the reaction being expressed by the equations:—

$$Na_2FeFe(CN)_6 + 2NaOH = Na_4Fe(CN)_6 + Fe(OH)_2 ;$$
$$Fe_2Fe(CN)_6 + 4NaOH = Na_4Fe(CN)_6 + 2Fe(OH)_2$$

The precipitated ferrous hydroxide presents the unwelcome feature of causing difficulties in respect of settling down and filtration, and necessitates recourse to the filter press again, in which connection the protracted washing of the press cakes—which, moreover, yield a very weak liquor—is highly inconvenient, the further concentration of the liquor taking up much time and patience. For these reasons the method is now seldom used, unless it be desired to extract further small quantities of cyanogen from the spent liquors.

The Kunheim and Zimmermann process accomplishes the same object in a much simpler and quicker way. In presence of alkali- or ammonium salts, in the warm, calcium ferrocyanide furnishes insoluble double salts, according to the equations:—

$$Ca_2Fe(CN)_6 + 2NH_4Cl = Ca(NH_4)_2Fe(CN)_6 + CaCl_2$$
$$Ca_2Fe(CN)_6 + 2KCl = CaK_2Fe(CN)_6 + CACl_2.$$

2. PRECIPITATION WITH AMMONIUM SALTS.

The reagent consists of a solution of ammonium chloride, which, according to the character of the preliminary dissociation process, is either added *per se*, or else the liquor from the filter boxes is manipulated in such a way that it contains sufficient ammonia to carry out the reaction. This latter will generally be the case when the spent purifying material has not been lixiviated before dissociation. In these circumstances, sufficient hydrochloric acid is added to neutralize the ammonia, but if the material has been previously lixiviated, a sufficient amount of unlixiviated material is added, for the dissociation treatment, to introduce sufficient ammonia to precipitate the double salt from the whole of the crude liquor. The precipitation is effected in apparatus provided with mechanical stirrers. The liquor is heated by direct steam, and the precipitation of the double salt begins when the temperature reaches 75° C. When the deposition is completed, the steam is turned off and the stirrers are stopped, the clear liquor being drawn off when the salt has settled down. This latter is repeatedly washed with water, by decantation, and is finally put through the filter press. It may occasionally be profitable to precipitate the cyanogen, present in the washings and mother liquor, in the form of "blue". The precipitated double salt is a white substance with a bluish tinge, and it may either be reconverted into the calcium salt, or else transformed direct into potassium ferrocyanide. In the case of very good double salt, a marketable article can be produced direct; but in other cases the calcium salt has to be prepared as the intermediate product. For this purpose a suitable quantity of lime is added to the solution of the double salt, in a stirrer apparatus of the kind already described, the liberated ammonia being worked up into one or other of the preparations referred to earlier. The reaction corresponds to the equation:—

$$Ca(NH_4)_2Fe(CN)_6 + CaO = Ca_2Fe(CN)_6 + 2NH_3 + H_2O.$$

When all the ammonia has been driven off, the resulting liquor is concentrated to 20-21° Bé. and put aside to crystallize, the black sludge formed during concentration being removed in a filter press. The calcium ferrocyanide is treated in exactly the same way as the crude liquor precipitated with potassium chloride. As already stated, the ammonium double salt can be converted direct into potassium ferrocyanide, for which purpose a corresponding quantity of potassium carbonate is placed in the stirrer apparatus, together with the requisite amount of lime. The reaction corresponds to the equation:—

$$\begin{aligned}&Ca(NH_4)_2Fe(CN)_6 + CaO + 2K_2CO_3\\ &\quad = K_4Fe(CN_6) + 2CaCO_3 + H_2O + 2NH_3.\end{aligned}$$

After the expulsion of the ammonia, the liquor is concentrated to 31° Bé., filtered and set to crystallize.

3. PRECIPITATION WITH POTASSIUM SALTS.

The best method of obtaining good salts from the crude liquors is through the potassium double salt.

In the methods discussed above, hydrochloric acid—and sometimes ammonia—must be added and then got rid of again, on which account it is preferable to make direct use of the salts which are required to furnish the end product. It is true that the potash salt can also be prepared direct from the calcium salt by means of potassium carbonate; but, for reasons of economy, cheaper potassium salts should be employed wherever possible. This can be done, up to the formation of the double salt, with potassium chloride. The crude liquor is either treated direct with potassium chloride in the stirring apparatus, or else the liquor can first be concentrated to 23-25° Bé., separated from the deposited impurities, and run into the apparatus. In this latter it is treated with an addition of solid potassium chloride (3-5 per cent more than the theoretical quantity) at about 80° C., the mixture being stirred continuously. The double salt, formed in accordance with the equation:—

$$Ca_2Fe(CN)_6 + 2KCl = CaK_2Fe(CN)_6 + CaCl_2$$

settles down quickly after the stirring ceases, and the clear supernatant liquor can then be drawn off. The salt is placed on a filter, and washed with a little water, whilst the liquor is treated for the production of "blue," by precipitation with iron salts, after which it is discharged as effluent. When a sufficient quantity of "blue" has accumulated, it is pressed, and treated further by one or other of the methods described. The double salt is converted into potassium ferrocyanide by boiling it with potassium carbonate, in accordance with the reaction:—

$$CaK_2Fe(CN)_6 + K_2CO_3 = K_4Fe(CN)_6 + CaCO_3.$$

After the calcium carbonate has settled down, the clear liquor (density 27° Bé.) is concentrated to 30-31° Bé. in iron pans, and is then set to crystallize, whilst still hot, in pans, about 4½ feet deep and 3½ feet across, which are lagged with wood to prevent loss of heat. Across the top of each pan a number of rods are laid, to which are attached strings leading nearly to the bottom of the vessel. The crystals collect in clusters on these strings. The pans must be kept free from vibration during the crystallizing process, which takes about a fortnight to complete. The crystals are broken up and whizzed, the mother liquor being returned to the crystallizing pans until it is so rich in potassium sulphate that this salt begins to crystallize out first, whereupon the liquors are placed aside and concentrated separately. The resulting crystals still contain about 60-80 per cent of $K_4Fe(CN)_6 . 3H_2O$.

CHAPTER IX.

THE TREATMENT OF CRUDE AMMONIUM THIOCYANATE AND CUPROUS THIOCYANATE.

THE crude ammonium thiocyanate obtained in the lixiviation of spent purifying material is dissolved in water, and the heavy metals are thrown down, as sulphides, by means of barium sulphide, the sulphuric acid present precipitating the barium at the same time. The addition of barium sulphide is continued until the filtrate no longer gives a precipitate with the same reagent. The mixture is squeezed in the filter press, after which the liquor is concentrated to 20-25° Bé. and left to crystallize. The resulting salt is not a marketable commodity, but has to be recrystallized. This is done by dissolving it, throwing down any heavy metals, still present, with ammonium sulphide, drawing off the clear liquor and concentrating it to 18-20° Bé. The crystals separating out as the solution cools are removed from the mother liquor, whizzed and dried. The product is a pure, white ammonium salt.

In connexion with the lixiviation of the purifying materials it has been mentioned that the thiocyanogen in the liquor can also be thrown down by copper sulphate. This product, cuprous thiocyanate, serves as the raw material for other thiocyanates. Treated with barium sulphide solution in a stirrer apparatus, it is decomposed as follows:—

$$2CuCNS + BaS = Ba(CNS)_2 + Cu_2S.$$

The copper sulphide is separated by pressing, whilst the barium thiocyanate liquor is passed through a charcoal filter, concentrated to about 60° Bé., and placed in iron pans to crystallize. The salt is separated from the mother liquor by whizzing, and forms a marketable product.

To prepare potassium thiocyanate, the purified barium thiocyanate solution is treated with a corresponding amount of potassium sulphate, separated from the precipitated barium sulphate by pressing, and the liquor is concentrated to about 40° Bé. The salt obtained on crystallization is purified by recrystallizing.

CHAPTER X.

POTASSIUM FERRICYANIDE.

THIS salt is not prepared direct, but is obtained by the oxidation of potassium ferrocyanide:—

$$2K_4Fe(CN)_6 + O = 2K_3Fe(CN)_6 + K_2O.$$

The means of oxidation include chlorine, peroxides, persulphates, and finally electrolysis. The oldest process is that of oxidation with chlorine. It may be carried on in the dry, or even in the dissolved state. To oxidize the dry product, it is reduced to fine powder, and spread on racks in a chamber, a current of dry chlorine being passed over it until a sample is found no longer to contain any ferrocyanide. This test is applied by dissolving a crystal in water, dropping it on an unglazed tile and seeing whether any blue coloration is produced by ferric chloride solution. The potassium ferricyanide obtained by this process contains, of course, all the potassium chloride produced in the operation. It is, however, not customary to separate the two salts in this method, by fractional crystallization, the product being usually worked up into Turnbull's blue.

In oxidation with chlorine by the wet process, a current of washed chlorine is passed through a cold 10 per cent solution until the whole of the ferrocyanide has been oxidized. The end point of the decomposition must be carefully watched for, or difficulties will occur during crystallization. If the oxidation be insufficient, the resulting salt will be contaminated with ferrocyanide; whilst if carried too far, Prussian green will be formed, which adheres to the product with equal tenacity. When oxidation is complete, the solution is concentrated to 27° Bé (hot), and put aside to crystallize, an operation taking about five days. The mother liquor is further concentrated to 29° Bé. (hot). The crystals from the mother liquor are contaminated with potassium chloride; and this salt serves for concentrating a newly oxidized patch. A number of mother liquors from the second crystallization are concentrated until the potassium chloride separates out, the bulk of this salt being washed out of the crystals with cold water. In this method of working, a yield of 88-90 per cent is obtained.

The oxidation of potassium ferrocyanide by means of peroxides was introduced into practice by Schönbein. When the ferrocyanide is treated, at boiling temperature, with lead peroxide, it is oxidized, lead oxide and caustic potash being also formed. These two compounds are converted into carbonates by the introduction of carbon dioxide, the lead carbonate being precipitated. The potassium ferricyanide and potassium carbonate can be easily separated by fractional crystallization. The lead carbonate is reconverted into the peroxide, by means of bleaching powder.

A modification of this process has been brought forward by Kassner, who replaces the lead peroxide by calcium plumbate and carbon dioxide. The decomposition proceeds according to the equation:—

$$2K_4Fe(CN)_6 + Ca_2PbO_4 + 4CO_2$$
$$= 2K_3Fe(CN)_6 + 2CaCO_3 + PbCO_3 + K_2CO_3.$$

The potassium carbonate left in solution is utilized by oxidizing an equivalent amount of ferrocyanide without addition of carbon dioxide, and adding the product to this solution, whereupon potassium ferricyanide and calcium carbonate are formed. The latter settles down, and the clear supernatant liquor is siphoned off and concentrated to crystallization point. Since the calcium plumbate is prepared by calcining lead oxide and calcium carbonate, it serves to some extent as a carrier of atmospheric oxygen.

The method which is probably most widely used at present for preparing ferricyanide is that of oxidation by electrolysis. In the electrolysis of water, the oxygen is separated at the anode, and the hydrogen at the cathode; and it is this nascent oxygen which is utilized for oxidizing potassium ferrocyanide. The reactions are expressed by the following equations:—

$$H_2O = H_2 + O.$$
$$2K_4Fe(CN)_6 + O = 2K_3Fe(CN)_6 + K_2O$$
$$K_2O + H_2O = 2KOH.$$
$$\overline{2K_4Fe(CN)_6 + 2H_2O = 2K_3Fe(CN)_6 + 2KOH + H_2.}$$

The potassium ferricyanide is deposited, in a pure state, on the anode, the yield amounting to 95 per cent and over. A number of patents are based on this process (Buschweiler, Petrie, Dubosq, etc.). The electrolysis is suspended as soon as all the ferrocyanide has been oxidized, a condition which is recognized by the circumstance that the liquor no longer decolorizes potassium permanganate solution.

According to the process of the Deutsche Gold und Silberscheideanstalt (Ger. Pat. 59,014), a mixture of potassium ferrocyanide and calcium ferrocyanide is oxidized. The use of calcium salts, in addition to potassium salts, in the decompositions corresponding to the reaction, is stated to ensure a purer product being obtained, since the whole of the potassium combines with the ferricyanic acid, and any lime that may be left behind in solution can be completely precipitated with carbon dioxide. The reactions are expressed by the equations:—

$$3K_4Fe(CN)_6 + Ca_2Fe(CN)_6 + O_2$$
$$= 4K_3Fe(CN)_6 + 2CaO;\ 2CaO + 2CO_2 = 2CaCO_3.$$

The use of ammonium- and sodium persulphates for oxidation is dealt with in Beck's German Patents 81,927 and 83,966, the reaction corresponding to the equation:—

$$2K_4Fe(CN)_6 + (NH_4)_2S_2O_8$$
$$= 2K_3Fe(CN)_6 + 2(NH_4)KSO_4$$

The potassium ferrocyanide, which is dissolved in water (1:1), is oxidized with ammonium persulphate at 60° C., 270 parts by weight of ammonium persulphate being required to every 1000 of ferrocyanide. In consequence of the heat generated by the reaction, the solution must be well cooled. When the decomposition is complete, the salts are separated by fractional crystallization, the ammonium-potassium sulphate, as the least soluble salt, crystallizing out first.

When sodium persulphate is used as the oxidizing agent, a ferrocyanide solution of 1 : 1·5 is taken, 282 parts of the persulphate being added per 1000 of ferrocyanide. The reaction is conducted at 50° C., and the resulting salts are separated by fractional crystallization.

CHAPTER XI.

THE CYANOGEN PIGMENTS.

THE cyanogen pigments consist of complex compounds of iron salts and hydroferri- or hydroferrocyanic acid. The chief representatives of the series, which are met with in commerce as Prussian blue, Berlin blue, and Paris blue, have the formula, $Fe_7(CN)_{18}$.

Chemically speaking, they are identical, differing only in their degree of purity. Paris blue is the purest form. It has an intensely blue colour and a peculiar coppery metallic lustre. The other members: Prussian blue, Berlin blue and mineral blue, are prepared from less pure salts and, in addition to containing such impurities as gypsum and carbonate, are adulterated with variable proportions of alumina, chalk, starch and even heavy spar. These substances naturally render the colour correspondingly paler, and also impair the bronze lustre.

There are two methods of making Paris blue. In the one, a solution of pure potassium ferrocyanide is treated with ferric salts, thus forming a precipitate of pure Paris blue; whilst in the other, the precipitation is effected with ferrous salts, which are cheaper, and the pale blue to dirty green precipitate is oxidized afterwards. The former method naturally furnishes the purer product.

A solution of ferric nitrate is added to one of potassium ferrocyanide until a sample no longer gives any further precipitate with the nitrate solution. The ferri-ferrocyanide thus formed separates as a completely insoluble substance and settles down. The supernatant liquid is siphoned off, and the precipitate is washed with water, by decantation, until all the potassium chloride has been extracted. It is next pressed, while still moist, cut up into cubes and dried. The first stage of drying is conducted at air temperature or up to 30° C. (86° F.), and it is only when the product is air-dry that the drying is finished off at 100° C. (212° F.), whereupon the copper-red ("bronze") metallic lustre, characteristic of the pure article, develops.

In the preparation with ferrous salts, followed by oxidation, ferrous sulphate is employed in practice. The following may be given as the most suitable proportions: ferrous sulphate 9 parts by weight; sulphuric acid (60° Bé.) 15 parts (dissolved in 100 parts of water); potassium ferrocyanide (yellow prussiate), 10 parts, dissolved in 100 parts of water.

The addition of sulphuric acid is intended to prevent the precipitation of iron carbonate by the carbonic acid in the water. The two solutions are poured into a wooden vat, only a slight excess of the ferrous salt being present. The liquid should be kept constantly stirred during the pouring process. The resulting white precipitate, which always has a slight bluish tint due to small quantities of ferric salt, is oxidized with 20 parts of nitric acid (1·3298) added in small quantities at a time, steam being admitted simultaneously. The heating is continued until no more nitrous fumes can be observed. In this way the precipitate is oxidized in a very short time. The Paris blue is allowed to subside and, after the clear supernatant liquid has been drawn off, is washed with water. The subsequent treatment of the precipitate is identical with that described above.

Hochstätter employs bleaching powder and hydrochloric acid as the oxidizing agent. In these circumstances he has to start with ferrous chloride, and dispense with the use of sulphuric acid, since otherwise the finished product would be contaminated with gypsum. Any oxidizing agent can be used for turning the white precipitate blue, manganese chloride being a highly suitable means. After separation from the solution, the precipitate is treated with a solution of manganese chloride in excess; and as soon as the colour of the product attains its maximum intensity, the oxidation is complete.

Berlin blue differs from Paris blue solely by reason of impurities, in consequence of which it is inferior in "bronze". Instead of working with pure salts, a crude salt, such as that obtained in making potassium ferrocyanide, is used. This contains considerable quantities of potassium carbonate and sulphate. Alum is generally added to the ferrous sulphate solution used for precipitating the blue, the object being to neutralize the carbonate and, at the same time, to increase the volume of the precipitate, the carbonate reacting with the alum and forming a precipitate of alumina. Oxidation in an acid solution would cause the precipitate of alumina to redissolve, and therefore the oxidation must be carried out with atmospheric oxygen. A better plan is to oxidize the ferrous sulphate beforehand. In other respects the manufacture of Berlin blue does not differ essentially from that of its purer congener, Paris blue. The depth of colour diminishes in accordance with the proportion of impurities present, which in "mineral" blue attain as much as 80 per cent. Mineral blue is made from the inferior crude liquors from the potassium ferrocyanide process. The cyanogen pigments are met with in commerce in the form of cubes, powder and paste. Their shade depends on the quantity of added substances and the method of precipitation employed.

Berlin blue is also put on the market in soluble form, and is now largely used for injecting anatomical preparations. At one time it was also used as a colouring matter for ink, but has now been entirely superseded by the aniline dyes.

In its preparation, the ferrocyanide must be present in large excess in the solution, the following proportions being given by Brücke: Potassium ferrocyanide 2170 parts, dissolved in 11,000 parts of water and treated gradually with a solution of 100 parts of ferric chloride in 1000 of water. The iron solution is mixed with twice its volume of a saturated solution of Glauber salt (sodium sulphate). The resulting precipitate is filtered off, and is washed with water so long as the washings exhibit a bluish tinge. The residue is then dried, and is sold in the form of powder. This blue, which is chemically the same as Berlin blue, is completely soluble in water.

Guignet utilizes the solubility of Berlin blue in oxalic acid, for preparing a soluble blue. A saturated solution of oxalic acid is shaken up with a large excess of Berlin blue in paste form, and filtered, the solution being then left to itself for two months, during which interval the dissolved Berlin blue gradually settles down, leaving the solution as clear as water. The blue obtained in this way is also soluble in water. In addition to oxalic acid, tartaric acid and molybdic acid have the faculty of dissolving Berlin blue.

Apart from Berlin blue and its varieties, mention may be made of the copper salt of potassium ferrocyanide, which is of a brown colour, and is met with in commerce as Hatchet brown. It is prepared by precipitating a solution of potassium ferrocyanide with copper sulphate, the shade of the product varying in accordance with the excess of copper sulphate used.

CHAPTER XII.

SULPHUR AND SULPHURIC ACID.

If it be desired to recover sulphur, as such, from the spent gas-purifying materials, this is preferably effected before the said materials are treated for the preparation of cyanogen compounds. The manner of extracting the sulphur has already been dealt with, carbon disulphide being the only solvent used. The process is exactly similar to that used in the extraction of fat from bones, and there is therefore no need to go into further details.

In the main, the sulphur from spent purifying material is transformed into sulphuric acid by roasting, the material treated in this way being, of course, such as has previously been freed from the other valuable constituents. The lixiviated and dissociated material chiefly contains ferric hydroxide or oxide, ferrous hydroxide, sulphur and lime (from the dissociation treatment), in addition to the substances (sawdust, etc.) required for loosening the material and facilitating the passage of the gas to be purified. In the roasting process, the ferric oxide remains behind, and the sulphur is liberated as sulphur dioxide. The roasting furnaces do not differ essentially from those used for pyrites and other sulphur ores. The entire process of making sulphuric acid from spent gas-purifying materials does not entail the use of any typical special appliances, and therefore it is sufficient here merely to mention that sulphuric acid, also, is one of the by-products of the manufacture of coal gas.

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INDEX

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