tar yield from bituminous coal. They further give the upper limit to which coal may be heated in rapid working to avoid tar losses by partial decomposition.

(*f*) DIFFERENTIATION BETWEEN VARIOUS PRIMARY TARS AND OTHER TARS

1. *Low-temperature and High-temperature Tars from Bituminous Coal.*[18]

The need has been expressed for some chemical criteria by which primary tars can be readily distinguished from ordinary tars. The characteristics given below may not definitely exclude the numerous varieties ranging from useless, solid and pitch-like producer tar to coke-oven tar, vertical retort tar, Mond gas tar and finally to low-temperature tar of high value, and there may be a need for a closer definition of true primary tar later on. The points specified below, however, will suffice as a guard against the crudest intentional sophistication.

(1) *General Characteristics.*

A good genuine primary tar * from bituminous coal should satisfy the following general conditions :—

1. It should be fluid at room temperature, with possibly slight segregations of paraffin wax.
2. Its specific gravity at 25° should be 0·95 to 1·06.
3. In a thin layer it should be an oil of a golden-red or port-wine colour.
4. Freshly made it generally smells of hydrogen sulphide or ammonium sulphide; it should never smell of naphthalene.

(2) *The Naphthalene Test.*

These characteristics are, however, not sufficiently safe indications of a low-temperature or primary tar. To justify its name the low-temperature tar should have been produced by low-temperature carbonisation, *i.e.*, it should not have been exposed to temperatures exceeding 550°, either during its formation or subsequently. A properly prepared primary tar *does not contain any naphthalene.*† Naphthalene is only formed secondarily from primary tar at temperatures upwards of 750°.[19] A tar containing naphthalene must therefore have been heated higher than the production of primary tar necessitated, and cannot rightly be defined as such. On this fact is based the simplest method of discriminating between primary and other tars. The higher temperature to which the naphthalene owes its existence changes the former in essential respects. The typical constituents of primary tar are paraffins,

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* By a good primary tar we mean a complete tar which still contains all the low- and high-boiling fractions.

† This fact was known to Börnstein. Having tested its accuracy we propose the naphthalene test for the discrimination of tars. Small traces have recently been found, but they are not shown by Fischer's test, which therefore holds good for the evaluation of a primary tar.

olefines, naphthenes and phenols, and only to a small extent aromatic hydrocarbons. To the first four types of compounds is due its low specific gravity. The conversion of these constituents into aromatic compounds, to which they are liable at temperatures above 550°, causes an increase in specific gravity. The latter fact provides a further means for distinguishing primary tar from tar which has been exposed to excessive temperatures.

For these reasons it is advisable to examine a tar which satisfies the general tests, but is still of doubtful low-temperature origin, for naphthalene, in the first instance. This is done in the following way: 200 c.c. of tar are distilled in a flask of 1·5-litre capacity in a moderate current of steam at 100°, the vapours being cooled in a very long Liebig condenser or two such condensers arranged in series, so that the distillate is perfectly cold. It is advisable to collect three separate fractions of about 250 c.c. each, which will all show a layer of oil on the water.

If the oil layer of one of the distillates solidifies to a crystalline mass, naphthalene is undoubtedly present, and the distillation may be stopped. In the case of a tar containing only a small percentage of naphthalene, the crystals appear only in the last of the three receivers or possibly only after cooling in an ice chest. The occurrence of naphthalene crystals unmistakably indicates that the tar has been exposed to too high a temperature and has consequently also been changed as regards other original constituents.

When subjected to steam distillation in this way, primary tar yields merely oily distillates, which will not show crystalline deposits, even after prolonged cooling in ice. By this test, additions to a genuine primary tar, of ordinary tar or inferior low-temperature tar containing naphthalene, can, of course, also be recognised.

(3) *Determination of Density.*

In cases where naphthalene is found to be absent, a more detailed test is required.

Tar free of naphthalene is not always a primary tar, since superheating may not have been pushed to a point where naphthalene is formed, so that, though free of naphthalene, the tar has yet undergone some thermal decomposition. A method of distinction in such instances is based upon differences of solubility and specific gravity of the individual constituents. As already mentioned, the thermal history of a tar can be learned from the nature of its constituents and its specific gravity. The hydrocarbons offer a convenient means of studying these phenomena, whilst the phenols, on account of their varying proportions with different coals, are not suitable for this purpose.

The tar should first be shaken with petroleum ether in order to precipitate pitch and asphaltic matter. The solution in petroleum ether is then freed of its acid constituents by means of alkali, and distilled up to 200°. The oils coming over from 200° to 300° are collected separately, and the specific gravity of the distillate and residue is determined. The specific gravity at 20° of the fraction from a primary tar, boiling from 200° to 300°, is below 0·95; in the case of other tars it is close to 1·0, or higher.

With a primary tar, the residue boiling above 300° solidifies to a pasty consistency, owing to segregation of paraffin wax; it is completely soluble in petroleum ether and in ether, and has at 50° a specific gravity below 1·0, *i.e.*, it will float on water of 50°. The corresponding residue from a superheated tar (although initially entirely soluble in petroleum ether) is, after distilling off the fraction 200° to 300°, only partially soluble in cold petroleum ether, leaving some solid matter undissolved. It is not completely soluble in ether and has at 50° a specific gravity above 1·0, *i.e.*, it sinks in water of 50°.

(4) *Examples.*

The following example may be cited :—200 c.c. of a commercial primary tar are vigorously shaken in a flask for a few minutes with 300 c.c. of petroleum ether (boiling from 30° to 65°). The solution, of a brownish-orange colour, is poured off the black, highly viscous deposit and is shaken in a separating funnel with 200 c.c. of 5*N*-sodium hydroxide. The aqueous layer is drawn off and is replaced by the same quantity of fresh lye, followed by further shaking and separation. The petroleum ether solution is now washed with an equal quantity of water and separated. It is filtered in order to remove any traces of water, and the petroleum ether is completely distilled off from a small flask on the water-bath. The residue is then freed of all constituents boiling below 200°, in a smaller flask resting on an asbestos plate. The residue is transferred to a still smaller flask of about 100 c.c. capacity and is distilled over a free flame up to 300°. The fraction boiling from 200° to 300° amounted to about 20 c.c.; the residue to about the same quantity. This mode of working was adopted for all the experiments summarised in Table VII and yielded the following data :—

TABLE VII

	Commercial primary tar.	Vertical retort tar.	Mond gas tar.
Spec. grav. at 20° of fraction 200° to 300°	0·9100	0·9850	0·9306
Spec. grav. at 50° of residue above 300° (determined in pycnometer) .	0·9606	1·0931	0·9713

The distillation residues from the primary tar and from Mond gas tar solidified to ointment consistency by the segregation of paraffin wax. Both were very readily soluble in the cold in ether and in petroleum ether; by triturating a sample with an equal volume of acetone the paraffin wax could be directly separated in the form of white flakes.

The residue from a vertical retort tar gave by comparison with the primary tar a negligible separation of paraffin in the form of a thin film; triturated with petroleum ether, it left a brown, insoluble mass. Ether left a very dark flaky mass undissolved.

(5) *Discussion*

On the strength of these distinctions it is no doubt possible to recognise by simple means how far any tar has undergone changes by subsequent heating, and to judge whether or not the product should be considered a true primary tar. To attempt to draw too narrow limits would not be advisable at present, in view of the variety of carbonising plant and of the coals used. The majority of tars should be distinguishable from primary tars without difficulty by the naphthalene test. It is therefore advisable to apply this test in the first instance.

The above-mentioned general characteristics of primary tar such as colour, etc., need, however, not be complied with in all cases. It may, for instance, occur that a primary tar is not liquid at the ordinary temperature. For if it was not separated by sufficiently energetic cooling, the low-boiling constituents which reduce its viscosity will be absent, and a pasty consistency will result owing to the separation of paraffin, although the tar still contains the valuable high-boiling lubricating oils. If high viscosity is caused by paraffin wax, the product should regain its fluidity at its melting point, 50°. The specific gravity of such a tar is naturally higher since the lighter constituents are absent.

(a) *Mond Gas Tar.*—The examination of a Mond gas tar proved that the general characteristic No. 3 may also be misleading, since the tar was quite black. The naphthalene test was, however, negative, and the tar could not have undergone any excessive heating. The figures for Mond gas tars in Table VII, for specific gravity of the distillate from 200° to 300° and of the residue boiling above 300° also indicated that it could be considered a primary tar which was merely devoid of the lighter constituents. To mistake such a tar, owing to the separation of paraffin wax and its pasty consistency, for a brown coal tar is hardly to be feared, since brown coal tars on account of their paraffinoid character have a much lower density than those from bituminous coal. In this case the general appearance did not characterise the product as a primary tar, although it had to be considered as the high-boiling portion of such a tar, still suitable for the recovery of lubricating oils; the reverse case may occur of what appears to be a primary tar being really a high-temperature product.

(b) *Vertical Retort Tar.*—A case in point was that of a vertical retort tar from the Breslau Gas Works. The tar decidedly resembled in its appearance a good primary tar; it was of relatively low viscosity, did not smell of naphthalene, and a thin layer showed the characteristic golden-red colour. Here the density of 1·084, exactly as given by Lunge [20] for vertical retort tar, was at once decisive. The naphthalene test was, moreover, positive though the quantity of naphthalene found was small. The density determination of this tar, and further, its behaviour in petroleum ether, made it clear that this test allows of a definite discrimination, even in the case of a tar so closely related to primary tar as the vertical retort tar. This latter test, further, affords a means of estimating the high-boiling product of lubricating oil character; for it is conceivable that tars which have already been deprived of an appreciable proportion of these valuable compounds might make their appearance on the market. How far this test is generally applicable must be left to further experience.

2. *Distinction between Brown Coal Primary Tar and other Brown Coal Tars* [14]

Our present knowledge of the primary tars from brown coal is based upon the examination of tars obtained by low-temperature distillation in the rotary drum, from Central German brown coal and Rhenish lignite (Union Briquettes). Another primary tar was prepared from a lignitic brown coal from the Westerwald (Gewerkschaft Weiler I, Langenaubach). Of this tar, however (yield about 3 per cent. referred to dry coal), only the general properties were determined. We are, therefore, not yet in a position to say whether and to what extent lubricating oils were present in this tar. This tar differed, however, by appearance so widely from the others that it seemed not expedient on the strength of our present knowledge to define the general characteristics of primary tars from all varieties of brown coal. Whether or not this is at all possible will have to be settled by further practical experience with brown coal tars.

We have recorded for purposes of comparison the properties and results of some investigations of various brown coal tars. From these a few simple characteristics of really good primary tars are available for quick orientation. Table VIII is a summary of the results from comparative examinations of the following brown coal tars :—

(1) A primary tar from brown coal of the Riebeck Montanwerke, Halle, compared with a once-distilled primary tar and a commercial brown coal tar.

(2) A primary tar from Rhenish Union Briquettes and a once-distilled primary tar from the same coal.

(3) A good brown coal producer tar of the potash works Prince Adalbert A.-G. (Gewerkschaft Einigkeit II), Oldau.

For the sake of comparison a few data concerning the primary tar from the lignitic brown coal are added.

(1) *General Properties of Primary Tar.*—The primary tars from Central German brown coal and Rhenish lignite, as well as commercial producer tar, are products of the consistency of fairly hard butter. They have, therefore, all rather high setting points, upwards of + 30°,* whilst the commercial brown coal tar and the once-distilled primary tars have setting points far below + 30° (see Table VIII). The specific gravity of the tars offers no characteristic features, on account of the great variation in paraffin wax and phenol content. Sometimes one can obtain primary tars with much lower setting points from brown coal, as is shown by the examination of the primary tar from lignite, which has a setting point + 12°. Such a tar contains consequently little paraffin wax, as might be anticipated from the low bitumen content of the raw material. Whether such tar will be suitable for the production of lubricating oil remains an open question.

One rule holds for the primary tar from brown coal as well as for that from bituminous coal, viz., it must not contain naphthalene. The presence of naphthalene in the tar would indicate with certainty that a portion had been subjected to a temperature of at least 750°. Brown coal tars examined by the method previously described were free of naphthalene.

(2) *Examination of Hydrocarbons of Boiling Range* 200° *to* 300° *Soluble in Petroleum Ether.*—We first tried to follow the lines used for the discrimination between primary and other coal tars. It had been established that the fraction 200° to 300° of de-phenolised tar does not exceed a certain specific gravity, and this test answered in cases where the naphthalene test gave a negative result.

200 grams of tar were shaken for a few minutes in a stoppered bottle with 300 c.c. of petroleum ether (35° to 65°). If, as in the case of brown coal tars, the amount of insoluble residue was small, it was filtered off and washed with about 50 c.c. When, however, as with primary tar and producer tar, there was a large residue insoluble in petroleum ether, the solution was decanted; the tar was then again shaken with 200 c.c. of the solvent, filtered and washed with a further 50 c.c. The petroleum ether solution was

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* In the paper by Schulz and Kabilac, "On the Brown-Coal Generator Tar from Gas Generators" (Mitteilung des Industriefœrderungsinstituts der Handels- und Gewerbekammer, No. 36, Prag, 1917) are given the setting points of generator tars from the gasification of various Bohemian brown coals, no exact origin being given. They range from + 31° to + 34° and correspond therefore to the primary tar from Rhenish brown coal in consistency. Spec. gravs. at 50° are from 1·002 to 1·015.

repeatedly extracted with 200 c.c. of 5*N*-caustic soda, washed with water, and filtered to remove moisture; the petroleum ether was then distilled off and the oil submitted to fractional distillation. The fraction boiling from 200° to 300° was collected separately and its specific gravity and that of the residue were determined. Table VIII shows that this course of examination was not completed in all cases. It is manifest that the specific gravity of fraction 200° to 300° does not discriminate between primary and other brown coal tar. It varies only from 0·859 to 0·895 in four samples and affords therefore no characteristic distinction. The same holds good for the residue after distillation to 300°. As it was noticed that the amounts of petrol-insoluble * varied with different tars, the further examination of the tars at our disposal was based on this observation.

TABLE VIII

	Tars from central German carbonising coal.			Tars from Rhenish Union-briquettes.		Tars from lignitic brown coal.	Producer tar.
	1. Commercial carbonising tar.	2. Primary tar.	3. Once-distilled primary tar.	4. Primary tar.	5. Once-distilled primary tar.	6. Primary tar.	7. From Prince Adalbert potash works.
Setting point . .	+15/16°	+ 37°	+ 18°	+ 33°	+ 17°	+ 12°	+ 35°
Spec. grav. at 50° .	0·877	0·886	0·864	0·950	0·936	1·125	0·953
Portion of tar soluble in benzene and insoluble in petroleum ether	4%	47·5%	8·5%	35%	2·5%	not det.	37%
Spec. grav. at 20° of fraction 200° to 300° of portion soluble in petroleum ether and free from phenol and bases . .	0·874	0·859	not det.	0·890	not det.	not det.	0·895
Spec. grav. at 40° of residue above 300° soluble in petroleum ether	0·776	0·875	not det.	0·979	not det.	not det.	0·924

(3) *Differentiation of Brown Coal Tars by the Amount Insoluble in Petroleum Ether.*—Before the treatment with petroleum ether the tar (50 grams) was first dissolved in hot benzene (100 c.c.) and filtered hot to remove impurities, which consisted mainly of coal dust. It was then washed with hot benzene. The benzene solution was evaporated, the last traces of benzene being driven

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* Obviously unchanged montan wax and the like.

off in a vacuum on the water-bath. Twenty grams of the residue were well stirred with 20 c.c. of petroleum ether (35° to 65°) in a beaker and passed through a weighed filter. The insoluble residue was washed with 20 c.c. of petroleum ether, freed from adhering petroleum ether by drying at 100°, and then weighed. This procedure seems to afford a quick method for detecting a primary tar. Thus, the primary tar from brown coal gave, in the first instance, about 48 per cent. of residue insoluble in petroleum ether, but only 9 per cent. after having been once distilled. This is intelligible, as a primary tar is considerably decomposed by a single distillation, changing in consistency and in paraffinoid and acid constituents towards the ordinary brown coal tar with conversion of the montan wax into the more soluble paraffin wax. Of the commercial brown coal tars after purification with benzene, 5 per cent. were insoluble in petroleum ether. Similar results were obtained with a primary tar from Union briquettes, and the once-distilled product, the former containing 35 per cent. and the latter 3 per cent. insoluble. Judged by the residue insoluble in petroleum ether, the producer tar must therefore also be classed as a primary tar.

It is important to carry out this test under standard conditions and particularly with the same proportion of petroleum ether, since the solubility of the components is only relative. We have carried out a few more experiments with larger proportions of petroleum ether to elucidate these relations further.

Thus, 10 grams of a primary tar from brown coal, previously purified with benzene by treatment with twice the quantity of petroleum ether (20 c.c.) and washing with a further 20 c.c., gave altogether 35 per cent. insoluble in petroleum ether. In another case, 10 grams of purified primary tar from Union briquettes was treated with five times its bulk of petroleum ether (50 c.c.) and washed with 50 c.c. This yielded 15 per cent. of insoluble residue. Ten grams of purified producer tar from the Prince Adalbert potash works, having been mechanically shaken with 10 c.c. of petroleum ether for 1 hour, yielded a total of 30 per cent. insoluble in petroleum ether. These experiments indicate that the amount of residue insoluble in petroleum ether depends upon the proportion of petroleum used. Yet even where ten times the quantity of petroleum ether was used, the amount of residue was much greater than, for instance, the quantity obtainable from a once-distilled primary tar from Union briquettes which in its behaviour would approximate to a commercial tar from the same brown coal.

In conclusion, it may be stated that a brown coal tar which contains naphthalene is not a primary tar. If free from naphthalene it should be purified as described above by extraction with benzene, and after evaporating the benzene completely it should be treated with petroleum ether. Thus examined, primary tars from brown coal give more than 30 per cent. and other brown coal tars less than 10 per cent. of products insoluble in petroleum ether.

3. *Differentiation between Primary Tar from Brown Coal and that from Bituminous Coal*

Primary tars from brown coal, leaving aside the special case of lignitic coal, differ from the primary tars of bituminous coal by their consistency. The latter, owing to their low paraffin content, are liquid (setting point 3·5°), while the former are of semi-solid consistency (setting point above 30°).[21] Benedikt and Bamberger, and also Franz Fischer and Tropsch,[22] have proved that bituminous coal is free from methoxyl, when examined by the Zeisel method for the determination of the methyl number, whilst brown coals contain methoxyl compounds.[23] This is recognised again in the primary tars. Thus, for instance, primary tar from bituminous coal was found free from methoxyl, whilst that from Rhenish Union briquettes contained methoxyl.[24]

(*g*) THE CHEMICAL COMPOUNDS FOUND IN PRIMARY TAR AND IN PRIMARY BENZINES

Most of the constituents of the primary tar have not yet been identified. Generally only those compounds are found which are already known from other sources; the unidentified compounds are apparently present in such complexity that their isolation has not yet been accomplished. The position is similar to that of petroleum, where, after many years of intensive research, only a few individual chemical compounds have been isolated, and these are often by no means characteristic of the petroleum because they frequently occur in negligible quantities. Coke-oven tar and lignite tar may also be quoted to exemplify how little such industrial products are really explored. In most cases only those products are known which obtrude themselves upon our attention by their particular behaviour; for instance, constituents which crystallise readily or are low-boiling, or which resist thermal decomposition. The more severely such tars are treated by heat, the fewer will be the surviving molecular aggregates. We know more concerning the low-boiling constituents of a tar than concerning the high-boiling, because the former are more easily disentangled, since in them the number of isomers is naturally smaller than in the higher boiling and highly substituted compounds. Hence primary tars, prepared by comparatively tender treatment and therefore retaining many labile constituents, offer particular difficulties to the elucidation of their constitution. To single out a few well-known and easily identifiable compounds is of little value for characterising a primary tar, unless their quantitative relation to the total tar can be proved. Unfortunately, some authors content themselves with the qualitative tests of a compound, and thereby give the uninitiated a false impression as if the composition of a tar, or of a particular fraction, had been cleared up. Even if a narrow fraction, boiling, say, from 79° to 81°, is found to consist of 50 per cent. of benzene, that would not prove any appreciable occurrence of this compound in primary tar. For it is manifest that, if there were only traces of benzene present, these traces would accumulate at or about its boiling point. The proportion of the total fraction should be stated. It must, however, be admitted that the quantitative estimation of a compound in a highly complex mixture is more difficult than its qualitative identification.

In the following description of the various compounds so far identified, two further objections claim consideration. The aromatic compounds found may have been formed at too high temperatures by the dehydrogenation of products originally more or less hydrogenated. Further, where identified as sulphonic acids or as nitro-bodies, these compounds, during sulphonation or nitration, may have undergone oxidation to aromatic compounds. For these reasons it appears expedient to examine their density and other physical properties.

The opinion has been expressed that little is to be done chemically with the complex mixture, say, of the fraction 200° to 300° and that it requires, in the first instance, conversion by cracking into the less complex constituents of coke-oven tar. This can undoubtedly be done, but the proposal has no practical importance, for the primary tars are prepared in the first instance for power purposes, where their higher hydrogen percentage and complexity are of advantage. Density, boiling range, setting point and calorific value are here mainly decisive. Nevertheless, the exact scientific determination of individual compounds in primary tar is of great importance for their possible chemical utilisation. Such compounds, however, must first be discovered. The identification of single compounds is of subordinate significance for general characterisation, unless their quantitative proportions are known, or are negligible, whilst the main bulk remains unrecognised.

For this reason it should not be assumed that the compounds whose presence has been established or made likely by the workers cited below would give a true picture of the constitution of primary tars.

Primary Tar from Bituminous Coal

Neutral Constituents.—According to Franz Fischer and Gluud,[25] the fraction 20° to 60° of the benzine contains predominantly saturated and unsaturated members of the paraffin series. The fraction 60° to 100° presumably consists chiefly of members of the naphthene series and a few paraffins. This fraction resembles Russian benzine.

The fraction 100° to 125° is of too low a density to contain appreciable proportions of toluene, but it probably contains hydro-aromatic products.

The fraction 150° to 300° of the primary tar hydrocarbons contains about 10 per cent. of constituents not attacked by fuming sulphuric acid, the remaining 90 per cent. being olefines, partially or fully hydrogenated aromatic compounds and other hydrocarbons. The hydrocarbons boiling above 300° consist of solid paraffins and highly viscous oils. The composition of the solid paraffins lies, according to Gluud [26] between $C_{24}H_{50}$ and $C_{29}H_{60}$, the members with 26 and 27 carbon atoms predominating. On the whole, the paraffin hydrocarbons, both liquid and solid, make up about 10 per cent. of the total fractions.

Schrader and Zerbe [27] found minimal quantities of naphthalene (0·01 per cent. of the total hydrocarbons).

In the neutral motor oil (200° to 300°) Weissgerber and Moehrle [28] found from 10 to 16 per cent. of paraffins and per-hydrogenated naphthenes, and from 50 to 60 per cent. assumed to be aromatic compounds by their solubility in sulphuric acid monohydrate. Of known compounds they found traces of naphthalene, and methyl- and dimethyl-naphthalene.

The unsaturated compounds have not yet been cleared up, though indene homologues are said to have been identified. Of aromatic compounds they identified pseudo-cumene, durene, α-methyl-naphthalene, β-methyl-naphthalene, 1 : 6-dimethyl-naphthalene. As regards the naphthenes, the presence of per-hydrofluorene, per-hydroacenaphthene and deca-hydronaphthalene appears probable.

Weissgerber [29] found ketones of the open, non-aromatic chain type in the neutral fraction 190° to 200° of primary tar oils. He presumes the presence of more or less hydrogenated acetophenone.

Schütz [30] found in the benzines unsaturated hydrocarbons and acetone, in addition to saturated hydrocarbons (pentane), mercaptan and sulphides; in the neutral oil boiling above 75°, benzene, toluene, *m*-xylene, but no naphthalene. Part of the aromatic bodies was probably formed by dehydrogenation through superheating of the tar, or by dehydrogenation during the sulphonation tests. This opinion is, however, not shared by Schütz.[31]

Of saturated hydrocarbons he identified *n*-butane, *n*-pentane, methylbutane, methylpentane, hexane, heptane and octane; of unsaturated hydrocarbons, ethylene, propylene, butylene, pentene; of diolefines, 1 : 2- and 3 : 4-butadiene, *cyclo*-pentadiene, acetone, methyl-ethyl ketone, acetonitrile, methyl-mercaptan, dimethyl-sulphide and minimal quantities of carbon disulphide.

Morgan and Soule,[32] investigating the primary tar produced by the "Carbocoal" process (see p. 65), found that the neutral oils, remaining after removal of the tar acids and bases, are distinguished by their low density ($D^{25} = 0{\cdot}891$) and low viscosity. They confirmed the absence of noteworthy quantities of solid aromatic hydrocarbons upon cooling down to — 30°. No individual hydrocarbon was found in predominating proportion. The unsaturated hydrocarbons when present in considerable amounts cause on standing a gradual darkening and an increase in the density of the oil. Treatment with sulphuric acid of 98 per cent. strength left the saturated hydrocarbons behind. These consisted of about two-thirds naphthenes and one-third paraffins, totalling about 14 per cent. of the neutral oils. The unsaturated hydrocarbons, isolated for purposes of examination by means of liquid SO_2, belonged, as the determination of density, refractive index and molecular weight indicated, to the same series of cyclic partially hydrogenated hydrocarbons as those occurring in vacuum tar. Solid aromatic hydrocarbons were absent, but liquid members present in traces.

Phenols.—It has been proved that carbolic acid is present in very small proportions only.[33] The cresols are chiefly represented by *m*-cresol, the proportion of *p*-cresol is exceedingly small, but *o*-cresol is slightly more abundant. The distribution of the isomers is therefore quite different in primary tar from that in coke-oven tar. Like the cresols, the xylenols seem to amount to about 1 or 2 per cent. of the total weight of the primary tar. Concerning the higher phenols little information is available; only pyrocatechol has been estimated, approximately in a proportion of 0·25 per cent. of the total tar. Pyrocatechol is also known to be present in brown coal tar, but not in coke-oven tar.

Weindel[34] investigated the phenols of the tar from a "Tri-gas" producer. According to him the phenols of this tar consist only partly of a regularly ascending series of homologues, those higher than xylenol being probably unsaturated in character. In addition, derivatives with more than one hydroxyl group are present, although in small quantities; they appear in the fractions from 240° to 275° (pyrocatechol). Among the higher members one may safely expect the presence of β-naphthol. Weindel did not isolate definite compounds, but he indicated the presence of homologues of cresol, viz. xylenol, propylphenol, butylphenol, and amylphenol.

Morgan and Soule[35] established that their primary tar contained little carbolic acid, but considerable proportions of cresols and xylenols. Half of their phenols boiled below 220°. The cresols consisted of 27 per cent. of *o*-cresol, 19 per cent. of *m*-cresol and 54 per cent. of *p*-cresol. The isomers were therefore found in proportions quite different from other cases. Besides, the presence of xylenols was proved.

Bases.—Fischer and Gluud ascertained that the proportion of bases amounts to about 1 per cent. of the tar.

Gollmer,[36] investigating the bases of the tar from a "Tri-gas" producer, found little pyridine, but mainly bases of higher boiling point, the larger portion boiling above 240°. Referred to the proportion of hydrocarbons, the total amount of bases would be from 2 to 3 per cent., referred to the tar, 1 to 2 per cent. Apart from the symmetrical collidine, no definite compounds were determined owing to the complexity of the mixture.

Morgan and Souls [32] conclude from their investigation of the nitrogenous bases that 80 per cent. are tertiary and 20 per cent. secondary; primary bases were not found. The specific gravity of the mixture of bases was $D^{15} = 0{\cdot}993$. Whilst in coke-oven tar bases quinoline predominates, they did not find any base preponderating in primary tar. The lowest boiling fraction contained pyridine, the higher-boiling bases have lower specific gravity and higher molecular weight than those of ordinary tar. They seem to contain partly hydrogenated nuclei and longer side-chains than the bases of coke-oven tar.

Brown Coal Tar

Graefe [37] states that the tar from brown coal boils from 150° to 400°, and consists essentially of liquid and solid members of the paraffin and olefine series. Among aromatic bodies he finds traces of phenol, cresol and substituted phenols to the amount of about 15 to 20 per cent. Marcusson has proved the presence of large quantities of ketones.

Ruhemann and Avenarius [38] found in the primary tar from a brown coal producer no carbolic acid, but *m*-cresol and 1 : 4 : 5-xylenol.

Fromm [39] established the presence of pyridine and considered that of picoline probable. Among the constituents soluble in alkali, carboxylic acids are only present in his tar in exceedingly small quantities. Of the phenols he could only identify *m*-cresol. Most phenols, of which he prepared urethanes, could not be identified with those already known. Apparently he had to deal essentially with unknown phenols.

Pfaff and Kreutzer [40] found thiotolene in the low-boiling fractions of ordinary brown coal tar which resembles the primary tar from brown coal, fraction 105° to 106° containing about 3 per cent. They further determined the presence of 2·2 per cent. ketones in the light oil from brown coal (100° to 200°), 3·3 per cent. of ketones in fuel oils (180° to 320°), and 4·5 per cent. of ketones in the dark paraffin oil (200° to about 400°).

On summing up the proportion of compounds definitely identified in primary tar, they are found not even to represent 10 per cent. of the total constituents. Matters are not much better in the case of the long-known coke-oven tar, the bulk of whose constituents have not yet been identified. The still unidentified portion probably consists of compounds of unknown constitution, hence the difficulty of their identification or isolation from the very complex mixtures.

(*h*) THE LIQUOR FROM LOW-TEMPERATURE CARBONISATION

In addition to the oily condensate an aqueous liquor is obtained in low-temperature carbonising, partly due to the moisture in the coal, and partly to water formed on decomposition. To restrict the yield of liquor, in order to facilitate its removal or to allow of a more complete recovery of products from it, the coal should be dried before distillation. This is an essential procedure in the case of brown coal. This problem will be dealt with in detail in a separate section (p. 91). The gas liquor from low-temperature carbonisation reacts acid in the case of both bituminous and brown coal, and it differs in this respect from the coke-oven and gas liquors which react alkaline owing to their ammonia content. The acid reaction of low-temperature carbonisation liquor is due to the fact that in this process almost the whole nitrogen remains in the semi-coke, and that therefore only minute quantities of ammonia are formed. Since at low temperature more than the equivalent proportion of acid products is formed, the gas liquor contains the small amounts of ammonia in the form of ammonium salts, and in addition free acids.

The bulk of the ammonia appears only at temperatures between 600° and 800°, that is, above the temperatures used in these processes, and then in amounts larger than the equivalent of the acids produced in low-temperature carbonisation. Hence, in coke-ovens and gas works liquor the acids are neutralised by ammonia, and it contains in addition free ammonia and ammonium carbonate to which it owes its alkaline reaction.

Amongst organic compounds found in low-temperature liquor pyrocatechol may be cited in the case of bituminous [41] and brown coal. Methyl alcohol occurs in small proportions in the liquor from brown coal, whilst acetone has been found in small quantities in both cases. It would, however, appear that, at temperatures slightly higher than those strictly required for low-temperature carbonisation, the percentage of acetone is increased at the expense of other not yet identified bodies. This also applies to carbolic acid which, though contained in slight amounts in normal primary tar, is sometimes found dissolved in the liquor. The amount of liquor produced depends, as already mentioned, upon the moisture content of the coal. With dry coal, the yield of liquor wholly formed by decomposition equals that of the tar.

(*i*) COMPOSITION AND APPLICATION OF LOW-TEMPERATURE CARBONISATION GAS

The yield of gas amounts with most coals to from 50 to 80 cb.m. per ton. There is a considerable difference between the low-temperature gas and ordinary coal gas, as shown in Table IX :—

TABLE IX

Primary Gas.				Crude Coal Gas.			
CO_2	1–7%	H_2	16–22%	CO_2	2·0%	H_2	50·0%
C_nH_m	3-5%	CH_4	55–70	C_nH_m	3·75%	CH_4	31·0%
O_2	— %	N_2	3–4%	O_2	— %	N_2	2·25%
CO	1–6%	H_2S	4–5%	CO	9·0%	H_2S	0·75 %

The high percentage of methane hydrocarbons and the small percentage of hydrogen is characteristic for low-temperature carbonisation gas; further, unsaturated hydrocarbons predominate and may amount to 15 per cent. of the gas. Whilst coal gas contains benzol vapours, low-temperature gas contains benzine which is recovered in a similar manner to benzol. This product is designated "gas benzine" as distinct from "tar benzine" of a slightly higher boiling point, which in the dry distillation of coal is condensed together with the primary tar. Otherwise the distribution of benzine between gas and tar merely depends upon the conditions of the tar condensation. The more effectively the tar is cooled, the more benzine it will contain and the less will be found in the gas. According to various statements by practical men, the low-temperature gas of bituminous coal does not contain any hydrogen, and its yield is 150 cb.m. per ton. The former statement is certainly incorrect, for numerous reliable investigators have agreed in proving the presence of hydrogen in low-temperature gas from the most varied kinds of coal. The statement as to the gas yield is also open to doubt, and it will be desirable to settle this question, since the possible gas yield is of economic importance.

Table X, due to Foerster,[42] is interesting in that it illustrates the liberation of the various gases at rising temperatures.

TABLE X

Gas sample taken	$CO_2 + H_2S$. %.	C_nH_m. %.	CO. %.	H_2. %.	CH_4. %.	C_2H_6. %.	N_2. %.
up to 420°	15·4	9·6	8·4	10·4	33·6	21·2	5·6
,, ,, 500°	6·2	4·6	6·2	24·8	40·3	14·4	5·7
above 500°	5·0	2·2	5·2	34·3	41·4	6·8	6·2

The table shows that hydrogen makes its appearance below 420°, and that its proportion increases with rising temperature.

Similarly, Burgess and Wheeler found the following gases in an English coal:

	At 450°.	At 500°.
H_2	7·0%	16·6%
CH_4	25·0%	37·6%
C_2H_6	34·1%	27·6%

Here also considerable evolution of hydrogen was observed even at low temperature.

In accordance with its composition, low-temperature carbonisation gas has a very high calorific value. Thus it has been established that the calorific value of low-temperature gas from bituminous coal, as prepared in the laboratory in the rotating retort, as free as possible from air, lies between 8000 and 9000 calories. Such values were obtained even when the gas had been stripped of its benzine vapours by washing with paraffin oil under pressure. In large-scale rotary retorts lower calorific values were obtained. This is due either to the production at the higher temperatures of a gas richer in hydrogen at the expense of the hydrogen content of the tar or semi-coke, or to leakage of air into the retort, which can scarcely be avoided in practice.

The gas from low-temperature carbonisation with its high calorific value can be used for many purposes. Compressed it may, for instance, be utilised for the illumination of railway carriages, since its calorific value is almost double that of ordinary coal gas. Gas holders of equal capacity, contain therefore at equal pressure twice the amount of energy, which means either improved illumination or a longer lighting period. In work of a lighter class it can be utilised in combination with oxygen for autogenous welding in place of acetylene. With a yield of 50 to 80 cb.m. of gas per ton of coal, *i.e.* only about a quarter or one-third of the yield of high-temperature gas, this valuable gas will easily find sufficient application. It will, however, not be used for heating the retorts as long as it can be otherwise employed. For this purpose gases of lower calorific power, like blast furnace gas or producer gas, are much more advantageous, since high temperatures are not only unnecessary but may lead to damage of the retorts or drums; moreover, these poorer gases are cheaper.

Alcohols or Naphthenic Petroleum from the Unsaturated Constituents of Low-temperature Gas

Various statements are found in the literature as to the possibility of the conversion of the unsaturated constituents of low-temperature gas such as ethylene and propylene, which may amount to 5 per cent. of the gas, into ethyl or propyl alcohol. The same problem has been investigated in relation to coke-oven gas for many years. The coke-oven gas is poorer in unsaturated constituents, and is therefore less suitable for the production of alcohol than low-temperature gas. Extensive experiments [43] have been made with concentrated sulphuric acid as absorbent, but in the coke-oven industry [44] no plant