Engler. The forerunnings and residue were then remixed and kept in an autoclave at 355° to 360° for 48 hours. Twenty-four hours later the autoclave scarcely showed any pressure; after 48 hours the pressure had risen to 20 atm. After cooling the autoclave, the gas copiously liberated was allowed to escape; it burned with a bright non-smoking flame. The oil made was again heated in an iron pot; at 80° a light oil began to come over; 75 c.c. were collected up to 265°. This oil was of a reddish-yellow colour and an intense green fluorescence. The remaining oil boiling above 265° had at 50° a viscosity of 33·4° Engler (against 2° Engler before), a very remarkable change which was also apparent from its colour, which had turned into a deep dark brown; the setting point was + 7·5°. This oil, being free of phenols, and the product of a thickening process, should be suitable for various lubrication purposes.[88]

Distillation at Ordinary Pressure and Chemical Treatment

The fraction 150° to 300° of the primary tar from bituminous coal, obtained by distillation at atmospheric pressure, and the corresponding fraction of brown coal tar are treated in exactly the same way,[89] *i.e.*, by first removing the phenols with 5 per cent. caustic soda and then the bases with dilute sulphuric acid. They both yield mixtures of hydrocarbons of close similarity, which by fractionation and refining with concentrated sulphuric acid can be separated into practically the same products. These products are tabulated below.

TABLE XVIII

	In tar.	Boiling range.
Tar benzine	5·0%	Below 150°
Solar oil	5·5%	150–220°
Cleaning oil	1·0%	220–250°
Gas oil	8·8%	250–300°
Neutral lubricating oil	6·0%	300–325°
Paraffin wax	0·5%	—

To these yields must be added the phenols extracted by caustic soda from the fraction 150° to 300°, amounting to 24 per cent. of the tar. Another portion of the phenols originally in the tar is in the pitch residue which amounts to 37 per cent. of the tar. As pointed out above, the hydrocarbons of primary tar from bituminous coal give the same products (solar oil, cleaning oil, yellow oil, red oil, gas oil, etc.), as those from brown coal tar. Particularly striking and complete is the resemblance between the solar oils from the two kinds of coal. Since solar oil in suitable burners is used as a lamp oil, the production of oil for illuminating purposes from bituminous coal is proved. The two oils tally in colour, specific gravity, ultimate composition, calorific value and viscosity, provided that the tar has really been prepared under true low-temperature conditions. A superheated tar is not likely to yield such a solar oil. Further details of these experiments will be found in *Abh. Kohle*, 1918, 3, 46.

Working-up of Primary Tar by Means of Superheated Steam and Chemical Treatment [90]

In order to prevent the decomposition of the viscous oils in primary tars care should be taken not to exceed a temperature of 300°. One mode of achieving this, by means of superheated steam, will be first described. Starting from the primary tar of gas flame coal, the phenolic constituents may be first extracted with caustic soda. As the tar contains about 50 per cent. of phenols, its volume will thus be halved. From the remaining hydrocarbons (neglecting the small amount of bases) the tar benzine is distilled off, up to 200°. Superheated steam is then introduced, when non-viscous oil comes over, until the vapour temperature reaches about 190°; as the temperature rises viscous oils are obtained; finally at 240° the products become resinous.

Results from fat coal are similar; the products have a better appearance, but the drawback is that the fat coal yields relatively little tar. The yields are summarised in Tables XIX and XX.

TABLE XIX

Fat coal. 100 kg. coal gave about 3 kg. tar.	%
Valuable viscous oils (lubricants)	15·2
Paraffin wax	0·4
Non-viscous oils	33·5
Phenols	14·0
Resins	4·2
Pitch	19·2
Loss and water	13·5
	100·0

TABLE XX

Gas coal. 100 kg. coal gave about 10 kg. tar.	%
Valuable viscous oils (lubricants)	10·0
Paraffin wax	1·0
Non-viscous oils	15·0
Phenols	50·0
Resins	1·0
Pitch	6·0
Loss and water	17·0
	100·0

Owing to the presence of paraffin wax, the viscous oils obtained by simple distillation have a high setting point. This may be lowered by removing the paraffin wax. By dissolving the oils in acetone, cooling the solution to − 10°, filtering the paraffin wax on the pump, evaporating the acetone and fractionating the wax-free oil with the aid of superheated steam, lubricating oils of the properties summarised in Table XXI were obtained.

the separation of paraffin wax; badly de-paraffined lubricating oils from petroleum show the same defect. Deficiencies in other properties, like oxidisability, etc., are also due to careless distilling, and the true history of such an oil would probably show that it had been driven over at high temperature and with strong decomposition, instead of having been submitted to a very cautious distillation as described.

"As long as products which have not been treated with care can find a ready sale and command high prices, it is intelligible that the preparation of primary tar is not carried out with the requisite attention. As soon as the competition of superior products makes itself again felt, the inferior products from primary tar will be forced from the market, and this contingency is rapidly approaching. The manufacture of superior products will then needs follow, the feasibility of which has been sufficiently emphasised.

"The economic necessity for improved methods will be found when the price of primary tar drops and therefore the raw material itself does not form an easy source of profit. The margin between raw material and finished product will then become wider and create an incentive for improvements in refining. Complaints of the quality of products from primary tar at present, I consider a good sign which can only make for improvement and will do away with the easy profits and the unnaturally high prices. It is not correct to ascribe the fault to the character of the tar, or the principle of its production; it really lies in the want of care bestowed upon the working-up of the products."

Gluud's arguments must be agreed with, but should be supplemented by recent experience in the primary tar industry. The objection that lubricants cannot be made from it must not be advanced against true primary tar. The difficulty lies in that the commercial products are frequently not true *low-temperature* tars, but are partly dehydrogenated, as explained in the section on "Influence of Retort Design." Even the most skilful distiller cannot get good results from such tars.

Viscous lubricants being high-priced products, the oil from coal will best be submitted to some hydrogenation process, as used in fat hardening or in tetraline manufacture. The process of Bergius will hardly be applicable, as it requires a temperature above 300°, where decomposition into non-viscous products takes place.

Examination of Primary Tars for Lubricating Components.[82]—In testing a tar for its content of viscous oils, the following method may be resorted to if high flash points are not wanted, and in the absence of suitable apparatus for distillation in superheated steam.

The tar is first submitted to steam distillation in order to remove the more volatile constituents. The residue is well shaken with two or three times its volume of petroleum ether (boiling range 90–100°). The viscous oils are dissolved, leaving behind the bulk of acid and asphaltic compounds. The solution is then shaken in turn with alkali, water, dilute sulphuric acid and again with water, and so freed of its acid, basic and resinous substances. The petroleum ether solution is evaporated at reduced pressure and finally at 100°, leaving as residue the viscous oils which mostly congeal to ointment consistency on account of their paraffin wax content. For the separation of paraffin wax the product is mixed with several times its volume of acetone, and cooled to – 10°; the paraffin is filtered off, and the acetone evaporated in a vacuum, raising the temperature to 100°. The viscous oil obtained still contains traces of acetone and petroleum ether.

The industrial working-up will be on somewhat different lines from that of our gas flame coal experiments in Tables XIX and XX. The whole tar is distilled and the phenols extracted from some selected fractions only. Under certain conditions partial extraction of the most acid phenols, with a restricted amount of caustic soda, will be preferable; the phenols which pass over together with the lubricating oils are also very viscous, and even more so than the hydrocarbons of the same boiling range. The non-viscous oils serve as liquid fuel, and after refining possibly as solvents. The highest fractions are of a resinous character and contain paraffin wax.

Freshly distilled, they are of yellow colour, which quickly darkens. The proportion of pitch left in the still can be reduced at will, by forcing the resinous compounds over. If it should be possible to remove from the resinous portion those constituents which cause the darkening, or to prevent it by hydrogenation, very valuable products would be obtained.

Improvement by means of hydrogenation both of resins and lubricants is one of the problems of the future. The difficulty is that the usual catalysts are rapidly poisoned by sulphur-containing materials, while hydrogenation without catalyst, according to Ipatiew or Bergius, is inapplicable owing to the high temperature required. Something might perhaps be achieved by electrolysis of the solutions or emulsions with cathodes, for example of lead, at high voltage.*

It has already been explained that primary tar from brown coal is altered by distillation at ordinary pressure, owing to the decomposition of the viscous constituents. It will be shown below that this tar is also a source of highly viscous lubricants when treated with care.[92] For this purpose a fair quantity of primary tar from Central German brown coal was prepared in the rotating drum. This tar differs materially from commercial brown coal tars. The yield is 100 per cent. of that given by analysis, whilst in the production of brown coal tar in the Rolle retort 60 per cent. is usually taken as a basis (Scheithauer, "Shale Oils and Tars," 2nd edition). A commercial brown coal tar has a setting point of + 15°; the primary tar prepared from the same coal showed a

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* de Hemptinne's "Voltol" process, using silent electric discharges, need hardly be considered here.

TABLE XXI

Condensed from 170° *to* 193° (*temp. of vapour* 210–235°)

65 grams medium viscous lubricating oil:

Flash point	152°
Setting point	−12°
Viscosity at 20°	7·2° Engler
„ at 50°	1·73° „

Condensed from 193° *to* 205° (*temp. of vapour* 235–255°)

100 grams viscous lubricating oil:

Flash point	182°
Setting point	−5°
Viscosity at 20°	19·2° Engler
„ at 50°	5·4° „

Condensed at 205° (*temp. of vapour* 255–265°)

90 grams very viscous lubricating oil:

Flash point	194–195°
Setting point	+4·5°
Viscosity at 50°	28·3° Engler
„ at 100°	1·9° „

Characteristic of these viscous oils are their deep golden-red colour and feeble green fluorescence; further, their pleasant aromatic, yet strong fatty smell. The smell resembles somewhat that of oils directly extracted from coal (see Chapter I, Extraction). The quantity of viscous oils also recalls the conditions of the extraction. Fat coal yielded 3 per cent. of tar, and the tar itself contained 15 per cent. of viscous oil, or 0·45 per cent. of weight of coal. Gas flame coal yields 1 per cent. of highly viscous oil. The yields are of the same order of magnitude as those by extraction of coal with anhydrous sulphur dioxide, and it is quite feasible that the oil which existed preformed in the coal should be found in the tar distillate, if all superheating has been avoided during carbonising and in distilling; the characteristic smell will at once attract attention. The oils obtained by distillation also contain constituents formed by the decomposition or de-polymerisation of the bitumen in coal.

If a solution of 100 grams of the viscous oil in petroleum ether is extracted with concentrated sulphuric acid, 10 grams of a viscous, quite colourless oil are obtained. But it is not necessary to push the acid treatment so far, and it is never done in practice. It suffices to remove the compounds particularly liable to resinification. As regards the value of the lubricant from primary tar, Gluud [91] wrote as follows :—

" Very discordant opinions are held by practical men regarding the lubricating oil obtainable from primary tar. The responsibility for failures is mostly ascribed to the tar, but should be more properly placed on the distiller. Too high a setting point indicates that proper attention has not been paid to setting point of about +38°. This is due to the higher percentage of solid products (paraffin, montan wax, etc.) which have undergone less decomposition, owing to the lower temperature and to the quick removal of the vapours from the drum by the steam current. The results of the working-up of the primary tar from brown coal by means of superheated steam are summarised in Tables XXII and XXIII.

TABLE XXII

Central German Brown Coal rich in Bitumen (Carbonising Coal)

	100 kg. coal (dry basis) gave 24 kg. primary tar.		% of tar.
I.	Viscous oils composed of:		
	(a) highly viscous oils: (V_{20} = 67·0° Engler) .	1·73%	
	(b) medium ,, ,, : (V_{20} = 11·4° ,,) .	13·01%	
	(c) slightly ,, ,, : (V_{20} = 5·4° ,,) .	2·47%	
		17·21%	
	total: (V_{20} = 13·5° Engler, V_{50} = 2·85° Engler) . . .		17·2
II.	Solid products (hard and soft paraffin wax, etc.)		29·4
III.	Non-viscous oils (free from creosot)		28·9
IV.	Tar acids		10·5
V.	Resinous substance		2·2
VI.	Pitch.		3·2
VII.	Loss		8·6
			100·0

TABLE XXIII

Results of Fractionation with Superheated Steam of Viscous Oils

	V_{20}	V_{50}	Setting point.	Flash point.	Tar yields.
below 180°	below 5° Engler	—	—	—	2·41%
180–210°	5·28° ,,	1·68° Engler	−12°	135°	5·65%
210–235°	45·4° ,,	6·02° ,,	− 4·5°	199°	3·61%
235–255°	—	49·5° ,,	+21°	176°	3·79%

Working-up in a High Vacuum

Primary tar from brown coal and its products are at present made on a very large scale by the Deutsche Erdöl A.-G. Works at Rositz,[93] in high-vacuum plants designed and built by the Brünn-Königsfelder Maschinenfabrik. "The distillation is effected in large continuous stills of 40 cb.m. capacity, arranged in groups of eight; the tar, freed of a certain fraction, flows into the next still from which the next fraction is taken."—"The temperature difference between two adjacent stills amounts to about 15°. Distillation begins at the temperature at which the preheated raw material enters the first still, *i.e.*, at about 200°, and finishes at 320°. Owing to the high vacuum of 680 mm. a goodly proportion of the tar passes over. The off-takes between the stills must be of ample diameter so as to equalise the vacuum in all the stills; otherwise there might be serious disturbances in the circulation of the tar from still to still.

"The tar enters the higher still, which is at the lowest temperature, and runs from it into the second, which is mounted 30 cm. lower; the difference between the levels of the first and the last still thus amounts to 7 × 30 = 210 cm. Each still yields two fractions, one coming down in the preheater, and one in the condenser. Apart from the light distillates which are taken up in the preheaters, sixteen fractions are thus obtained. All these fractions are not kept apart; for the further working-up, the light and the heavy distillates free of paraffin wax, as well as those containing wax, are combined in a smaller number of groups."—"The stills are heated by means of producer gas which is taken from the producers in which the tar is produced. Owing to the high vacuum, the lubricating value of the hydrocarbons of the brown coal tar is much better preserved than with the former method of working. The producer tar is anyhow less decomposed than the brown coal (Schwel-) tar, and by further distilling it with every care, oils are obtained of a lubricating value which could not be obtained with ordinary brown coal tar. The Deutsche Erdöl A.-G. has put brown coal tar lubricants on the market, which though as regards lubricating power, purity, smell and cold point are not quite equal to the corresponding petroleum products, yet have done a great deal towards the reduction in imports of lubricants into Germany from other countries. Two such lubricating oils had the following properties :—

TABLE XXIV

	Machine oil I.	Machine oil II.
Viscosity at 50°	3–4° Engler	4–5° Engler
Ignition point	165–180°	170–185°
Specific gravity	0·970–0·980	0·970–0·985
Solidification point	+7° to +8°	+7° to +8°

"The large quantities of paraffin wax which are obtained in the working-up of the brown coal producer tar are also important, as the existing supplies from the brown coal carbonising industry do not meet the home consumption. The methods of production and refining of paraffin wax have also been changed from those formerly customary in the brown coal industry."

The Gesellschaft für Teerverwertung, of Duisburg-Meiderich, has erected a plant for working-up primary tar from bituminous coal on the high vacuum system. An exhibition of its products formed part of the Heating Exhibition at Essen in 1922.

3. *Separation and Utilisation of Phenols*

The Disadvantages of Phenols and their Corrosion of Metals

The particular applicability of aliphatic hydrocarbons of high boiling points in internal combustion engines of the Diesel type is due to the decomposition of the injected oils by heat, which takes place more readily the larger the molecule. For this reason kerosene has a lower ignition point than benzene.* The larger kerosene molecules form, by the action of heat, scission products of olefinic character which are more oxidisable and inflammable. To a certain extent the hydro-aromatic hydrocarbons share this property; they also are subject to scission, or at any rate split off hydrogen. On the other hand, aromatic compounds, with which the phenols found in primary tar must be classed, are highly resistant to heat. They are decomposed above red heat only, and then into carbon (soot) and hydrogen. For that reason a Diesel engine cannot be run on phenols, unmixed with more easily ignitible substances. It is therefore clear that gas oil from brown coal tar, which is poor in phenols, is more suitable for this purpose than the corresponding fraction of primary tar from bituminous coal, almost half of which consists of phenols. The presence of phenols is objectionable when they are present in large quantities. In that case they may have to be removed, entirely or in part, unless it is

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* The spontaneous ignition point must not be confused with the flash point. Whilst the flash point indicates to which temperatures an oil must be heated so that the layer of vapours above the oil is ignited by a small flame, the ignition point marks the temperature at which drops or sprays of the oil, falling or injected into air, spontaneously catch fire. The ignition point is important for Diesel engine oils. The most recent data are tabulated below :—

TABLE XXV

Fuel.		Ignition point °C.	
		in oxygen.	in air.
Petroleum distillates :	Benzine	272	383
	Kerosene	251·5	432
	Gas oil	254	358
Crude oil :	Californian	262	420
Shale oil :	Motor oil	253	333
Coal tars :	Primary tar	307	508
	Horiz. retort tar	454	—
	Coke-oven tar	495	—
Tar distillates :	Xylene	484	—
	Toluene	516	—
	Benzene	566	—
	Coke-oven tar oil	478	—

The ignition points are considerably higher in air than in oxygen. The ignition point of primary tar approaches that of petroleum more closely than that of coke-oven tar; the latter has a relatively high ignition point, like all aromatic hydrocarbons. It is noteworthy that the high-boiling gas oil has a lower ignition point than the low-boiling benzine, whilst the sequence of flash points is reversed (Daiber, *Zeitschrift des Vereins deutscher Ingenieure*, 1921, **65**, No. 50).

expedient to reduce their concentration sufficiently by the admixture of petroleum products.

The behaviour of phenolic oils must also be studied for other reasons, in particular as to the corrosion of the metal of the engines. The different opinions expressed do not as a rule allow any definite conclusions, because the circumstances are not stated; for instance, whether the corrosion was observed when hot, in the presence of water or of air. It appeared, therefore, useful to study the behaviour of these oils in contact with the different metals used, under conditions favouring corrosion.

Ehrhardt and Pfleiderer [94] investigated the corrodibility of different metals by such oils in the presence of atmospheric oxygen and water. The primary tar oil which they applied had a boiling range of 150–270°, and contained about 40 per cent. of phenols. The oil was first saturated with water by shaking; the water not taken up was removed. The metals to be studied were used in the form of strips of sheet metal, or else in lumps. In order to ensure a strong reaction, the specimens were enclosed in glass tubes with the oil and air, and were kept agitated on a shaking machine during daytime for four weeks.

TABLE XXVI

Metal.	Loss of weight mgm./sq. cm.	Metal.	Loss of weight mgm./sq. cm.
Copper	6·5	Lead	1·1
Brass	0·6	Aluminium	0·0
Nickel-silver	0·9	Tin plate	0·22
Zinc	1·2	Sheet iron	0·51
Galvanised iron	0·73	,, ,, pickled	0·04
Nickel (wire)	0·09	Ferro-silicon (18%)	0·0
Nickel-plated brass	0·17	V2.A steel (Krupp)	0·0

According to Table XXVI aluminium, ferro-silicon and V2.A steel are not attacked by phenolic oils at ordinary temperature. For tubes and sheets, aluminium should therefore be used; for rods and bolts, V2 steel; and for castings, silicon-iron. Iron and nickel were also found to be very resistant. Cast iron was not examined; it is likely that it would hardly be corroded, and that it would behave like the pickled black sheet. It is not certain to which constituent the corrosion is really due; apart from phenols, sulphur compounds must be considered. For the practical problem it was less important to ascertain which constituents have a corrosive action than which metals would resist it under all conditions. If the corrosive ingredients are really among the phenols, they would probably be those which are somewhat soluble in water. It might then suffice to remove these by treatment of the primary tar oils with superheated water.

The Utilisation of the Phenols

Before proceeding to discuss the various possibilities of recovering the phenols from the tar oils, which must be done cheaply, their particular mode of application must be considered. In view of the high content of tar acids and the fact that carbolic acid, at present the most valuable, only occurs in negligible proportions (see p. 41), their removal and utilisation is of the highest importance for the working-up of primary tar, especially that from bituminous coal. It may be recalled that the gas flame coals which are richest in tar yield primary tars with nearly one-half of all fractions consisting of tar acids.

In the absence of other applications, the tar acids may be utilised as liquid fuel. Their use as impregnating oils is doubtless more profitable. For this purpose, the higher boiling phenols, which are not soluble in water and therefore not liable to be washed out of the wood by rain and moisture, are the most suitable. The phenols may be condensed with formaldehyde to resins similar to bakelite,[95] for which there is a considerable demand. Their manufacture on a large scale is impeded by the insufficient supply of formaldehyde and consequently its high price. As soon as a cheap method of preparing large quantities of formaldehyde from methane or carbon monoxide is found, a large-scale conversion of phenols into bakelite will be possible. It would be of particular value to convert the phenols into useful fuels, since this is the purpose for which the production of primary tar is largely undertaken. That this is at present within the range of possibility will be demonstrated in one of the following chapters.

Methods of Separation of Phenols hitherto in Use

The simplest way of recovering the phenols from the distillates of a primary tar, of the fractions of which they may make up to 50 per cent. or more, consists in shaking the oils with dilute caustic alkali and separating the aqueous alkali solution. Such a method of working is easy in the laboratory, but would be expensive on a large scale owing to the high cost of caustic soda. The alkali, after use, must be recausticised with lime, which is quite feasible, but undesirable. This is the way at present applied in works practice; the phenolate solutions are decomposed with carbon dioxide, sodium carbonate formed being reconverted into caustic soda.

Attempts to separate the oils by means of formic acid,[96] which is a good solvent for phenols, but hardly dissolves hydrocarbons at all, are successful in the laboratory, but out of the question in practice, as concentrated formic acid is too costly and moreover awkward to handle. Formamide behaves similarly, but is also too expensive.

Glycol and glycerin are solvents for phenols,[96] but not for hydrocarbons. One might dissolve the phenols in glycerin, and then dilute the glycerin solution with water, when the phenols separate; this would involve concentration of the glycerin solution with unavoidable losses, which makes the process uneconomical.

More advantageous is Krey's extraction with aqueous alcohol, which dissolves the phenols preferentially though not exclusively. This process is in constant use in the brown coal carbonising industry in plant designed by Kubierschky.

On mixing liquefied carbon dioxide under pressure with primary tar oil, two layers are formed; the upper layer consists chiefly of carbon dioxide and, strangely enough, hydrocarbons, whilst the lower contains mainly phenols. The separation is by no means complete, but might be adequate when repeated. The possibility of recovering and recompressing carbon dioxide quantitatively is a point in favour of this process, but the high pressure of 60 atm., at which it must be operated, is against it.

A peculiar reaction is observed when gaseous hydrochloric acid is passed into primary coal tar. The experiment is successful only with the tar itself, not with the oil fraction. Within a few minutes the tar separates into a thickish black paste and a light-coloured more fluid oil. The action becomes noticeable with as little as 0·5 gram of gaseous hydrochloric acid in 50 grams of tar; even a smaller quantity of acid would probably be sufficient. On centrifuging, the acid tar separates readily and sharply from the more mobile oil, in proportions of 60 per cent. of acid tar to 40 per cent. of thin oil. On extracting the separated oil with caustic alkali, the volume reduction indicated 15 to 18 per cent. of tar acids against more than twice that amount in the untreated tar.

The impression is gained that the acid tar is a better solvent for the phenols (and possibly for oxygen compounds in general) than the thin oil. The distribution ratio of the phenols is therefore such that the phenols pass mostly into the acid tar, whilst the thin oil is deprived of phenols.

A check experiment in which 2 c.c. of concentrated hydrochloric acid was applied per 50 grams of tar, in the place of the gaseous acid, gave the same result after a short while on a shaking machine. The distribution ratio between acid tar and thin oil after centrifuging was the same as in the experiment with gaseous hydrochloric acid. The phenol content of the thin oil was diminished to the same extent as in the previous experiment.

The oil purified with gaseous hydrochloric acid gave rise to a renewed deposition of solid resinous compounds when subsequently shaken with a little concentrated sulphuric acid.

A sample of fresh primary tar, shaken with a few drops of concentrated sulphuric acid, gave a similar deposit as with gaseous hydrochloric acid, though the oil was perhaps less fluid. Whether in this case the phenols accumulated in the acid tar was not ascertained; nor whether the lubricating oils of the tar were to be found in the acid tar, or in the thin oil.

It would be useful to continue these experiments. The acid tar might be