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ON THE CHEMISTRY OF THE ESTONIAN OIL SHALE „KUKERSITE"

A MONOGRAPH

BY

PAUL N. KOGERMAN

TARTU — 1931 — DORPAT

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KOMISJONIS J. G. KRÜGER'I JUURES TARTUS

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TARTU 1931

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Preface.

This Monograph is merely a summary of results of experiments carried out by the author since 1920. The chapters on the thermal decomposition of kukersite, the isolation and the properties of phenols, the composition of light oil, and the gum formation in light fractions of shale oil have been published by the author, but the pressure of academic work and research in other fields of chemistry have prevented him so far from publishing the rest of his researches *in extenso*.

The few works published by other investigators on the subject are reviewed in this Monograph.

The author desires to record his thanks to Mr. *M. Arvisto* for experimental assistance in connection with the study of the initial decomposition of kukersite, to Dr. *J. Hüsse* for checking the combustions of acids, to Mr. *E. Zastrov* for checking the combustions of bases, to Mr. *A. Wähner* for checking the experiments on refining of light shale oils. Acknowledgment is extended to Messrs. *M. Raud* and *J. Kopwillem* for their permission to publish Figs. 1 and 19, to Mr. *K. Weske* for the preparation of the drawings, and finally to Mr. *John Roberts*, D. I. C., for reading the manuscript.

University of Tartu,
March 3rd, 1931.

Contents.

Introduction.

Civilization and the progress of mankind have always been dependent on the use of energy in its various forms, among which heat stands out as the most important. Since pre-historic times the natural organic raw materials, like wood, coal, and vegetable and mineral oils, have been used for the production of light and heat.

The rapid development of the automobile industry in recent years has enormously increased the demand for liquid fuels. On the other hand, the fact that the reserves of well-petroleum are not inexhaustible has induced the petroleum technologists to look for substitutes for it (McKee[45]).

The possible subtitutes for petroleum oils are: —

(i) vegetable oils and alcohol, (ii) synthetic fuels like synthol and others (Fischer[9]), (iii) low-temperature coal tars, and (iv) shale oils.

Since the industrial importance of oil shales has been thoroughly discussed by many eminent technologists and chemists (Gavin[11], Alderson[1], Cunningham-Craig[6]), the author need not go into a discussion of the subject in this Monograph. It is worth mentioning that the American oil technologists usually regard oil shales as the most important substitute for well oil (Alderson, 1926[2]). Although the technology of oil shales, especially the retorting of it, has made notable progress in many countries, as, in Scotland, in France ,in the United States, in Estonia (Kogerman and Roberts[35]), and elsewhere, purely scientific research on oil shales seems to have been somewhat neglected. Only recent researches have shed some light on this dark subject. To elucidate the chemical nature of an oil shale is not easy, because the classical methods of organic analysis are but partly applicable to this case, and some new methods have to be discovered.

The study of the chemical nature of an oil shale requires the knowledge of not only organic chemistry, but also colloidal and physical chemistry, geology, biology, and other branches of science.

The following scheme illustrates the complexity of the question and shows the relation of the chemistry of oil shales to other sciences:

Chemistry of Oil Shales	Genesis of Oil Shales	Limnology and biology
		Geology and paleontology
		Biochemistry
	The Nature of Oil Shales	Colloidal Chemistry (absorption, etc.)
		Organic "
		Inorganic (Ash.) "
	Utilization	Chemical Technology & Engineering
		Economics.

The Genesis of the Estonian Oil Shale.

The genesis of the Estonian oil shale (so-called "kukersite") has been discussed by the author in a paper read before the Naturalists' Society at the University of Tartu, Estonia, (K o g e r m a n, 1927 [20]). The main conclusions drawn from the geological, limnological, and chemical evidence are as follows:

1. The organic matter of microscopic algae and other plankton organisms, which formed the organic matter, or kerogen, of kukersite seems to be highly altered. The chief constituents of these organisms, the proteins, have totally disappeared, the percentage of nitrogen in kukersite being practically nil (about 0.2 per cent).

2. In the formation of kukersite compounds have participated which are most resistant to decomposition, *i. e.* waxes and resins, with decomposition products of proteins and cellulose on one side, and putrefaction products of undigested organisms on the other, but the first group of substances seems to predominate. Part of the kerogen of kukersite might be regarded from the genetic point of view as a coprogeneous substance.

The so-called "algae", as recognized under the microscope at present might well be synthetic formations, as has been shown by S t a c h [56] in the case of pollen-like bodies in coal.

3. In nearly all theories dealing with the origin of oil shales the biochemical changes in the raw material in the "predeposition" period, based on recent limnological observations, are usually neglected.

4. The greater part of the kerogen in kukersite is (from a chemical point of view) probably "gummified" or resinous. In this connection the word "resin" does not mean compounds analogous to natural resins or resins found in coal, but gums or resins of "synthetic character", *viz.* condensation products like aldehyde resins, etc.

These main conclusions, arrived at by the author, might well be true in the case of other oil shales, similar in nature. Dr. Manning [43], in his dissertation on the *Genesis of Oil Shales*, published in New York in 1927, and dealing with the American oil shales, comes to the conclusion that "the predominating substances concerned in the origin of kerogen are residues from vegetation of past eras, and these residues are in part resinous". The Estonian oil shale is planktonic in its origin.

The chemical investigations of the Estonian oil shale and its products fairly well support the hypothesis of the present author.

The chief aim of the author was to determine the nature of kerogen from the chemist's point of view. Therefore, geological and limnological facts were dealt with to such an extent as to make it possible to form a working hypothesis. Words like "sapropel", "katabitumen", etc., used by German geologists and chemists to characterize the nature of oil shales and coals, are omitted in the present work, because they do not refer to any group of chemical compounds.

PART I.

THE OIL SHALE.

General. The Estonian oil shale is one of the oldest and richest oil shales in the world. The shale deposits occur in

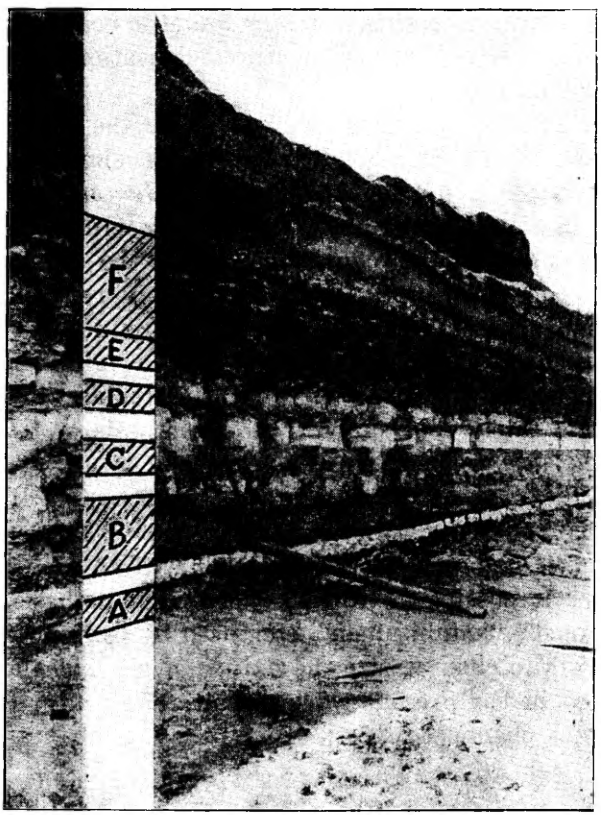


Fig. 1. A section of the oil shale mine at Kohtla.

the Middle-Ordovician strata (Plate I), the whole formation attaining a total average thickness of 2.2 metres, over an area of about 2500 square kilometres. Where the oil shale is typi-

cally developed, it consists of seven beds or seams, referred to locally as the A, B, C, D, E, F and G seams, respectively, the lowermost being the A seam. The seams are inter-stratified with limestone beds. Some of the oil shale beds are highly fossiliferous. A typical section, as developed in the Kohtla area, is shown in Figs. 1 and 2.

Fig. 2. A corner of the Käva-Kohtla Mine.

The colour of kukersite varies from greenish-yellow to reddish-brown. In thin section, under the microscope, the kerogen is amber-yellow. Contrary to the view of Narbutt [48], who describes the ash-free shale substance as a dark-brown powder, the present writer finds that the fairly pure kerogen has a yellow colour when the mineral matter is cautiously removed, for instance, by flotation and with dilute (5%) nitric acid. The treatment with concentrated hydrochloric and hydrofluoric acids, which was used in Narbutt's experiments, affects the kerogen chemically. The darkening of the colour of kerogen is probably a sign of chemical change in the shale substance.

The hardness of kukersite exceeds that of coal. The freshly mined mineral is hard, only the weathered shale is soft and brittle (K o g e r m a n, 1925 [21]).

The density of kukersite varies from 1.30—1.80, and the density of kerogen is slightly above 1.0 (1.08).

The Composition of Kukersite.

The average proximate composition of kukersite is given in Table I:

Table I.

Proximate Analysis of Kukersite.

Kukersite	Water per cent	Ash per cent	CO_2 per cent	Ash + CO_2 per cent	Organic matter per cent	Calorific value cals/kg.
Freshly mined .	18.2	30.0	7.9	37.9	49.9	3000—3500
Air dry	1.5	36.1	9.5	45.6	52.9	4200—4500

The chemical composition of the kerogen of various seams of kukersite does not vary much, as is evident from Table II (Luts[42]).

Table II.

Chemical Composition of the Shale Seams (Kohtla-Järve District).

The Ultimate Composition (per cent of C, H, S, Cl, O + N) only of Pure Kerogen is given.

Seams	A	B	Bituminous limestone B/C	C	D	E
C	77.49	76.25	77.56	76.47	76.87	76.93
H	9.13	9.10	9.42	9.20	9.32	9.30
S	1.78	1.58	1.75	1.87	2.01	2.22
Cl	0.68	0.50	11.27	0.64	0.63	0.54
O + N	10.92	12.57		11.82	11.17	11.01
Percentage of ash in rich samples	7.77	5.09	6.56	6.27	6.07	3.19
Per cent of mineral ash in the dry shale	41.3	33.3	54.4	41.7	47.3	30.3
Per cent of CO_2	11.7	8.9	37.0	10.7	11.5	5.7
Per cent of total ash . . .	53.0	42.2	91.4	52.4	58.8	36.0

The ultimate composition of the kerogen varies within the following limits:

C, 76.5—76.7 per cent., H, 9.1—9.2 per cent; N, 0.2—0.4 per cent; S, 1.6—2.2 per cent; Cl, 0.5—0.7 per cent and oxygen (by difference) 11.2—12.2 per cent, C/H ratio =

= 8.4. The composition of the kerogen of kukersite nearly corresponds to an empirical formula $(C_8H_{11}O)n$.

The composition of the ash in seams E and B is given in Table III:

Table III.

Composition of the Ash.

	Seam E	Seam B
SiO_2	30.8 %	28.8 %
Fe_2O_3	5.5 %	7.2 %
Al_2O_3	10.7 %	6 8 %
CaO	40.1 %	42.9 %
SO_2	7.9 %	9.3 %
MgO	1.5 %	1.8 %
$K_2O + Na_2O$ . . .	3.7 %	3.6 %
	100.2 %	100.4 %

The ash content of the oil shale can be reduced by flotation and by treatment with dilute (5%) nitric acid to about 5 per cent. (Compare Table II).

K l e v e r and M a u c h [17], in a recently published pamphlet on kukersite, give the following figures for the ultimate composition of the kerogen: C, 72.55; H, 10.44; N, 0.55; S, 1.79; O, 14.64.

They assume that a high percentage of oxygen in kukersite is caused by oxidation or weathering of the shale. This is not the case. It has been found that the oil shale from underground mines has the same percentage of oxygen as the mineral from open quarries, except that from the top seams, which lie close against the glacial deposits and the soil. The high percentage of oxygen in kukersite is characteristic of the mineral, and is in full accordance with its chemical nature.

Methods of Analysis of Oil Shales.

As in the case of coal and other solid fuels, the methods of chemical investigation of oil shales may be classified as follows:

1. Action of reagents.
2. Action of solvents.
3. Action of heat.

The combination of 1. and 2., and 3. and 2. has been found the most effective in the case of oil shales.

The Action of Reagents.

Of the reagents used for coal research we may mention here concentrated sulphuric and nitric acids, sodium and potassium hydroxides, halogens, a mixture of potassium chlorate and dilute hydrochloric acid, oxygen, and ozone (Stopes and Wheeler[57]). These reagents are mainly oxidizers and they have been applied in a few cases to shale research. In the opinion of the author the value of reagents for fuel research was perhaps underestimated by Stopes and Wheeler[58], when they said, "Considered by themselves, the facts elicited from the study of the action of reagents on coal are not very informing (we except, of course, the facts relative to the formation of ulmin-compounds), *nor are the prospects for future work in this direction very promising*" *). Fortunately the authors have changed their views later on [57].

So far, a very limited number of reagents have been employed for this purpose. At any rate, certain facts obtained by the treatment of kukersite with reagents are important for determining the chemical nature of the shale.

The Action of Potassium Hydroxide. The action of solutions of different strength of potassium hydroxide on kukersite has been studied by Fokin[10], Kogerman[22], and Klever and Mauch[17]. The amount of humic acids, determined recently by Klever and Mauch is practically nil, *i. e.* the average percentage of three determinations was 0.06 per cent. This must be regarded as one of the most significant differences between oil shale, coal, and lignite. In the *peat-lignite — bituminous-coal — anthracite* series the contents of alkali-soluble substances diminish as the content of carbon or the C/H ratio increases, but in the case of oil shales the C/H ratio bears no relation to the solubility in potassium hydroxide solution.

The temperature of fusion has a great effect upon the reactivity of kukersite with potassium hydroxide. At 230—240° C the shale yields only about 4 per cent of water-soluble extract; at 260—280° C about 8 per cent, but at the latter temperature the shale substance undergoes a marked de-

*) The italics are ours.

composition. The water extract was treated with dilute hydrochloric acid, and a brown precipitate was formed, which had a very faint smell of phenols. The precipitate was washed with dilute acid and a small amount of water, and dried in a desiccator. The precipitate amounted to about 6 per cent of the weight of the dry shale. On drying, the precipitate formed a white crystalline mass, with some amorphous dark-brown substance in it. The general character of the mass did not remind one of the so-called ulmins or humic substances.

The filtrate, which still had a yellow colour, was extracted with ether. After the ether was evaporated, an orange semi-solid mass of acids was obtained with a very distinct smell of butyric acid. Unfortunately, the amount of acids was too small for the identification of individual compounds (Kogerman [20]).

Fusion with Sulphur. Samples of powdered shale were heated in sealed tubes at 180—200° for two hours; during the heating a considerable amount of pressure was developed, and one tube exploded. When the tubes were opened, a strong smell of H_2S was noticed.

The oil shale treated in this way was extracted with various solvents, *viz.* benzene, toluene, and pyridine. The extracts contained mainly sulphur. The most interesting was the pyridine extract, ruby-red in colour; on the evaporation of the pyridine a greenish white mass remained, which contained about 98 per cent of sulphur. A portion of the pyridine extract was concentrated by evaporation *in vacuo* and extracted with alcohol. The alcohol extract, also ruby-red, left on evaporation a sticky reddish substance, about 1 per cent of the weight of the fused mass. When the alcohol extract was poured into water, grey globules of soft rubber with a smell of freshly vulcanized rubber were precipitated.

Oxidation of Kukersite. Lindenbein [41] oxidised finely ground kukersite, the ash content of which was reduced to 4.45 per cent, with a mixture of $KClO_3$ and conc. nitric acid. After 12 hours warming on a water bath the shale powder formed a lemon-yellow "flaky" suspension in the liquid; after 48 hours of oxidation the shale turned to a yellow crust floating on the liquid. The yellow substance was filtered and washed; on dry-

ing at about 100° C it swelled and melted, and transformed into a mass which resembled the fused sulphur. The ultimate analysis of the substance gave the following figures (calculated on ash-free basis): C, 51.78%; H, 5.94%; N, 1.80%; O, 40.50%, C/H ratio = 8.6.

Nitration of Kukersite. Kogerman and Ohtla[32] investigated the action of nitric acid on kukersite. The shale powder was preliminarily treated with dilute (3 per cent) hydrochloric acid in order to decompose the carbonates, and in this way to avoid the effervescence of the reaction mixture on treatment with conc. nitric acid. It was found that the action of the acid is dependent upon its strength, the temperature, and the time (duration) of the reaction.

In Table IV particulars of some of the experiments are given: —

Table IV.

Nitration of Kukersite.

Nos. of experiments	Time	Temperature	Amount of shale taken	Weight of shale after nitration	Extraction with acetone		
					Amount of nitrated product taken	Weight of extract	Percentage of extract, calc. on the carbonate-free shale
	hours	°C	grams	grams	grams	grams	
1	2	16—20°	9.887	10.130	5.000	0.114	2.33
4	4	„	9.689	9.957	4.978	0.169	3.50
7	6	„	10.040	10.461	5.000	0.205	4.27
10	8	„	10.024	10.427	5.000	0.244	4.84
16	4	50°	10.000	10.099	5.000	0.434	8.77
19	1	100°	10.000	8.168	5.000	1.107	18.04
26*	1	100°	10.000	6.792	2.000	1.304	44.28

Comparing the results of the action of nitric acid on kukersite and alum shale, Prof. B. Holmberg[14] says: "It is of interest to note that the Estonian oil shale "Kukersite", which on destructive distillation yields a large amount of oil, does not give greater amounts of soda-soluble substances on oxidation

*) In the experiment No. 26 a mixture of concentrated nitric and sulphuric acids was used.

with nitric acid in the same way as that adopted for the alum shale, and that the substances obtained are quite different from the nitro-shale acids. It seems, therefore, that the organic material of "Kukersite" may be characterized as bituminous, humic substances hardly being present at all; this is all the more remarkable as the oil obtained from the Estonian shale is almost as rich in phenols as the low-temperature tar from coal, while the oil from the highly humic Swedish alum shale only contains a few per cent".

Bromination and Chlorination of Kukersite. In a preliminary experiment samples of dried oil shale from different seams were finely ground and sifted through a 1 cm^2/5000 mesh sieve. As a typical case, the shale from seam B is referred to here. The shale powder was suspended in pure CCl_4, and a known amount of bromine in chloroform was then added.

1 g. of shale powder was put into a 120 cc. glass bottle provided with a glass stopper, then 100 cc. of bromine solution was added. A blank experiment was carried out every time.

The suspensions of kukersite in chloroform were shaken at successive intervals of 24, 36, 48, and 60 hours in a shaking apparatus. Half an hour after each shaking, the solution was titrated: from the clear solution three samples were taken for analysis.

For control, the bromination tests were repeated with the shale ash, and the amount of bromine absorbed by the inorganic substance was only 0.37 per cent.

Table V shows the results of bromination.

Table V.

Bromination of Kukersite.

Hours	Weight of shale taken in grams	Weight of bromine in 100 cc. of Soln.	Weight of bromine absorbed	Average percentage weight of bromine absorbed, calc. on dry kukersite	Average percentage of Br_2 absorbed, calc. on pure kerogen
24	1.0112	1.1359	0.4933	48.65	—
36	1.0081	1.0868	0.5396	53.35	—
48	0.9995	1.0716	0.5510	54.96	106.3
60	1.0102	1.0613	0.5604	55.34	107.0

For chlorination, about 10 g. of pulverized kukersite was suspended in pure chloroform (250 cc.). The chlorine was bubbled through the suspension at a rate of 110—120 bubbles per minute. The duration of chlorination was 24—36 hours. The results of chlorination are given in Table VI:

Table VI.

Chlorination of Kukersite.

Hours	Duration of drying of chlorinated shale in hours	Weight of kukersite taken in grams	Weight of chlorinated kukersite in grams	Average percentage increase in weight of kukersite	
				Calculated on dry shale	Calc. on kerogen
24	84	10.0145	12.1228	21.28	
36	84	10.0061	12.1840	21.56	41.7
36	12	10.0061	12.4842	24.27	46.9

The chlorinated kukersite was dried in a partial vacuum (under 40 mm Hg) at 70° C. On drying, a portion of halogenated shale seemed to be volatile and only after about 80 hours of drying a constant weight was obtained. The sulphuric acid in the desiccator had turned brown.

The samples of halogenated kukersite were extracted with absolute alcohol. Halogenated shale powder shows a marked solubility in absolute alcohol, about 26 per cent, whereas the untreated shale powder yields only about 0.31 per cent of extract with the same solvent under the same conditions. The shale powder was extracted for 36 hours in a Soxhlet apparatus; 10 g. of shale was taken, 350 g. of ethyl alcohol was used. The colour of the alcohol siphoned was yellow in the beginning, but it turned dark brown after 36 hours of extraction.

The extracted shale was dried under 40 mm pressure at 70° C until constant weight was obtained. The colour of the chlorinated shale was yellow. The yield of extract reached 26.8 per cent of the weight of the shale.

A careful examination of the extract showed that it contained also calcium salts (calcium chloride) in considerable quantity.

The amount of chlorine was determined in chlorinated shale and in the residue after extraction. Schiff's method was

used for the determination of chlorine. The average percentage of chlorine in chlorinated shale was 17.69, the average percentage of chlorine in the residue 10.65. This analysis shows that a greater portion of the original chlorine remained in the residue.

A very important fact was discovered on chlorination of some enriched or washed samples of shale, containing only about 4.5 per cent of ash: the action of halogen was not as marked, and the yield of extract was much less than in the case of untreated shale powder. Probably the mineral matter acts catalytically during chlorination. Further, it was found that

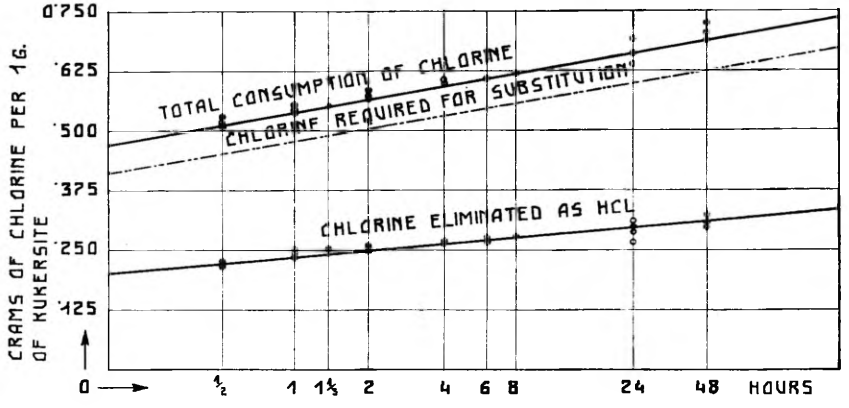


Fig. 3. Chart showing the rate of chlorination of kukersite.

both reactions, *i. e.* addition and substitution, proceed simultaneously.

1 g. of shale powder, containing 4.5 per cent of mineral matter, requires for addition 0.051 g. of Cl_2 and for substitution 0.250 g. of Cl_2 during 1 hour. The amount of chlorine added is nearly constant in all samples, which shows that the degree of unsaturation is nearly the same in all samples of kerogen.

Fig. 3 shows the amounts of chlorine required for addition and for substitution. To avoid losses of alcohol extract on washing it with water for removal of inorganic salts, ether was used in recent experiments of extraction of chlorinated kerogen. A special apparatus was used for extraction of chlorinated kerogen with ether (Kogerman and Raudsepp [34]).

The ether extract of chlorinated kerogen is a brown viscous liquid, with an "aromatic" odour; it is soluble in chloroform, benzene, acetone, and partly soluble in alcohol and petroleum ether.

On distillation, even under a reduced pressure, the ether extract begins to decompose at about 130° C, and, therefore, the extraction with certain solvents, *viz.* alcohol and petroleum ether, was applied to separate the ether extract into fractions.

By this method five fractions were obtained, and their ultimate composition is given in Table VII.

Table VII.

Fractionation of Ether Extract of Chlorinated Kerogen.

Nos. of Fract	Solubility	Consistency and odour	Composition %			Percent from total extract	Remarks
			C	H	Cl		
1.	Insoluble in alcohol and ligroin, b. p 35—50°	Brown colophony-like substance; odourless	49.46	5.40	36.59	21	Begins to soften at about 50° C
2.	Soluble in alcohol, insoluble in ligroin		50.48	5.54	32.55	33	Begins to soften at about 40°
3.	Soluble in alcohol, partly soluble in ligroin	Odourless brown, highly-viscous (soft) substance	49.23	5.48	34.76	6	
4.	Soluble in alcohol and ligroin	Brown viscous liquid	48.42	5.90	36.49	30	Does not distil below 100° at 20 mm Hg
5.		Yellow mobile liquid, aromatic odour	65.30	10.78	14.15	5	Passes over at 100°/20 mm Hg

The amounts of fractions were so small that they did not allow of any closer examination of their chemical nature, but taking into consideration the ultimate composition of the fractions, one may assume that the compounds forming the ether extract belong to derivatives of hydroaromatic hydrocarbons.

The Action of Solvents.

The action of solvents is fully discussed in the author's paper, "The Chemical Composition of the Estonian M.-Ordovician Oil-bearing Mineral Kukersite" [22].

An improved form of Soxhlet apparatus was employed for the extraction of shale. About 10 g. of powdered shale was taken for each extraction, and about 250 cc. of solvent was used. The experiments were carried out in an atmosphere of nitrogen. The main results of the extraction experiments are given in Table VIII.

Table VIII.

The Extraction of Kukersite with Solvents.

Solvent	Hours of extraction	Per cent of extract	Colour of extract	Remarks
Acetone	120	0.27	Light yellow	
Chloroform	120	0.22	„ „	
Benzene	124	0.43	Orange, green fluorescence	
Carbon disulphide	100	0.49	Yellow	
Petroleum Ether	119	0.49	Nearly colourless	
Toluene	124	0.52		
Xylene	120	0.77	Yellow	
Pyridine	48	0.70	Dark red	Probably decomposition occurred. Residue black.
Tetrachlorethane	70	2.20	Dark brown	Decomposes shale. Elimination of HCl was observed.

All results calculated on pure organic substance.

Even the extraction of kukersite with benzene under pressure at about 250° C yielded less than 1 per cent of a very viscous oily substance (Schneider [54]); Klever and Mauch [17] extracted powdered kukersite for 12 hours at 240—250°, and obtained 1.86 per cent of a dark-brown, neutral asphalt-like substance, which they regard as a decomposition product of the kerogen.

The Action of Heat.

Heat is the most effective agent for the depolymerisation of kerogen of kukersite. As in the case of coal, the distillation

of oil shales has supplied more facts for the elucidation of the chemical nature of the kerogen than any other method described so far.

It is well known that the character of liquid distillates is not only dependent on the nature of a fuel, but also on the temperature and manner of distillation.

The depolymerising action of heat was thoroughly studied on samples of kukersite from B seam.

The following series of experiments were carried out:

(i) The yield of volatile substances over a wide range of temperature.

(ii) The increase of solubility of kerogen in CS_2 on heating up to about 180° C.

(iii) The yield and properties of the vacuum oil.

(iv) The yield of oil and gas at various temperatures, *e. g.* 400—900° C.

Some writers assume that the distillation of kukersite begins at a temperature as low as 100° C, and they propose to dry kukersite at 90° "to avoid loss by distillation" (J a n n s e n [16]).

To determine whether on drying only water is given off or occluded gases as well, samples of pulverized kukersite, weighing about 1 g., were dried in air and in a current of inert gas (CO_2).

The samples were dried at 18°, at 40°, at 60°, etc., until constant weight was obtained. The results of drying in air are given in Table IX.

Table IX.

Loss of Weight of Kukersite on Drying in Air.

Intervals of temperature °C	Percentage loss of weight (calc. on original weight)	Remarks
18—40	2.29	
18—60	2.63	
18—80	2.80	No change in colour of the shale powder
18—110	2.83	
18—147	2.83	
18—178	3.33	
18—181	4.88	Darkening in colour
18—210	10.41	
18—223	23.14	

The last figure is somewhat high and is probably caused by slow oxidation and elimination of oxides of carbon and water.

From the results of these drying experiments an important conclusion can be drawn, *viz.* that on drying within the temperature 80—147° the weight of the shale remains practically constant and no decomposition is observed.

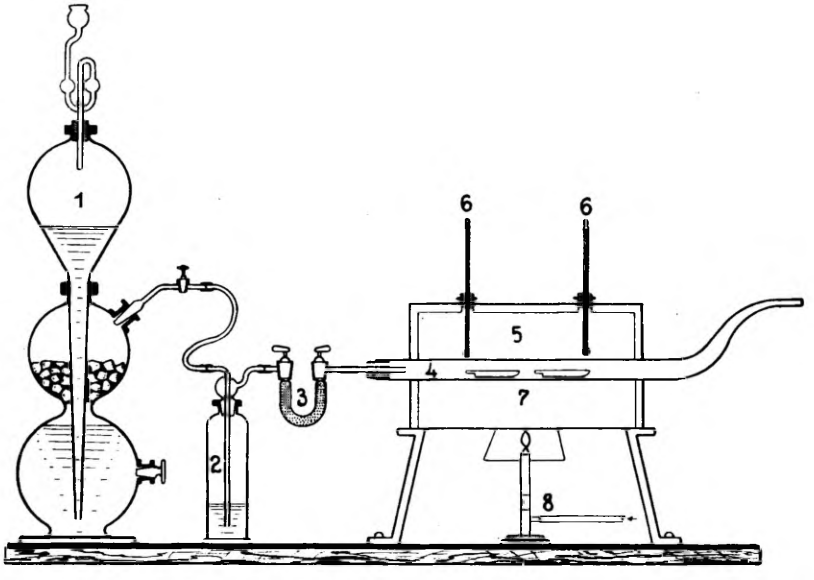


Fig. 4. The drying of kukersite in CO_2. 1 — Kipp's apparatus for generating CO_2; 2 — wash bottle; 3 — $CaCl_2$-tube; 4 — glass tube with two boats (7); 5 — drying chamber; 6 — thermometers; 8 — burner.

In another series of experiments the pulverized shale was heated in a stream of carbon dioxide. The scheme of arrangement of apparatus is given in Fig. 4.

First of all, the shale was kept in CO_2 and weighed. Then the boats with the shale were heated to 61°, 81°, etc., until constant weight was obtained. The rate of flow of CO_2 was about 90 bubbles per minute. The results are given in Table X.

The percentage loss of weight plotted against temperature appears as a smooth, nearly straight line between the temperatures 80—150° C (Fig. 5). The loss of weight within the limits 80—150° C in this case is 0.09 per cent per 10° C, or about 0.1 mg. per 1°, which is greater than the experimental

error in our case. The percentage loss of weight on drying in air for the same interval of temperature is much less, *i. e.* only 0,0043 per cent per 10° C.

Table X.

The Results of Drying Powdered Shale in CO_2.

Temp. intervals, beginning f. 16° C	Percentage loss of weight calc. on dry substance			Remarks
	I Expt.	II Expt.	Average	
At 16°	1.32	1.41	1.36	No
Up to 61°	1.89	2.02	1.96	change
„ „ 81°	2.05	2.21	2.13	in
„ „ 101°	2.22	2.39	2.30	colour
„ „ 151°	2.69	2.84	2.76	
„ „ 171°	3.28	3.42	3.35	Colour darkens

These results clearly indicate that on drying in air the powdered shale loses not only water (up to 80°) but also a

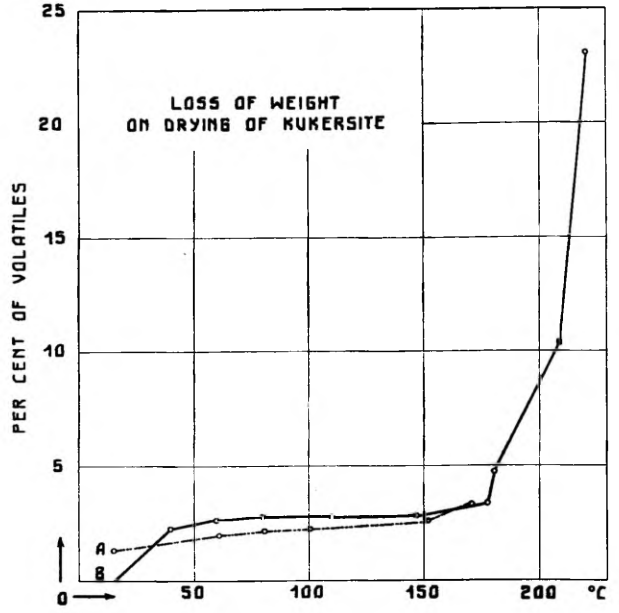


Fig. 5. A — drying in CO_2; B — drying in air.

volatile substance, probably the oxides of carbon, which were found by the present writer in the gases eliminated at the temperature of initial decomposition.

At 150° the loss of weight in both cases is the same; up to this temperature no change in the organic matter of the shale is observed.

The Increase of Solubility of Kerogen in CS_2 after Heating to Temperatures below the Initial Decomposition Point. C. Engler and F. Fischer [8] showed experimentally that coal and some oil shales show marked solubility after being heated for several hours at temperatures far below their decomposition point. To investigate the action of heating on the solubility of kerogen of kukersite the following experiments were carried out.

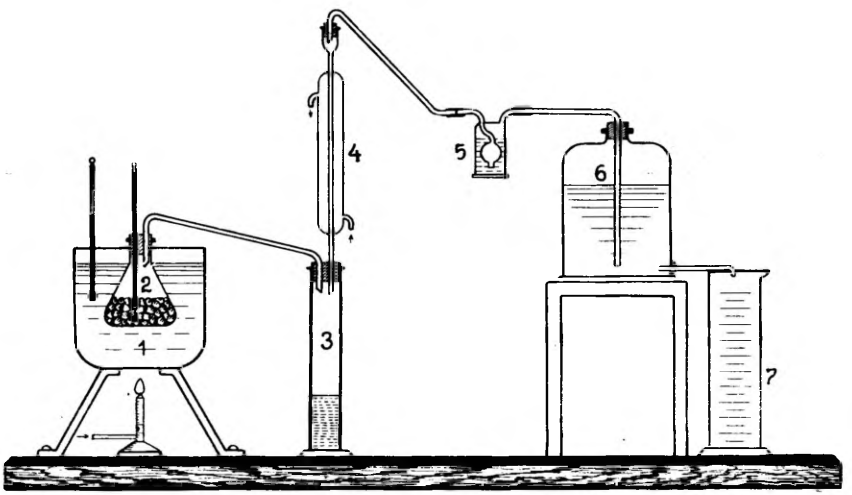


Fig. 6. Apparatus for studying the initial decomposition of kukersite: 1 — oil bath; 2 — Erlenmeyer flask with shale powder; 3 — graduated cylinder; 4 — condenser; 5 — bubbler; 6 — gas-holder; 7 — measuring cylinder.

1. About 20 g. of pulverized kukersite were heated in an Erlenmeyer flask on an oil bath for 6 hours at 220° C (see Fig. 6). The shale lost 2.6 per cent of its weight, and its solubility in CS_2 increased to 2.11 per cent (in a Soxhlet apparatus).

2. Three samples of pulverized shale were heated in Pfungst's oil autoclave at 200—208° C. The duration of heating was 2, 4, and 6 hours respectively. After the heating no appreciable change in the appearance of the shale powder

was observed, but the powder had the characteristic smell of charred kukersite (K o g e r m a n and A r v i s t o [30]).

The heated shale powder was then extracted in a Soxhlet apparatus with carbon bisulphide. The solvent was removed by distillation on a water bath: the extract remained as a red "mobile" oil, which solidified on standing in contact with air. The particulars of the extraction experiments are given in Table XI:

T a b l e XI.

The Loss of Weight on Heating and Extraction of Kukersite.

No of experiment	Rate of increase of temperature per min. °C	Duration of heating of the shale at 200—208 °C: h	Loss of weight on heating; per cent	Duration of extraction of the heated shale with CS_2 in mins	Weight of extract; per cent calcul. on the heated shale	Total loss of weight on heating & extraction; per cent
1a	0.6	2	2.5	275	2.65	5.15
2a	0.8	8	2.6	435	5.30	7.90

The results show that extending the duration of heating increases the amount of extract.

All the methods described so far reveal the structure of a very small portion of kerogen. There is no so-called "free bitumen" in the kukersite, and the oils obtained on distillation of the shale are decomposition (or to a certain extent depolymerisation) products of the kerogen.

Pyrolysis of Kerogen.

Initial Decomposition.

The opinions of different writers as to the definition of the "temperature of initial decomposition" of fuels are very divergent. Some authors consider the appearance of a "characteristic odour" as a sign of initial thermal decomposition, others pay attention to the "free decomposition", as determined by the rapid evolution of gases, still others assume as the most important sign the beginning of the distillation of liquids [57].

Recently Holroyd and Wheeler[67] introduced a new expression *viz.* the "temperature of active decomposition", which seems to be identical with the initial decomposition temperature of Porter and Taylor (rapid evolution of gases).

Valghis and Strunnikov[60] in their paper on "The Drying of Oil-Shales" assume that the decomposition (similar to distillation) of kukersite begins between 170° and 180° C. The experiments of the present author show that, although a darkening of colour of kukersite is observed, when heated at temperatures between 170° and 180° C, there are no other signs of decomposition. A rapid evolution of gases from kukersite is observed at about 320° C. At the same temperature oil vapours appear in considerable quantities.

Distillation at Various Temperatures.

The yield of gases and oils from kukersite at various temperatures was studied by the author many years ago, and the results of some of these experiments are summarized in Table XII[22].

Table XII.

Distillation of Oil Shale at Various Temperatures.

Temp. °C	Percentage yield	Yield of Oil. Galls per ton	Yield of Gas cu. ft. per ton at 0° & 760 mm	Yield of Ammonia %	Calorific value of Oil in B. Th. U.
410	27.1	63.3	1900	—	—
500	29.7	72.9	2250	—	17028
600	30.8	74.8	3000	0,02	17528
700	27.5	65.0	4500	0,04	—
900	21.7	49.7	7200	0,11	—

The ultimate composition of the oil obtained on distillation at 500° was as follows: C, 82.14%; H, 10.43%; the coke contained: C, 27.87% and H, 1.14%.

The results of experiments on the pyrolysis of kerogen of kukersite, to be published *in extenso* elsewhere, are summarized in Table XIII.

Table XIII.

Pyrolysis of Kukersite.

Temp. °C	Zones	Characteristics	Thermal effect of reactions
170—180		Beginning of partial decomposition or depolymerisation of kerogen	
320—340	Zone of depolymerisation of kerogen	Beginning of rapid evolution of gases and oil vapours	
380—390		End of depolymerisation and beginning of cracking of depolymerisation products	
415—420	Zone of distillation or cracking of depolymerisation products	. . . . .	endothermic
420—440		. . . . .	exothermic
440—470		. . . . .	endothermic
above 470		. . . . .	exothermic
470—550		Maximum yield of liquid products (oils)	[See Fig. 7]
above 750	Cracking of distillation products	Rapid increase in the yield of gas; "aromatisation" of liquid distillates*	

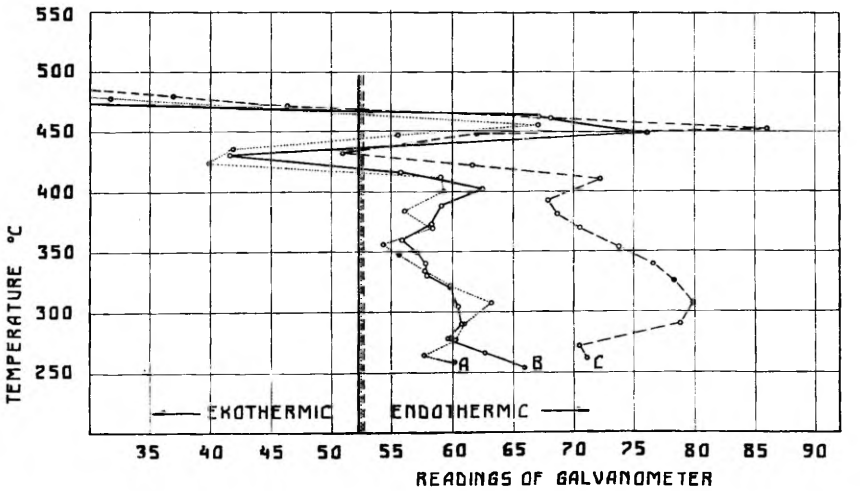


Fig. 7. Chart showing the thermal effect of reactions of decomposition.

*) Compare the data on cracking of shale oils by Weiderpass [60] and others.

The yield of gas per 1 g. of dry kukersite is given in Table XIV and Fig. 8.

Table XIV.

The Yield of Gas.

Temp. °C	cc. of gas, at 0° and 760 mm Hg.
250—260	1.53
320—340	41.20
400—410	51.35
500	60.30
600	82.60
700	120.00
900	265.00

The composition of gases obtained on distillation of kukersite in glass or silica tubes at various temperatures is given in

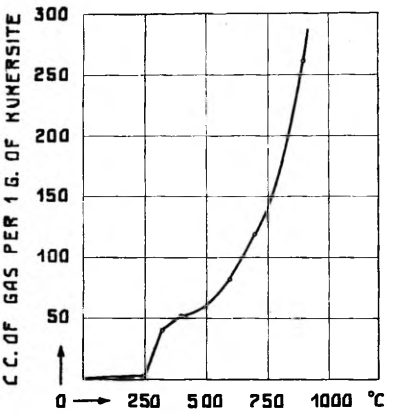


Fig. 8. The yield of gas.

Table XV. For comparison the analyses of gases, obtained on carbonisation of kukersite on a large scale at low and high temperatures, are included in the Table.

Table XV.

The Composition of Gases obtained on Distillation of Kukersite.

Temp. °C	Percentage Composition of Gas							
	H_2S	CO_2	C_nH_{2n}	CO	C_nH_{2n+2}	H_2	N_2	O_2
500	—	22.5	28.2	9.3	34.0	4.2	1.8	Air excluded
600	2.1	19.6	24.8	11.2	26.6	10.8	7.8	
700	2.2	15.6	22.0	12.5	19.6	22.9	5.2	
900	—	7.4	20.2	16.4	12.9	33.0	9.1	
1. Low-temperature gas, from "Eesti Patendi A/S" retort	29.8		15.0	4.5	33.8	14.7	2.0	0.2
2. High-temperature gas, from gas-retorts *)	—	13.3	7.2	19.3	22.64	26.18	11.38	—

The Effect of Retorting upon the Yield and Character of Liquid and Gaseous Products.

The character of liquid distillates and gases obtainable on the retorting of oil shales is not only dependent upon the chemical nature of the kerogen of the shale but also on the temperature and manner of distillation.

The problems of retorting of kukersite have been dealt with by the author elsewhere [24; 25], and therefore only the yields and properties of oils, obtained by different large-scale processes are given in Tables XVI and XVII.

Description of retorts. *A.* — Vertical modified Scottish retort, externally heated, superheated steam used also, internal temp. about 450° C; *B.* — "Fusion" retort; *C.* — J. Pintsch's producers; *D.* — Estonian patent retort (Messrs. Wuht & others), with transport screw, externally heated, but superheated steam used as well, temp. about 600° C; *E.* — horizontal gas-retorts at Tartu gas plant. *F.* — Davidson rotary retort. (See: Plate II and Figs. 9 and 10.)

*) See: papers by H. v. Winkler [68] and Dr. A. Puksov [50].

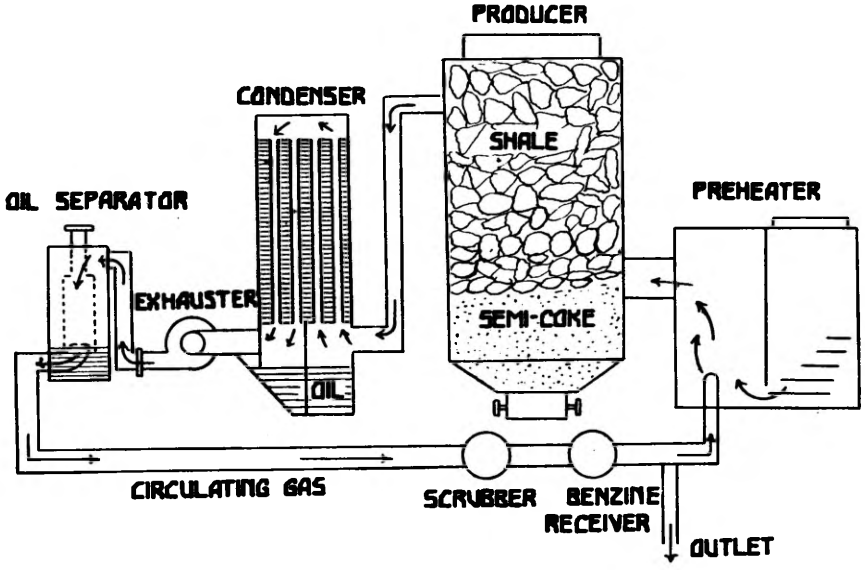


Fig. 9. Scheme of the Kohtla experimental oil shale distillation plant.

Table XVI.

Properties of Some Crude Oils Obtained from Kukersite by Different Methods of Retorting.

Oils	A	B	C	D	E	F	Remarks
Sp. gravity at 15° C	0.946	0.950	1.007	0.997	1.170	0.939	
Viscosity at 50° (Engler apparatus)	1.6	1.6	4.7	3.7	—	—	
Flash point (Martens-Pensky) . . .	30°	21°	92°	37°	—	14°	
Unsaturation (1 vol. oil + 1 vol. benzine + 4 vols. of 80 % H_2SO_4) . . .	41	27	45	55	—	—	Vol. percentage given; average % of two determinations
Phenols (vol. %) .	36	34	39	50	—	30.6	1 vol. of oil + 1 vol. of benzine + 2 vols. 10 % NaOH
Moisture	0.9	1.1	0.5	14.3	—	0 .8	Water contents given in cc. per 100 g. of oil
Dust or free carbon; % by weight . . .	0.02	0.54	0.54	0.82	—	0.01	
Yield of oil % (approximate figures).	15	18—20	18—20	19—22	5	24	The yield of oil is dependent upon the moisture content, ash content etc.

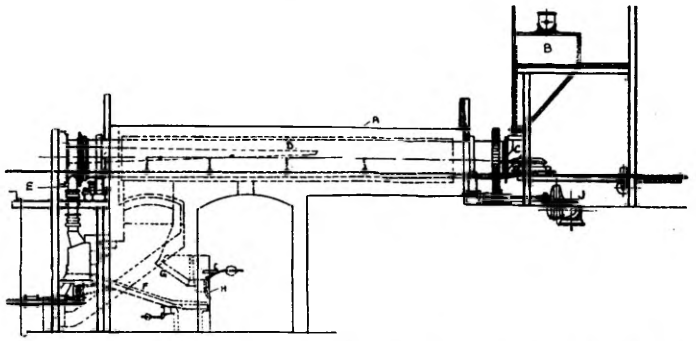


Fig. 10. Davidson rotary retort: a type of externally heated retorts.

All samples of shale oil were distilled in an Engler apparatus under the same conditions. The results of distillation tests are given in table XVII and Fig. 11.

Table XVII.

Engler Distillation of the Shale Oils.

Amount of Oil given in cc., except in Column F.

Temp. °C	A	B	C	D	E	F**)	Remarks
Initial B. P.	83°	70°	98°	79°	107°	—	
Up to 150°	11.9	7.7	0.3	3.4	0.5	8.07	
150—175°	6.3	5.9	0.1	2.9	0.4	4.96	
175—200°	9.8	4.6	0.7	3.6	0.5	3.82	
200—225°	8.1	6.0	3.8	4.9	2.4*)	4.05	The fractions marked with an asterisk (*) crystallised partly on standing (gas tar)
225—250°	8.1	5.9	6.1	4.0	5.9*)	5.24	
250—275°	7.0	6.9	5.2	6.9	6.3*)	6.27	
275—300°	7.9	6.4	8.6	5.5	7.4	7.65	
Over 300°	40.9	54.0	72.8	66.2	81.5	53.4	Amount of residue left (B. P. over 300°) is given in grams.
Amount of oil taken in grams	94.4	92.2	96.4	95.2	107.5	94.0	

It follows from Tables XVI and XVII that the oils produced by different processes vary greatly in composition; the oils obtained in an externally heated retort at low temperature usually contain a larger portion of light (*i. e.* benzine) oils. Of course, in one and the same retort, the quality of oil is dependent upon the manner of operation. Thus, for instance, in the retort,

**) All amounts in the column F are given in grams.

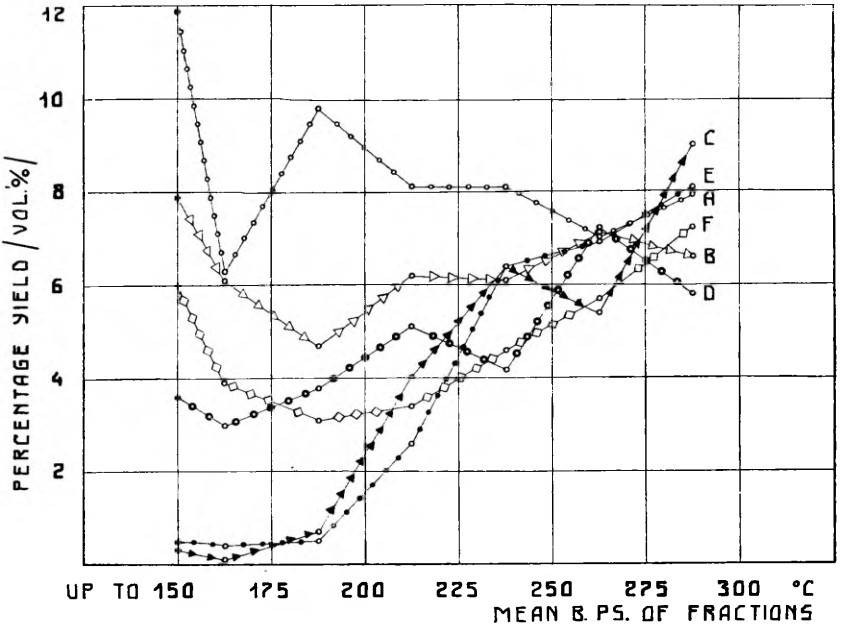


Fig. 11. Distillation curves of various crude shale oils.

described as *A* above, a still lighter crude oil has been obtained, *viz.* sp. gravity 0.907 at 15°. The particulars of the fractionation of this crude oil are given in Table XVIII.

Table XVIII.

Particulars of a Crude Shale Oil: Sp. gravity at 15°—0.907. Fractionation of the Crude Oil.

Fract.	Temp. °C	Percentage yield	Sp. gr. at 15°
1.	Up to 150	9.9	0.790
2.	150—200	27.5	.831
3.	200—250	17.5	.879
4.	250—280	7.5	.925

The heavy oil boiling above 280°, sp. gr. about 0.98, was then distilled with superheated steam (at 240°), which carried over 14% of oil.

The particulars of fractionation of crude shale oils, obtained on distillation of kukersite in different types of large-

scale retorts, show only the distribution of different constituents of shale oils in various fractions, but do not show the difference in the chemical composition of corresponding fractions. On broad lines, it may be assumed that the chemical compounds forming a certain fraction of an oil are identical in all cases, provided, of course, that the temperature of retorting was the same, but the quantities of compounds in various crude kukersite oils vary greatly, being dependent on the manner of operation and the efficiency of the condensing plant.

The Distribution of Sulphur in the Products of Distillation.

The distribution of sulphur in the products of destructive distillation of kukersite was studied by Wittlich and his coworkers [70], and in the laboratory experiments at 520° it has been found as follows:

	% S
Gases	42.4
Oil	9.3
Pitch	3.9
Coke	44.4
Total	100.0

(Total sulphur in the shale = 100).

Klever and Mauch [17] later carefully analysed the products of low-temperature carbonisation of kukersite with regard to sulphur contents, and their figures are given below:

	% S
In low-temperature oil	28.4
„ semi-coke, organic	32.3
„ „ „ as Pyrite	3.15
„ „ „ as Sulphide . . .	13.4
As free H_2S (gas)	23.5

(Total sulphur in the shale = 100%.)

The Vacuum Distillation of Kukersite.

The chief method of investigation of the constitution of oil shales and coals is the indirect method of thermal decomposition. The effect of the temperature of distillation on the yield of decomposition products is discussed by the writer in the previous chapter; the effect of pressure, especially decomposition under considerably reduced pressure, will be briefly dealt with in this chapter.

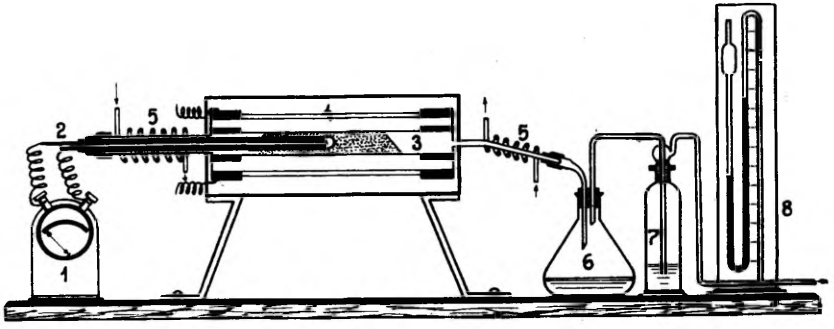


Fig. 12. Laboratory retort for vacuum distillation of oil shale: 1 — milliveltmeter with Pt/Pt-Rh couple (2); 3 — iron retort; 4 — silicide-sticks; 5 — coil-condensers; 6 — receiver; 7 — wash-bottle; 8 — manometer.

According to the researches of McKee and Lyder[46] the transformation of kerogen of shales to oil proceeds in two phases: firstly, a semi-solid intermediate product is formed; secondly, on further heating this intermediate product decomposes into gas, shale oil, and carbonaceous residue.

It is evident that on distilling the shale under considerably reduced pressure a very viscous oil will be obtained, the composition of which resembles more the intermediate product than the ordinary shale oil.

The scheme of the apparatus for vacuum distillation used in the preliminary experiments is shown in Fig. 12. The shale was placed in a horizontal iron tube. The temperature was observed by means of a Pt/Pt, Rh thermocouple. Table XIX gives the rate of distillation and yield of oil.

Table XIX.

The Vacuum Distillation of Kukersite.

Rate of Distillation						Yield of Oil %		Yield of Coke %		Remarks
I Experiment			II Experiment							
Time	Temp. °C	Pressure mm Hg	Time	Temp. °C	Pressure mm Hg	I Exp.	II Exp.	I Exp.	II Exp.	
0h.00′	—	5	0h.00′	—	9.8					
1h.1′	220	„	0h.32′	290	11.3					
1h.28′	250	„	0h.42′	370	„					
2h.8′	300	„	0h.47′	380	14.0	19.5	18.17	42.1	43.13	
2h.23′	340	22	1h.27′	440	12.6					
2h.32′	390	„	2h.43′	490	„					
3h.50′	700	28	3h.8′	640	22.0					
4h.00′	700	—	3h.38′	640	—					

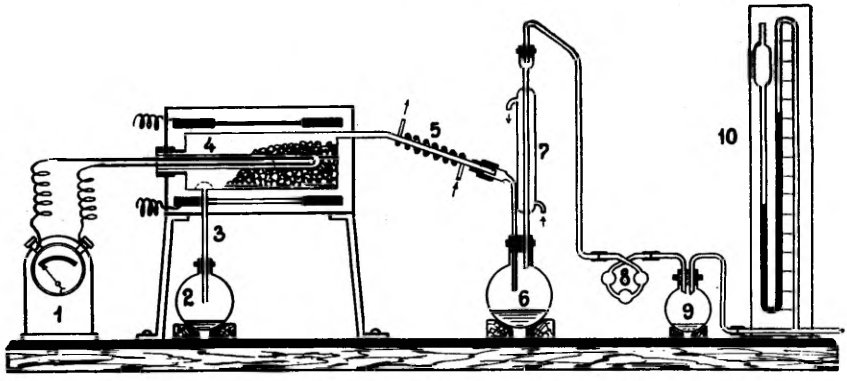


Fig. 13. Another type of retort for distillation under reduced pressure: 1 — pyrometer; 2 — receiver for heavy oil or soft pitch; 3 — outlet for heavy oil; 4 — retort; 5 — lead coil-condenser; 6 and 9 — receivers; 7 — condenser; 8 — bubbler; 10 — manometer.

On inspection, after the distillation, some heavy oil was found in the distillation tube. Therefore, in the second series of experiments another type of iron retort was used for distillation. This retort is shown in Fig. 13. Tube 3 allows the heavy oil to flow out.

In this apparatus only a reduced pressure of about 50 mm was maintained. 355 g. of the shale was taken for distillation. In the course of four hours the temperature was raised to 460°. The total yield of oil in this case was 28.8%. This figure is

close to the figure given by Lindenbein for the yield of vacuum oil from kukersite.

The vacuum distillate is a brown, highly viscous liquid, with a pleasant "aromatic" odour. Lindenbein[41] found the following constituents in the vacuum oil:

Acids	3.35%
Phenols	21.42%
Bases	0.23%
Alcohols	0.25%
Unsaturated hydrocarbons. .	74.74%

It is very difficult to determine the contents of unsaturated compounds of the vacuum oil: the oil is miscible with liquid SO_2 and conc. H_2SO_4.

In the writer's experiments the content of phenols was found to be about 19%.

The composition of the vacuum shale oil is very close to that found by Klever and Mauch for the pressure extract of kukersite.

Table XX shows the composition of vacuum oil, pressure extract with benzene, kerogen of kukersite, and some natural asphalts.

Table XX.

Comparative Data of Ultimate Composition of Kerogen, Pressure Extract, Vacuum and Low-Temperature Oils of Kukersite and some Natural Asphalts.

Substance	Ultimate Composition					Softening point (K. S.)	Nos. of papers in Bibliography
	C	H	N	S	O		
Kerogen	76.6	9.1	0.3	1.9	11.8	320—330°	42 and M*)
Pressure Extract .	81.43	8.69	0.32	1.42	8.14	75°	17
Vacuum Oil . . .	83.31	9.76		6.93		—	41
Low-Temp. Oil . .	81.26	10.15	0.25	1.08	7.26	—	M
Mexican Asphalt .	82.34	9.14	—	6.25		—	17
Asphalt from Abruzzi	81.83	8.28	1.06	8.23		—	17
Blown Asphalt from Kukersite Oil . .	83.96	8.73		7.31		22°	M

*) M — This Monograph.

The results of distillation of kukersite under atmospheric and reduced pressures may be summarized as follows: —

(i) The vacuum distillation of kukersite does not increase the yield of oil.

(ii) The vacuum oil is more viscous and probably more unsaturated in character than the ordinary shale oil.

(iii) The phenol content of the vacuum oil seems to be lower than that of ordinary shale oil.

Comparing the ultimate compositions of pressure extracts and vacuum oils of an "asphalt-base" oil shale (kukersite) with some natural asphalts, a close similarity is observed, and one might assume that *the asphalt-base oil shales may be the source of some asphalts in nature* *).

*) A few weeks ago Mr. K. Luts, chief chemist of the Kohtla Oil Shale Works, informed the author of a discovery of thin layers of black asphalt in the kukersite seams at the Kukruse Mine.

PART II.

THE CHEMICAL COMPOSITION OF THE ESTONIAN SHALE OILS.

When the commercial distillation of kukersite was started at Kohtla, the author took the opportunity to investigate the chemical nature of the shale oil. This research shed much light on the composition of shale oil, and made possible the comparisons between the composition of this oil and that of low-temperature coal tars and well-petroleum.

The method of operation of the Kohtla retorting plant is described by the author elsewhere [21]. The Kohtla shale oil may be regarded as a primary product of distillation or a low-temperature oil: it differs greatly from the high-temperature tar obtained by distilling the shale in gas retorts.

General Characteristics of the Oil. The crude oil used for the present research was obtained from the Kohtla experimental distillation plant, where an internally heated retort, designed by Messrs. J. Pintsch and Co., of Berlin, was in operation. In 1926 the plant was rebuilt and equipped for refining of shale oil.

For checking some of the earlier results, the oil obtained from the new Kohtla plant (operating on the same principle) was used. The analysis did not show any marked difference between those two crude shale oils.

The specific gravity of this shale oil varies within the limits of 0.990 to 1.009 at 15° C. The average ultimate composition of the oil used for the experiments was as follows: — C, 81.26 per cent; H, 10.15 per cent; O, 7.26 per cent (by difference); S, 1.08 per cent, and N, 0.25 per cent.

The dry oil contained: neutral oils (chiefly hydrocarbons), 72.1 per cent; phenols, 22.4 per cent; carboxylic acids, about

4.0 per cent; and bases 0.2 per cent (loss 1.3 per cent). These figures give only a rough idea of the composition of the shale oil, and are dependent upon the methods used for analysis.

The ultimate composition of the pressure extract, as analysed by Klever and Mauch, is given in Table XX. The pressure extract contains chiefly neutral substances; it does not contain free acids. Compared with the natural asphalts, the oxygen content of the pressure extract is somewhat higher.

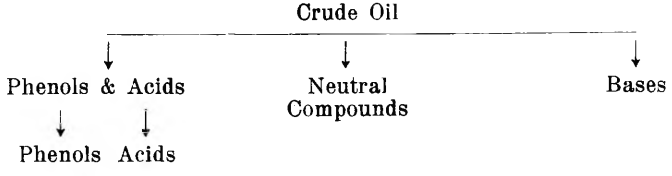
The crude shale oil is miscible with various crude well-oils, especially with asphalt-base oils.

Methods of Analysis.

Of all known methods of analysis of crude well-oils and low-temperature coal tars but few are applicable to the kukersite oil. The partial precipitation methods used successfully for the analysis of some crude well-oils and coal tars (E d w a r d s [7]) fail to give any results in the case of kukersite oil.

The kukersite oil is soluble in 95 per cent alcohol, in benzene, in chloroform, in petroleum ether, and in other organic solvents; it is also soluble in liquid sulphur dioxide. Only the acid bodies and bases can be removed by extraction; the greater portion, containing a complex mixture of neutral compounds, can be separated only by fractional distillation. The crude kukersite oil was therefore separated into three portions: *viz.* acid compounds soluble in alkali, bases, and neutral compounds. Each portion was analysed separately.

The scheme for analysing kukersite oil was as follows: —



In another series of experiments the crude kukersite oil was first fractionated into four fractions, and the fractions were then analysed by both methods, *viz.* extraction and fractional distillation.

The Phenols of Kukersite Oil.

The crude shale oil was extracted with a 5 per cent solution of NaOH; the resulting mixture of sodium salts and sodium phenolates was treated with carbon dioxide, which decomposed the phenolates, and from the acidified solution the phenols were extracted with ether [26].

Comparison of some Quantitative (Technical) Methods for Determination of Phenols in Kukersite Oil.

The methods for the determination of phenols can be divided into two goups: (a) volumetric, and (b) gravimetric.

Volumetric Methods. — For volumetric determination many reagents have been proposed: sodium hydroxide solution, formic acid, glycerol, alcohol (diluted), superheated steam, etc. Of these reagents, sodium hydroxide solution and formic acid have only a relatively quantitative value, the others do not give any reliable results; for instance, glycerol extracted only about 30% of the total amount of phenols in kukersite oil.

The phenols and acids are extracted by sodium hydroxide solution of 5—20% strength. When applying this method to the determination of phenols in oils and tars, two facts ought to be taken into consideration: (1) the partial solubility of phenoxides in neutral oil and, conversely, the solubility of neutral oils in phenoxide solution; (2) and (as the kukersite oil contains unsaturated hydrocarbons, ketonic and aldehydic compounds), the formation of condensation and polymerisation products.

On shaking the oil-phenoxide solution in contact with air, the yellow colour gradually darkens, until a dark brown solution is formed, although the amount of phenoxides does not increase. The methods based upon the solubility have not a strictly quantitative value . Usually the percentage of phenols obtained by volumetric methods is slightly higher than the actual figures.

Experimental.

To make the separation of layers easier, the crude kukersite oil was mixed with benzene (1 : 1). Portions of 60 cc. each of this mixture were poured into 250 cc. graduated cylinders;

solutions of sodium hydroxide (9—15% strength) saturated with benzene were added from burettes. The cylinders were thoroughly shaken and kept for 2 hrs. at 60°. After 24 hrs. the quantities of oil were recorded (at 18°). In reflected sunlight the layer of oil has a greenish colour and the layer of phenoxides is nearly black. The results of determinations are given in Table XXI.

Table XXI.

Ratio: $\frac{\text{Oil+Benzene}}{\text{NaOH soln.}}$	Percentages of oil in alkali soln. (phenoxides and salts)			
	9 % NaOH.	11 % NaOH.	13 % NaON.	15 % NaON.
60 : 10	—	—	—	23.5 *)
60 : 20	—	—	26.6 *)	24.7
60 : 30	32.3 *)	33.2 *)	34.2	39.5
60 : 40	33.4	35.4	38.4	44.8
60 : 50	34.4	35.6	41.9	46.0
60 : 60	34.8	35.5	42.8	—
60 : 70	35.0	—	—	—
60 : 80	34.0	—	—	—

Using sodium hydroxide solutions of 9% and 11% concentration, a maximum is reached at the ratio 60 : 60 and 60 : 70 (about 1 : 1).

The phenoxide-alkali solutions were then distilled with steam, and the volatile oils collected in measuring cylinders. The results were as follows: —

Solution used NaOH%.	*Oil %.*
9	4.0
11	4.2
13	7.0
15	7.8

The amount of oil dissolved in sodium hydroxide solution increases with the quantity and the concentration of the solvent.

More concentrated solutions, *i. e.*, above 15%, were not used, because the formation of condensation products was too great and the layers were difficult to separate.

*) Average figures of two determinations.

When the fraction of *b. p.* 230—270°/760 mm. was treated in the same way the variations were not so wide, ranging from 17.6 to 19.4%. Increase of the quantity of the solvent above the amount given in Table XXI does not increase the volume of the acid substances obtained.

Gravimetric Methods. — Using the method of extraction with sodium hydroxide solution, the error due to polymerisation and condensation occurs here too, but the solubilities are different. The best gravimetric methods were developed by Breuer and Broche[3], Lazar[39], and Noack[49].

If the procedures prescribed by Breuer and Broche and by Noack are used, the following scheme should be adopted: (a) the neutral oil is repeatedly washed with water; (b) the aqueous solution containing phenoxides and salts of carboxylic acids is washed with ether to remove the neutral oil; (c) the salts are extracted from the ether solution with water.

As a result of the action of sodium hydroxide solution, "resinified" phenols are thus mixed with the neutral oil. The phenoxides and salts are to a certain extent soluble in ether. Further, some of the oils are volatile (in ether) at 100°, as shown by the following test.

If 1 vol. of oil, *b. p.* 230—270°, from which the phenols have been removed, and 8 vols. of ether are placed in a 200 cc. flask, and the flask is warmed on a water-bath at 50—60°, the ether vapour on cooling falls on the rings of the bath and is volatilised again; at the end of the evaporation the rings on the water-bath are covered with a film of oil.

The method of Breuer and Broche was applied for the determination of phenols and acids in crude kukersite oil. In five determinations the following results were obtained: 22.4%, 26.3%, 23.2%, 21.5%, 26.1%; mean difference ±2.4%.

Noack's method gives more satisfactory results. Four determinations, under the same conditions, gave the following results: — 23.2%, 21.4%, 22.8%, 21.8%; mean difference ± 0.9%.

An Improved Gravimetric Method. — In view of the wide differences in the results obtained by the methods described above, and taking into account the possible sources of the errors, it was decided to carry out the determination of the

amount of acid substances in kukersite oil in two separate portions, under the same conditions, using equal weights of oil in all determinations. In one sample, the water content was determined by distillation with xylol, also the amount of constituents insoluble in ether. The second sample was distilled in an air-bath up to 160°, the remaining oil dissolved in a measured amount of ether and extracted three times with 10% sodium hydroxide solution. The extract was washed with ether and the washings were added to the oil; the ether (equal portions having been taken) was evaporated *in vacuo*. During the evaporation the temperature dropped to — 4° (or — 2°). The flask containing the oil was put into hot water and kept there for 10 minutes, cooled, and weighed, and the water was determined by xylol distillation. Working in this way, the differences between the determinations are reduced, as the following figures show: — 22.7%, 22.4%, 22.9%, 22.5%, 22.4%; mean difference ± 0.25%.

By this method small differences (*i. e.*, about 0.5%) in the phenol contents of different fractions can be determined.

For further investigations, and for the isolation of some phenols, the fraction of *b. p.* 230—270°/760 mm. was chosen. This fraction forms 8% of the crude kukersite oil, and has d^{20} 0.889, viscosity 1.5° (Engler at 20°), flash point (Martens-Pensky), 81°. The freshly-distilled fraction has an orange-yellow colour, but darkens on being kept in contact with air. Ultimate composition: — C, 83.28%, H, 11.00%, S, 1.01%, O, 4.71%. (Kogerman[27]; Weiderpass[63]).

The fraction was successfully washed with (i) sodium hydroxide solution (5% to avoid "resinification" as far as possible) until the volume of oil did not decrease; (ii) water; (iii) 5% sulphuric acid; and (iv) water again. The neutral oil was dried over calcium chloride.

The acidified solutions of phenoxides and salts were extracted with benzene, and distilled with superheated steam, the acids were separated from the phenols with carbon dioxide, and the phenols were extracted with dry ether and dried over anhydrous sodium sulphate. The fraction contained: — Phenols, 17.2%; acids, 2.5%; bases, less than 1%. The neutral oil has a yellow colour and a green fluorescence; d^{20} 0.857. The neutral oil redistilled *in vacuo* at 60 mm. has d^{47} 0.847.

Cresols. — The phenols were fractionated at 60 mm., and the cresols determined by the methods of Lederer[40] and Raschig[52]. The results of these determinations are given in Table XXII.

Table XXII.

Percentage of Cresols in Different Fractions of Phenols.

No. of fractions	B.P./760 mm. °C	Yield g.	Cresols %			Method L = Lederer R = Raschig	Total % of cresols.
			ortho-	*meta-*	*para-*		
I	188—193	17.50	7.59	10.84	1.26	L	9.69
II	193—196	28.00	6.40	19.50	1.58	L	27.48
III	196—201	120.50	6.50	31.20	1.50	L	39.20
IV	201—204	93.50	2.42	22.50	1.34	L	26.26
V	204—208	99.50	—	21.60	—	R	21.60
VI	208—215	116.30	—	7.77	—	R	7.77

For the isolation of cresols 100 kg. of kukersite oil were treated. The fraction *b. p.* 230—270° (*b. p.* 135—175°/60 mm.) yielded 1400 g. of phenols; of this amount 1200 g. were fractionated into 17 fractions, of which the six given in Table XXII contained cresols.

Xylenols. — In the fraction of phenols of *b. p.* 208—215° xylenols were determined in the form of xylenoxyacetic acids.

Procedure. — A mixture of 15.0 g. of the fraction with 15.0 g. of monochloroacetic acid and 50 cc. of 25% sodium hydroxide solution was warmed for 2 hrs. on a water-bath. The mixture was extracted with ether and poured into dilute hydrochloric acid. The crystals were separated and dried. Yield of crystals, 11.5 g. From the ether extract 3.6 g. of oily products were obtained. The crystals were extracted with light petroleum (*b. p.* 60—80°) in a Soxhlet apparatus and by fractional crystallisation separated into six "fractions", of *m. p.* I. 81.9°; II. 86.0°; III. 95.0°; IV. 102.8°; V. 95.0°; VI. 93.6°. The fractions I. (0.65 g.), III. (3.50 g.), and VI. (0.63 g.) show on analysis C, 66.57, 66.55, 66.55%; H, 6.68. 6.76, 6.78% respectively. Required for xylenoxyacetic acids ($C_{10}H_{12}O_3$): C, 66.66%; H, 6.66%. Another portion of the fraction (15.0 g.) was treated in the same way, but the crystals were extracted with light petroleum, and the insoluble portion

was dissolved in cold carbon disulphide; 4.25 g dissolved in light petroleum. On recrystallisation from the same solvent the crystals had *m. p.* 117.5°, which corresponds to 1 : 4 : 2-xylenol (2-hydroxy-1 : 4-dimethylbenzene). The insoluble portion of the crystals was extracted with hot benzene. After recrystallisation 1.4 g. of a substance which melted at 140° was obtained; this corresponds to 1 : 3 : 4-xylenol (4-hydroxy-1 : 3-dimethylbenzene). The portion soluble with difficulty in hot benzene had *m. p.* 160,5°, which corresponds to 1 : 2 : 4-xylenol (4-hydroxy- 1 : 2-dimethylbenzene).

The next higher fraction, *b. p.* 215—220°, also contains xylenols. The fraction of *b. p.* 240—245° (C, 80.05%; H, 9.14%) was treated in the manner described above, and the phenols were converted into derivatives of phenoxyacetic acid. Two fractions of crystals were analysed: — Fraction I had *m. p.* 94.2°, C, 67.93%, H, 7.25%. Fraction II had *m. p.* 134.8°, C, 67.91%, H, 7.10%. On the basis of the analytical data given above, the presence of a mesitol ($C_6H_2Me_3.OH$) or propylphenol can be assumed. W e i d e l [66] investigated the phenols from a low-temperature coal tar; he assumes the presence of propylphenol and trimethylphenol.

The Phenol Ethers. — In the phenol mixture obtained from the fraction mentioned above, phenol ethers of guaiacol type are present. The Zeisel determination gives about 10—11% of methoxyl (or ethoxyl) compounds, but hitherto no individual compounds have been isolated. Qualitative tests show the presence of guaiacol.

The main results of the analysis of phenols are as follows: —

(1) The phenol content of a shale oil has been determined, and the effect of the concentration of NaOH solutions used on the results of analysis shown.

(2) For the first time a shale oil, very rich in phenols, has been examined carefully and different constituents isolated and identified; *o*-, *m*-, and *p*-cresols have been identified and determined almost quantitatively, while the presence of 1 : 4 : 5-, 1 : 2 : 4-xylenols, and higher phenols such as mesitol and propylphenol is assumed.

Pyrocatechol has been identified in the water obtained by distillation of the oil. Lately resorcinol was found in the mixture of phenols by ultimate analysis and qualitative reactions *).

Some of the phenols of kukersite oil correspond to those of low-temperature coal tars, but the former contains phenolic esters, which so far have not been reported in researches on coal tars. The phenolic esters have been found in lignite tars, and resorcinol is a constituent of the oil obtained on distillation of resins.

(3) The mean molecular weight of crude phenols and their ultimate composition lead us to assume that besides the phenols actually isolated, derivatives of naphthols and anthrols should be present.

(4) The crude phenols and phenoxides possess a high disinfecting power, and have proved to be suitable for impregnating timber, etc. (Weiderpass and Kogerman [64, 65]).

In connection with the high phenol contents of kukersite oil and in view of the facts mentioned in the chapter dealing with the genesis of kukersite, it is of interest to compare the hypotheses of the origin of phenols in low-temperature coal tars. There is no lignin nor humin in the kerogen of kukersite, and yet it yields phenols on destructive distillation, therefore, the source of phenols in low-temperature coal tars might be in some cases the same as in the case of kukersite oil, *viz.* products "resinic" in nature, but not of the type mentioned by Klever in his hypothesis ("aus fossilen Pflanzenresten neben fossilem Harzbitumen") [59].

Acids.

The acid contents of two fractions of the shale oil were investigated, and some fatty acids isolated. The fraction boiling

*) After this Monograph had been sent to the publishers, the author found a note on the occurrence of resocinol in the aqueous liquor from low-temperature coal tar. See: G. T. Morgan and A. E. J. Pettet, *J. Soc. Chem. Indust.* T. 72, 1931.

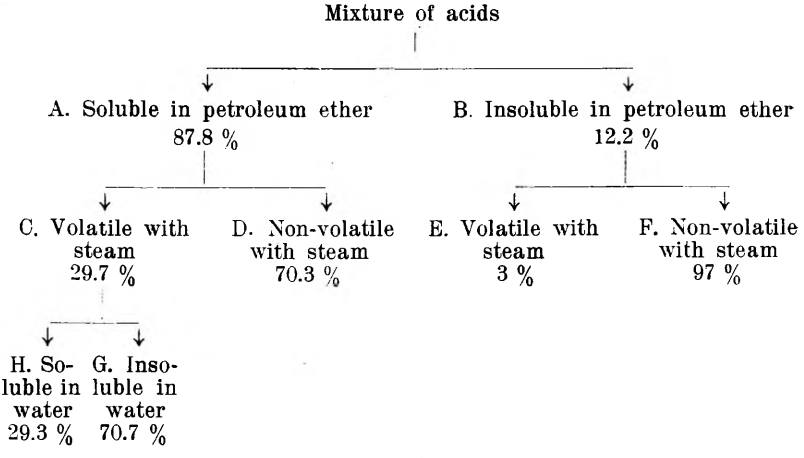
up to 200°/90 mm. Hg or up to about 260°/760 mm. contains about 2 per cent of acids; fraction of *b. p.* 175—225°/40 mm Hg or *b. p.* about 270—330° under atmospheric pressure, about 2.4 per cent.

Acids of the Fraction Boiling up to 200°/90 mm.

For fractionation 67 kg. of crude oil was used, and 8.9 kg. of the fraction obtained or 13.3 per cent of the crude oil. In a series of preliminary experiments it was determined how much NaOH is required to neutralise the acids and phenols. Then $^1/_6$ of the total alkali required for neutralisation was added to the oil, the mixture was well shaken, and allowed to stand. The water solution of the salts was then drawn off, acidified, and CO_2 was bubbled through the solution. The mixture of acids separates as an oily reddish-brown liquid having a smell of lower fatty acids. The liquid dissolves completely in alkali, and its properties are as follows: —

Specific gravity: 0.964; index of refraction: 1.4517; initial *b. p.* about 173°, about 70 per cent of the acids distils below 250°. The mean mol. weight of the mixture was 131.2.

The scheme for separation of acids is given below: —



The ultimate composition of the acids is given in Table XXIII below: —

Table XXIII.

Ultimate Composition of Acids.

Fractions (See scheme above)	Taken for analysis; grams	Obtained CO_2 g	Obtained H_2O g	C %	H %	Average C %	Average H %	Iodine value	Mean mol. weight
Mixture of Acids	1. 0.4409	1.0714	0.3844	66.26	9.71				
	2. 0.4292	1.0395	0.3768	66.02	9.76	66.14	9.74	72.6	131.2
A	1. 0.2257	0.5490	0.2061	66.34	10.14				
	2. 0.3575	0.8634	0.3270	65.87	10.16	66.11	10.39	53.4	136.3
D	1. 0.4578	1.1340	0.4164	67.55	10.11				
	2. 0.4910	1.2082	4.4457	67.11	10.08	67.33	10.10	—	145.2
E	0.1597	0.3692	0.1427	63.50	9.93	—	—	170	84.0
F	0.2398	0.5870	0.1442	66.76	6.68	—	—	64.5	
G	1. 0.4716	1.0857	0.4398	62.87	10.36				
	2. 0.4164	0.9559	0.3901	62.51	10.42	62.69	10.39	38.2	115.1
H	1. 0.3740	0.8374	0.3280	61.06	9.74				
	2. 0.3086	0.6856	0.2696	60.60	9.71	60.83	9.73	43.0	110.9
Crystalline acid	1. 0.1345	0.3511	0.0729	71.19	6.02				
	2. 0.1207	0.3131	0.0671	71.50	6.09	71.35	6.46	—	172.0

In the case of acids insoluble in petroleum ether (B) the "acid number" is about half the value of the "saponification number".

The amount of "active hydrogen" was determined by means of CH_3MgI. Further $AgNO_3$ solutions were applied for the precipitation of acids. (Sossi[55]).

The results of the above-mentioned experiments may be summarized as follows: —

(i) The acids of the fraction of crude oil boiling up to 260° are boiling between 175—250°, above that temperature decomposition begins.

(ii) The greater portion of the acids is soluble in petroleum ether.

(iii) On steam-distillation the acids of lower mol. weight pass over, the lowermost member containing 5 C-atoms.

(iv) The methods used for separation of higher saturated and unsaturated fatty acids are not applicable in this case.

(v) The acids volatile with steam can be isolated by means of fractional precipitation with $AgNO_3$.

(vi) The greater portion of the saturated acids passes over with steam, but in the bulk of the acids those of unsaturated character predominate.

(vii) Some acids are present probably in the form of anhydrides.

(viii) A part or the acids on oxidation give a crystalline compound, having the composition $(C_5H_5O_2)n$.

(ix) The acids belong to the series of aliphatic acids.

The Acids of the Fraction b. p. 175—225°/40 mm.

The fraction, *b. p.* 270—330° resembles in appearance the lower fraction (230—270°). The viscosity of the freshly-distilled oil was 2.2 *E.* at 20°. The ultimate composition of the fraction was as follows: C, 84.44 per cent; H, 10.27 per cent; S, 1.06 per cent; N_2, 0.19 per cent, and O_2, 4.09 per cent [27].

For the isolation of acids, 50 kg. of crude shale oil was fractionated, the fraction *b. p.* 270—330°, weight 8270 g., forming 16.5 per cent of the crude. The fractionation was carried out under 40 mm. pressure. The distillation of the fraction under ordinary pressure gave the following results: —

Table XXIV.

Temp. °C	Percentage yield
Up to 270	24.0
270—280	16.4
280—290	14.6
290—300	12.6
300—310	8.6
310—320	5.4
320—330	6.7
Over 330	11.0
Loss	0.7
Total	100.0

On standing in contact with air, the oil darkened rapidly. The change is practically finished after 9 days, as indicated by the change of physical properties.

For the determination of the amount of acids, the method of Marcusson and Picard[44] was used. The fraction contained:

Hydrocarbons & bases . .	75.5%
Phenols	20.7%
Acids	2.4%
Loss	1.4%
Total	100.0%

The mixture of acids was extracted with ether and washed with dilute sodium carbonate solution. The acids appear as a dark reddish viscous liquid of sp. gravity 1.0374 at 20° C. The iodine value of the crude acids was 85.3, and their composition was: C, 71.34 per cent; H, 10.87 per cent; O, 17.84 per cent.

About 45 per cent of the acids is volatile in steam; the steam-distilled acids have a peculiar odour and yellow colour; they contain C, 68.42 per cent; H, 10.76 per cent, and O, 20.82 per cent. The non-volatile acids are consequently richer in carbon.

For final purification the acids were fractionated in a partial vacuum, under 120 mm. Hg in a steam of CO_2.

Table XXV gives the particulars of the fractionation.

Table XXV.

Fractionation of the Acids.

Fraction	Percentage yield	Sp. gravity at 17° C	Indices of refract. at 17° C
Up to 170° C	1.5 %	—	—
170—180° C	2.9 „	0.9545	1.4406
180—190 „	7.7 „	0.9591	1.4490
190—200 „	5.5 „	0.9649	1.4554
200—210 „	12.2 „	0.9667	1.4637
210—220 „	13.5 „	0.9808	1.4749
220—230 „	11.1 „	1.0030	1.4886
230—240 „	8.4 „	1.0193	1.5051
240—250 „	8.8 „	1.0304	1.5105
250—260 „	9.3 „	1.0446	1.5261
Residue . .	17.0 „	—	—
Loss . . .	2.1 „	—	—

The composition of fractions thus obtained was determined by precipitation with $AgNO_3$. A part of the silver salts of these acids is soluble in ether. All fractions of the acids are soluble in alkali, ether, and alcohol.

Table XXVI shows the percentage of acids, the silver salts of which are soluble.

Table XXVI.

Iodine Numbers and Refractive Indices of some Acids.

Fraction °C	Iodine numbers		Per cent of acids which remain in solution	Refractive indices of the acids at 17° C
	of the fractions	of acids, not precipitated by $AgNO_3$		
170—180	50.8	—	—	—
180—190	56.9	76.3	15.8	1.4761
190—200	58.5	71.1	15.4	1.4949
200—210	59.2	67.3	16.8	1.4817
210—220	65.5	85.6	15.8	1.4991
220—230	68.4	93.4	17.2	1.5117
230—240	72.2	98.4	17.3	1.5218
240—250	81.3	108.1	18.2	1.5190
250—260	105.7	133.7	18.5	1.5264

As evident from the given analytical data, the amount of acids, the silver salts of which are soluble in ether, increases with the temperature. The soluble salts were treated with H_2SO_4, and the free acids extracted with ether. These acids, yellowish-brown liquids, form about 21 per cent of the bulk of crude acids.

The ultimate composition of the mixture of acids, the silver salts of which are soluble, was as follows: — C, 71.84%; H, 11.40%, and O, 16.68%; iodine value: 96.3. Assuming that these acids are monobasic carboxylic acids, the following empirical formula is obtained for this fraction of the acids: — $C_{11.5}H_{21.7}O_2$. The formula for the acids volatile in steam is $C_8H_{15}O_2$.

The ultimate composition of the fractions of acids is given in Table XXVII: —

Table XXVII.

The Ultimate Composition of Fractions.

Fractions under 120 mm Hg		C per cent	H per cent	O per cent
180—190°C	1.	65.21	10.65	24.14
	2.	65.31	10.49	24.20
	Average	65.26	10.57	24.17
190—200°	1.	67.67	11.23	21.10
	2.	67.51	11.17	21.22
	Average	67.59	11.20	21.16
200—210°	1.	68.58	11.21	20.21
	2.	68.70	11.29	20.01
	Average	68.64	11.25	20.11
210—220°	1.	69.90	11.13	18.97
	2.	69.72	11.25	19.03
	Average	69.81	12.19	19.00
220—230°	1.	71.12	11.36	17.52
	2.	71.18	11.20	17.62
	Average	71.15	11.28	17.57
230—240°	1.	71.75	11.35	16.90
	2.	71.67	11.38	16.95
	Average	71.71	11.37	16.92
240—250°	1.	72.86	11.45	15.69
	2.	73.00	11.57	15.43
	Average	72.93	11.51	15.56
250—260°	1.	73.94	11.61	14.45
	2.	74.10	11.53	14.37
	Average	74.02	11.57	14.41

The 2 per cent solution of sodium salts of the acids was precipitated with $^1/_5$ N solution of $AgNO_3$. A brown amorphous precipitate was formed, which darkened on standing. The precipitation with $AgNO_3$ was repeated many times.

The particulars of precipitation of fractions with $AgNO_3$ solution is shown in Table XXVIII below: —

Table XXVIII.

Precipitation of Acids with $AgNO_3$ Solution.

No. of precipitation	1	2	3	4	5	6	7	8	9
Fractions 120 mm	Per cent of silver in salts.								
190—200°	40.27	40.79	41.82	42.34	42.87	43.09	43.63	44.00	46.22
200—210°	39.16	40.02	40.77	41.83	41.99	42.03	42.80	43.74	44.17
210—220°	34.87	35.19	39.15	39.79	41.62	42.59	43.94	—	—
220—230°	33.70	34.25	37.42	39.18	39.73	40.82	—	—	—
230—240°	33.15	33.79	35.00	35.25	36.90	39.15	—	—	—
240—250°	32.10	33.17	33.71	34.15	34.28	35.45	36.63	—	—
250—260°	31.01	31.97	32.29	33.01	33.59	34.29	—	—	—

The summary of the results of experiments on the determination of acids in the fraction of oil, *b. p.* 175—225/40 mm., is given in Table XXIX: —

Table XXIX.

Properties of Acids of the Fraction 175—225°/40 mm.

Fractions 120 mm	Specific gravities at 17° C	Refractive indices at 17° C	Acid numbers	Iodine numbers	Average empirical formula	Basidity calc.	Per cent of acids; Ag-salts soluble	Iodine numbers of acids in the previous column
200—210°	0.9667	1.4637	352.9	59.2	$C_{9\cdot9}H_{17\cdot9}O_2$	1.02	16.8	67.3
210—220°	0.9808	1.4749	333.0	65.5	$C_{9\cdot8}H_{18\cdot7}O_2$	1.01	15.8	85.6
220—230°	1.0030	1.4886	304.5	68.4	$C_{10\cdot8}H_{20\cdot5}O_2$	—	17.2	93.4
230—240°	1.0193	1.5051	294.6	72.2	$C_{11\cdot3}H_{21\cdot3}O_2$	0.97	17.3	98.4
240—250°	1.0304	1.5105	273.2	81.3	$C_{12\cdot5}H_{22\cdot5}O_2$	1.03	18.2	108.1
250—260°	1.0446	1.5261	250.3	105.7	$C_{13\cdot7}H_{25\cdot5}O_2$	0.96	18.5	133.7

The basidity of the acids is about 1.0. From the analysis of silver salts, one may draw the conclusion that the acids of kukersite oil are chiefly saturated and unsaturated fatty acids. It is worth notice here that the acids obtained on fusion of the shale with KOH belong partly to the same group of acids.

The acid content of kukersite oil is one of its characteristic features, and in this respect it differs widely from low-temperature coal tars. That the acids are mainly fatty acids is in accordance with the present writer's view on the origin of kukersite.

Bases.

A preliminary experiment showed that the direct extraction of crude shale oil with dilute sulphuric acid does not lead to a complete separation of bases. If 5 per cent sulphuric acid is used, the acid remains practically colourless; sulphuric acid of 20 per cent strength extracts only a small amount of the bases present in shale oil. (K o g e r m a n [27]).

The crude shale oil was mixed with pure benzine (1 : 1) and treated with 10 per cent solution of NaOH to remove acids and phenols. The oil was next extracted with 20 per cent sulphuric acid and the acid extract was neutralized with sodium hydroxide solution. After the neutralization part of the bases

formed an oily layer on the top of the alkaline solution, but the rest was carried down with the hydroxides of iron and aluminium. The bases were so strongly adsorbed by hydroxides that a repeated extraction with ether failed to separate them.

For the complete isolation and purification of the bases the neutralized solution of sulphates of bases was repeatedly extracted with ether (Extract A). When the solution of sulphates of bases was shaken with ether and allowed to stand, the metallic hydroxides and adsorbed bases formed a yellow flocculent layer between ether and water. The water was then removed by a syphon and the hydroxide separated by filtration.

The hydroxides and adsorbed bases were steam distilled (superheated steam was used) and the bases extracted from the water solution (distillate) with ether (Extract B).

Ether extracts (A and B) were mixed and treated with 10 per cent sulphuric acid; all impurities and neutral oils remained in the ether.

The sulphates of the bases were washed with ether, and finally treated with superheated steam to remove the traces of hydrocarbons and sulphur compounds. The pure bases were set free by NaOH, dissolved in ether, and dried over Na_2SO_4.

The ether was distilled off on a water-bath, the last traces being removed *in vacuo* under 30 mm. pressure at 20—30° C.

The pure bases showed a negative sulphur test, and did not fluoresce; they formed a reddish liquid, with a quinoline-like odour; their sp. gravity was 0.9731 at 15° C; refractive index: $n^{19} = 1.539$.

The mean ultimate composition of bases was as follows: — C, 81.54 per cent; H, 9.59 per cent, and N, 8.59 per cent.

Altogether 175 kg. of crude shale oil was treated, and 260 g. of bases obtained, *i. e.* 0.15 per cent of the oil.

The distribution of bases in crude oil fractions was determined by another experiment, for which purpose about 6 kg. of shale oil was fractionated. Up to 250° C the fractionation was carried out under atmospheric pressure, above 250° C under 60 mm. pressure. The extraction of bases was carried out as described above. Table XXX shows the percentage distribution of bases in kukersite oil. All temperatures are reduced to atmospheric pressure.

Table XXX.

Distribution of Bases in Shale Oil.

Fractions °C	Per cent of bases
150—175	0.18
175—200	0.42
200—225	0.48
225—250	0.52
250—275	0.59
275—300	0.38
300—325	0.16
325—350	0.08
350—375	0.02
375—400	traces

The pure bases were fractionated under 756 mm., and 50 mm. pressure. Finally the corresponding fractions were mixed and refractionated twice under 50 mm. pressure. The results of fractionation are given in Table XXXI (All temperatures are reduced to atmospheric pressure).

Table XXXI.

Fractionation of Bases.

Nos. of fractions	Temperature °C	Sp. gravity at 16°	Refractive indices at 16° C	Amount in g.	Colour and odour
I	90—160	—	1.481	4.0	Colourless; pyridine-like odour
II	160—170	—	1.494	2.2	
III	170—175	0.9060	1.494	3.3	
IV	175—180	0.9145	1.496	3.4	
V	180—185	0.9222	1.496	6.2	
VI	185—190	0.9261	1.497	5.6	
VII	190—195	0.9280	1.498	5.8	
VIII	195—200	0.9300	1.499	8.3	
IX	200—205	0.9352	1.502	6.0	
X	205—210	0.9403	1.504	7.8	Yellow; quinoline-like odour
XI	210—215	0.9465	1.508	9.0	
XII	215—220	0.9517	1.512	6.6	
XIII	220—225	0.9489	1.515	7.6	
XIV	225—230	0.9618	1.524	7.2	
XV	230—235	0.9683	1.529	8.4	
XVI	235—240	0.9762	1.536	11.1	
XVII	240—245	0 9844	1.543	11.0	
XVIII	245—250	0.9277	1.551	14.0	Yellowish-brown
XIX	Over 250	—	—	9.2	

The sp. gravities were determined by a pyknometer (Landoldt's type) at 16° C and the refractive indices by a Zeiss-Pulfrich refractometer at 19° C (Prism No. 1, sodium light). The determination of nitrogen in the fractions gave interesting results: the percentage of nitrogen in the first fractions decreases up to the fraction *b. p.* 210—215°, then suddenly rises, and drops slowly again in higher fractions. The same phenomenon was observed by G o l l m e r [13] in the case of bases isolated from a low-temperature coal tar. The percentage of nitrogen in the fractions is given in Table XXXII below: —

Table XXXII.

Percentage of Nitrogen in Bases.

Fractions °C	Amounts taken g	N %	Average mol. weight
170—175	0.1015	11.15	125.6
180—185	0.0938	11.08	126.4
190—195	0.1305	10.46	133.9
200—205	0.1004	10.12	138.4
210—215	0.1104	9.56	146.5
215—220	0.1227	10.11	139.6
220—225	0.1430	9.76	143.5
225—230	0.1522	9.13	153.4
230—235	0.1030	8.96	156.3
240—245	0.1140	8.93	156.9

All the fractions of the bases changed colour (darkened) on standing, even in sealed tubes: after 8 days the colour of the light fractions turned yellow, the colour of the higher fractions to reddish-brown.

Reaction of the Bases.

(1) On warming the alkaline alcoholic solution of the bases with chloroform, the odour of isonitriles was very pronounced.

(2) Hoffmann's reaction gave positive results.

This shows that the primary amines are present.

(3) No crystalline derivatives were formed by the action of methyl iodide.

(4) With 10 per cent solution of $FeCl_3$ an intense reddish-brown coloration was produced.

(5) By the action of acetyl chloride no crystals were formed, but an oily liquid separated.

(6) A concentrated solution of metaphosphoric acid precipitated from the alcoholic solution of the bases an oily liquid.

(7) The fractions of the bases were treated with solutions of mercuric chloride and picric acid.

1 part of bases and 5 parts of 10% HCl were treated with 50 parts of hot $HgCl_2$ solution (135 g. in litre).

From the fraction *b. p.* up to 160°, crystals were formed, which after recrystallisation from alcohol melted within the temperature range 122.8—138.2° C. After four recrystallisations (twice from water and twice from alcohol) the crystals melted at 156—160°.

From the fraction 160—170° C yellow crystals were formed, which melted between 150° and 190°.

From the fractions *b. p.* 170—175° and *b. p.* 175—180° C a small amount of crystals was formed, but all higher fractions gave only a white emulsion with the $HgCl_2$ solution. The results of the treatment of the bases with a solution of picric acid were as follows: —

Fractions.	*Precipitate.*
90—180°	Double salts, crystals.
180—205°	„ „ crystals.
205—215°	„ „ crystals and oily liquid.
215—235°	„ „ oily liquid.
235—250°	„ „ crystals and oily liquid.

Pyrogenetic Decomposition of the Fractions b. p. 185—205°, and 225—245°.

The bases in these two fractions probably belong to two different groups of heterocyclic compounds, as shown by the results of nitrogen determinations. To prove this assumption the fractions were subjected to pyrogenetic (thermal) decomposition.

About 10 g. of the bases *b. p.* 185—205°, were placed in a small distillation flask, which was connected with a combustion tube filled with coke. The other end of the combustion tube was connected with a Liebig condenser; a small distillation flask served as the receiver. Before the start of the distillation the combustion tube was heated to a glowing red.

5.6 g. of a dark-coloured liquid collected in the receiver. This product of decomposition was fractionated: about 25 per cent of the liquid passed over at 90—125° C and had the characteristic odour of pyridine. With a solution of mercuric chloride the fraction formed a well-defined crystalline precipitate. After two recrystallisations the crystals had a melting point of 176° C, which corresponds to the melting point of the complex compound of pyridine and $HgCl_2$.

The rest of the oil passed over below 190° C.

12.7 g. of the fraction *b. p.* 225—245° was decomposed in the same manner; 7.7 g. of a liquid was obtained. The main portion of this distillate passed over at 180—200°; about 20 per cent boiled between 200—230°. The latter fraction had a strong smell of quinoline.

The results of the experiments on the isolation of bases may be summarised as follows: —

(1) The Kohtla shale oil contains about 0.15 per cent of bases, which boil within the limits of 160° and 260° C.

(2) The chemical properties of these bases differ from the bases of low-temperature coal tars.

(3) The greater portion of the bases does not alter (oxidize) on standing in contact with air.

(4) The bases belong to the derivatives of pyridine and quinoline.

The Neutral Compounds.

The ultimate analysis shows practically in every fraction boiling above 200° C the presence of oxygen-containing compounds. In some of the fractions, *viz.* 230—270° the qualitative reactions showed the presence of ketones. These compounds, however, were not isolated and identified and therefore only the hydrocarbons will be dealt with here.

The Saturated Hydrocarbons.

The preliminary experiments showed that the determination of the amounts of unsaturated and saturated hydrocarbons of the crude oil or of the phenol-free crude (neutral crude oil) is very complicated. About 90 per cent of the crude oil is absorbed by conc. sulphuric acid and with liquid sulphur

dioxide the crude oil forms an inseparable mixture. It has been found possible to separate the hydrocarbons only from the fractions of the crude oil.

All fractions boiling up to 230° (under ordinary pressure) were carefully refractionated, washed with alkali and acid, and treated either with sulphuric acid or with liquid SO_2 at about — 20° C.

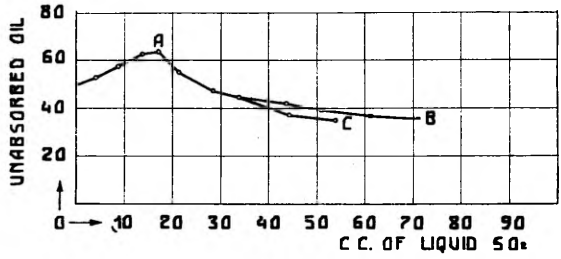


Fig. 14. Extraction of light shale oil with liquid SO_2: up to point A no separation into layers occurs; B — amount of oil absorbed after first extraction C — amount of oil absorbed after second extaction.

Three large fractions of the neutral oil were analysed, *viz. b. p.* up to 230° C, 230—270°, and 270—330°.

As regards the first fractions, it was later on found to be advantageous to work with the light oil obtainable at the Kohtla retorting plant. This oil was obtained from the Kohtla crude oil by steam distillation; its sp. gravity was 0.7726 at 15°, and $n_D^{20} = 1.4319$.

The Chemical Composition of the Light Oil. A portion of the oil was treated with liquid SO_2 at — 20° C: 3500 cc. of the oil yielded about 950 cc. of extract and 2350 cc. of unabsorbed oil. The properties of the products are given in Table XXXIII (cp. Figs. 14 and 15).

Table XXXIII.

Properties of Oils Obtained by Edeleanu's Method.

	Untreated Oil	Unabsorbed Oil	Absorbed Oil (Extract)
Sp. grs. at 15° C . .	0.7726	0.7567	0.8067
Refract. indices at 20° C	1.4319	1.4235	1.4495
Per cent. of saturation (1 vol. of Oil + 1 vol. of conc. H_2SO_4)	73 %	79 %	59 %
Colour	Orange	Yellow	Ruby-red

Both oils, absorbed and unabsorbed, were subjected to Engler distillation, and the results of the distillation were as follows: —

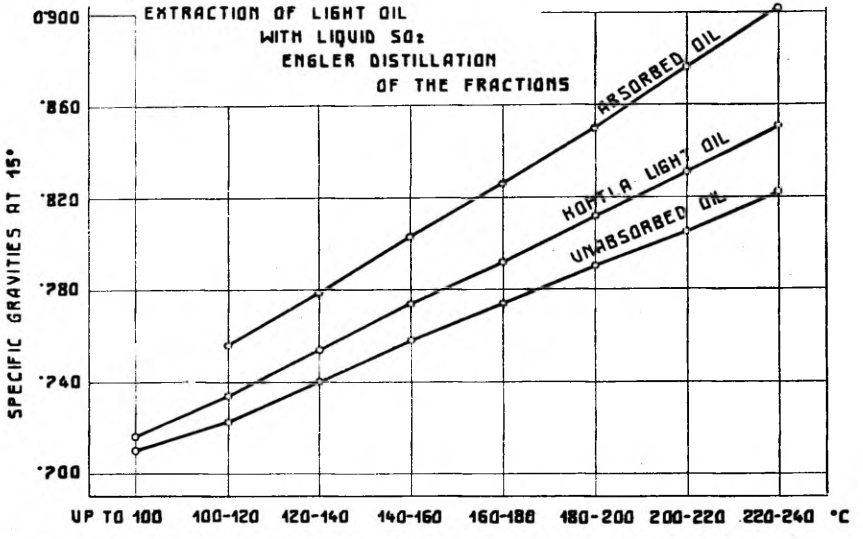


Fig. 15.

Table XXXIV.

Engler Distillation of Light Oil and its Products, obtained on Extraction with Liquid SO_2.

Fractions °C	Saturated portion of Light Oil			Light Oil (crude)		Unsaturated Oil (absorbed by liquid SO_2)	
	Amount cc.	Sp. gravity at 15° C	Saturation %	Amount cc.	Sp. gravity at 15°	Amount cc.	Sp. gravity at 15°
I. B. P.		81°			81°		90°
Up to 100	4.5	0.710	83	3.6	0.716	1.3	—
100—120	23.1	0.723	85	23.0	0.734	22.1	0.757
120—140	23.0	0.740	82	25.0	0.754	26.5	0.779
140—160	16.8	0.758	79	16.2	0.774	18.3	0.803
160—180	12.1	0.774	78	11.9	0.792	11.7	0.826
180—200	8.9	0.790	—	9.0	0.812	8.7	0.850
200—220	5.5	0.805	—	5.3	0.831	5.3	0.876
220—240	3.7	0.822	—	4.0	0.852	3.8	0.902
Residue in grams	2.0	—	—	2.2	—	3.1	

Another portion of the oil was treated with conc. sulphuric acid in the usual way: first with conc. sulphuric acid (sp. gr. 1.84) at O° C., then with fuming sulphuric acid at the same temperature, washed with dilute alkali and water, and refractionated. The fractions obtained after treatment with sulphuric acid had approximately the same physical properties as those obtained by extraction with liquid sulphur dioxide (the saturated portion). For the isolation of saturated hydrocarbons the light oil was treated with conc. sulphuric acid. A three-bulb distillation head was used during the fractionation.

After the first two refractionations only very slight differences were found in the amounts of individual fractions corresponding to equal intervals of temperature, but after about 40 refractionations the fractions "accumulated" at certain temperatures.

These large fractions were fractionated separately, and finally five fractions with fairly constant boiling points were obtained. The particulars of the analysis of these fractions are given in Table XXXV.

Table XXXV.

Constants and Composition of Saturated Hydrocarbons from Shale Oil.

	B. Ps. °C.	Sp. grs. at 20°C.	Refract. indices at 20°C.	Ultimate composition per cent.		Formulas.
				C	H	
1.	68.5—69.5	0.6647	1.3775	—	—	C_6H_{14}
2.	98.5—99.5	0.6933	1.3908	83.79	16.13	C_7H_{16}
3.	124.0—126.0	0.7147	1.4018	83.99	15.97	C_8H_{18}
4.	148.5—149.5	0.7323	1.4111	84.13	15.24	C_9H_{20}
5.	172.4—174.0	0.7509	1.4198	84.32	15.67	$C_{10}H_{22}$

Thus in the light shale oil the normal saturated hydrocarbons (about 35 per cent. of the oil) predominate. About 26.0 per cent. of the oil was absorbed by conc. H_2SO_4 and about 10 per cent was polymerized (K o g e r m a n [28]).

The untreated light oil distils completely over below 240° C, but after the treatment with conc. sulphuric acid about 40 per cent. of the unabsorbed oil boils at temperatures above 240° C. This polymerized oil was distilled *in vacuo* under 14 mm. pressure.

The results of the distillation are shown in Table XXXVI.

Table XXXVI.

Fractionation of Polymerized Portion of Light Oil. 1000 g. of oil was taken.

Nos. of Fractions	Temperature limits under 14 mm pressure	Corresponding temperatures under atm. pressure	Amounts in g.	Sp. gravities at 20°C.
1.	Up to 120°	Up to 250°	85	0.785
2.	120—155°	250—300°	250	0.840
3.	155—190°	300—350°	265	0.868
4.	190—215°	350—380°	225	0.880
Residue	—	—	120	—

All fractions had a light-yellow colour. The fractions 2, 3, and 4 were redistilled over metallic sodium. Table XXXVII shows the amounts and sp. gravities of fractions.

Table XXXVII.

Temperature °C under 14 mm	Weight of fractions in grams	Sp. gravity at 24°C
105—120	56	0.812
120—130	62	0.831
130—140	48	0.846
140—150	53	0.852
150—160	103	0.858
160—170	76	0.862
170—180	45	0.867
180—200	127	0.873
200—210	57	0.879
210—220	17	0.878
Residue and loss	100	—

These redistilled oils were colourless, very viscous, and practically odourless. The largest fraction was redistilled again and its main fraction (*b. p.* 150—160°) was analysed. This fraction contained C, 87.03 per cent; H, 12.65 per cent. The molecular weight was determined in stearic acid, and was found to be 221.0. The hydrocarbon is probably a dinaphthene, with the formula $C_{15}H_{28}$.

In the unsaturated portion of the light oil naphthenes were detected, and probably a naphthene of the general formula C_nH_{2n-2} under the action of conc. H_2SO_4 undergoes polymerization and forms a dimer.

Dr. Kopwillem[37] recently found the same polynaphthene in the oils, obtained by hydrogenation of the crude Kohtla oil.

Although the method of analysis described above allows chiefly the determination of normal hydrocarbons, one may conclude, on the basis of the amounts of the normal paraffins obtained, that in the light shale oil the normal hydrocarbons predominate.

It proved very difficult to obtain the higher boiling fractions completely free of oxygen and sulphur. The results of the analysis of some higher fractions are given in Table XXXVIII: —

The higher fractions of the refined neutral oil may be used as lubricants (Hüsse[15]).

Table XXXVIII.

Composition of Higher Fractions of Neutral Oil.

Fractions under 8 mm Hg °C	Sp. gravity at 15° C	Solubility in H_2SO_4 Vol. %	Solubility in dimethyl-sulfate, Vol. %	Ultimate Composition %					Mol. weight	Per cent of asphaltic matter	Iodine value	Per cent of coke	Viscosity at 50° C (Engler)
				C	H	S	Cl	O					
150—175°	0.9082	45.9	29.3	85.35	11.51	1.03	0.15	1.96	197	—	114.2	0.22	1.80
175—200°	0.9515	62.5	41.4	84.19	10.49	1.11	0.21	4.00	234	—	131.2	0.26	1.48
200—225°	0.9854	69.2	40.5	84.03	9.92	1.09	0.26	4.70	271	0.03	98.7	0.44	3.23
225—250°	1.0020	75.6	39.3	84.09	9.98	1.15	0.29	4.49	283	0.19	111.3	1.08	6.90
250—275°	1.0126	89.2	26.7	84.36	9.87	0.97	0.21	4.59	330	0.15	128.2	1.82	23.5
275—300°	1.0218	93.5	20.6	84.33	9.71	0.69	0.18	5.09	352	0.23	120.4	4.78	41.6

The portion of light oil soluble in liquid sulphur dioxide was carefully refractionated under atmospheric pressure, and in a partial vacuum.

The particulars of the fractionation are summarized in Table XXXIX: —

Table XXXIX.

Fractions: A: atmosph.-pressure; R: 60 mm pressure	Amount in grams	d_4^{20}	Refractive index n_D^{20}	Br numbers: g. of Br per 1 g. oil: added	Br numbers: g. of Br per 1 g. oil: substit.	Mean mol. weight	Ultimate Composition: C %	Ultimate Composition: H %	Ultimate Composition: O %	Formula
A. 100—105°	14.3	0.7606	1.4263	—	—	—	—	—	—	—
A. 110—115°	15.3	0.7759	1.4327	0.70	0.35	115	83.61	12.48	3.91	C_nH_{2n-2}
A. 115—120°	16.2	0.7704	1.4300	—	—	—	—	—	—	—
A. 120—125°	28.1	0.7630	1.4271	0.64	0.41	113	84.93	13.18	1.89	C_nH_{2n-1} and C_nH_{2n-2}
A. 125—130°	22.7	0.7787	1.4359	—	—	—	—	—	—	—
A. 135—140°	16.4	0.8099	1.4516	0.45	0.60	127	84.52	11.93	3.35	C_nH_{2n-3} and C_nH_{2n-4}
A. 145—150°	20.8	0.7967	1.4439	0.47	0.54	127	84.17	12.48	3.35	C_nH_{2n-2} and C_nH_{2n-3}
R. 90—94°	17.5	0.8261	1.4580	0.40	0.60	141	85.06	12.01	2.93	C_nH_{n2-4}
R. 102—106°	7.6	0.8482	1.4692	—	—	—	—	—	—	—
R. 106—110°	11.5	0.8473	1.4692	0.30	0.67	141	84.87	11.45	3.68	C_nH_{2n-4}
R. 118—122°	11.3	0.8744	1.4858	0.23	0.51	143	—	—	—	—

On the basis of experimental data available the presence of naphthenes is assumed.

Autoxidation and gum formation.

On standing in contact with air the light shale oil deposits a very viscous, yellowish-brown oil, and its colour darkens from yellow to orange-red.

To investigate the distribution of such gum forming compounds in the light oil about 3 litres of untreated oil were carefully refractionated 3 times into 2—5° C fractions and allowed to stand in corked glass flasks for about 18 months. After about six months the formation of polymerisation and oxidation products, so-called "gums", was noticed in certain fractions; those fractions were: 90—92°, 98—100°, 107—108°, and 110—111°.

These oxidation *resp.* condensation products were insoluble in the bulk of the oil and formed heavy amber-yellow layers on

the bottoms of the flasks. The amount of gum in certain fractions reached about 10 per cent of the weight of the fraction. (K o g e r m a n [28]).

The gum formation was practically limited to the lower fractions of the light oil, *i. e. b. p.* 72—125° C. The higher fractions showed no deposit of gum, although the colour darkened noticeably on standing. The colour of the fractions between the fractions with the gum deposit remained practically water-white during about 12 months. After that period a slight formation of gums was also observed in some of these "unoxidized fractions".

Table XL shows some physical constants of the fractions and the gums or liquid resins: —

T a b l e XL.

Properties of Oils and Fluid Resins Formed on Oxidation of Shale Oil.

B. Ps. °C	Colour	Oil		Fluid resin		Per cent. of resins by wt. of the fraction.
		Sp. gr. at 20°C	n_D^{20}	Sp. grav.	n_D^{20}	
90—92°	Pale yellow	0.7393	1.4077	—	1.4719	4.2
98—100°	„ „	0.7516	1.4141	1.0531/20°	1.4730	—
107—108°	„ „	0.7637	1.4178	1.0538/16°	1.4742	10.1
109—110°	Water white	0.7382	1.4158	No gum formed		—
110—111°	Pale yellow	0.7726	1.4207	1.0308/17.5°	1.4702	10.5

The ultimate analysis of the fraction *b. p.* 107—108° gave for the oil: C, 82.13 per cent., H, 13.48 per cent., S, traces, oxygen (by difference) 4.39 per cent., the so-called "gum" contained: C, 61.38 per cent., H, 9.20 per cent., S, 0.47 per cent. and 0_2 (diff.) 28.95 per cent.

After standing for about twelve months in four fractions (*viz.* 94—96° C., 104—105° C., 109—110° C., and 117—118° C.) the formation of white, needle-like crystals was observed (Fig. 16). No gum formation was observed in these fractions previously, nor did the colour darken. The crystals were soluble in water, the solution being strongly acid (reaction with litmus), m. p. about 87° C. Average mol. wt. was 134. Micro-combustion of the crystals gave the following figures for

hydrogen and carbon: C, 61.30 per. cent., H, 10.44 per cent, which corresponds to an empirical formula $(C_3H_6O)n$. Taking into consideration the mol. wt., the crystals seem to be a mixture of an aldehyde and of an acid or hydrates of peroxides.

The evaporation of the fraction *in vacuo* did not increase the amount of the crystals. The crystals sublime on heating, and liquefy on standing in a desiccator.

Fig. 16. Crystals of oxidation products in light shale oil (about × 1.5).

Brooks and Humphrey [4] suggest that "diolefines are probably the cause of the resinification which has been observed when highly cracked gasolines are permitted to stand for several months".

On the basis of his own experiments, the results of which have been published elsewhere [29], the present writer concludes that only diolefines with conjugated and probably with twin-double linkages absorb oxygen rapidly and undergo polymerisation, whereas the diolefines with the isolated double bonds, for instance, diallyl and 1,4-pentadiene do not absorb oxygen nor polymerise at ordinary temperature, in the absence of catalysts.

The absorption of air (oxygen) by shale oils has been investigated by Kogerman and Koern [19]. The amount of air absorbed by different fractions in 24 hours is given in Table XLI.

Table XLI.

B. p. of fraction (40 mm)	cc. of air absorbed per 100 g. oil
Up to 170° C	4.05
170—230°	12,88
230—270°	6.80
270—300°	3.60

The highest absorption of oxygen is observed in the fractions, rich in phenols.

The same investigators have studied the action of ozone and "voltolysis" upon the shale oils.

Asphaltic Substances.

The formation of asphalt from raw shale on heating under atmospheric and high pressure has been studied by many chemists. Recently P u k s o v [50] carried out an exhaustive study of asphalt formation from oil shale and shale oils. The main conclusions arrived at by Puksov are as follows:

(1) At higher temperatures the shale oil undergoes condensation or polymerisation; with the rise of melting points of these condensation products the amount of carbenes and free carbon increases.

(2) By air-blowing about 70 per cent of Kohtla crude shale oil can be converted into an asphalt-like substance; the amount of asphaltenes increases during the blowing, but the formation of free carbon and carbenes does not occur.

(3) The blowing-process can be carried out on a large scale. At 220° about 20 per cent (by weight) of oxygen is absorbed.

(4) Compared with the shale pitch of the same melting point, obtained on heat-treatment without blowing, the blown residue (asphalt) has a lower specific gravity, contains less carbon, more hydrogen, and its mol. weight is higher.

(5) The rate of increase of solubility of kerogen is dependent upon temperature and duration of heating; the optimum temperature for production of asphalt from raw shale is about 380—390°.

(6) It is possible to produce asphaltic substances from oil shale, which can compete favourably with natural asphalt, so far as technical requirements are concerned.

High-Temperature Shale Tar.

The high-temperature shale tar, obtained on retorting of raw shale in horizontal gas retorts, at the Tallinn Gas Works, resembles in many respects the high-temperature coal tars: it contains chiefly aromatic compounds, *viz.* naphthalene, anthracene and other hydrocarbons, phenols and cyclic nitrogen bases. (K o g e r m a n and P õ l l u m a n [33]).

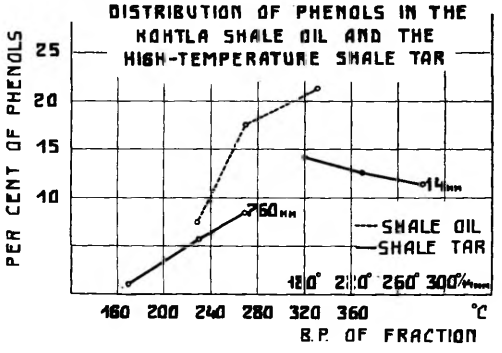


Fig. 17.

The high-temperature shale tars differ greatly from the Kohtla shale oil, as is evident from the following data:

T a b l e XLII.

	Kohtla Shale Oil	Shale Tar
Sp. gravity . . .	about 1.0	1.25
Free carbon . . .	none	over 27 %
C/H	about 8	about 14
Naphtalene . . .	none	considerable quantity

The difference between the contents of phenols and bases of low- and high-temperature oils is shown in Figs. 17, 18.

The light oil (benzol) from gas-retorts was analysed by W i n k l e r and R ü b e n b e r g [69]. On the basis of this ana-

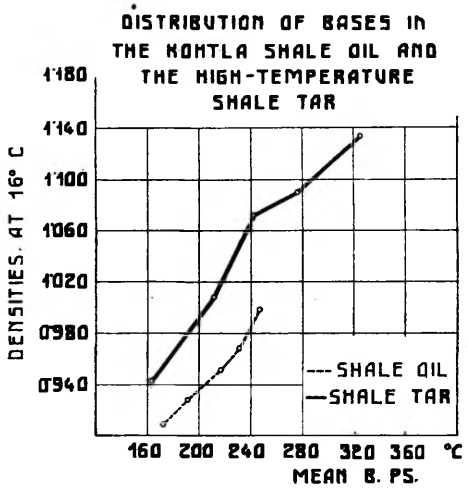


Fig. 18.

lysis the authors assume the presence of benzene and toluene in the light oil from gas-plants.

PART III.

1. — HYDROGENATION OF THE CRUDE SHALE OIL AND OF THE OIL SHALE. 2. — THE RELATION OF KUKERSITE OIL TO THE LOW-TEMPERATURE COAL TARS AND WELL-PETROLEUM.

I. — Some preliminary experiments on the hydrogenation of the shale were carried out by the present writer and M. H. Tamm [36]. On the suggestion of the writer, Dr. J. Kopwillem undertook a systematic study of the hydrogenation at the University of Zurich, Switzerland. Three series of experiments were carried out: (i) hydrogenation of the shale oil, (ii) hydrogenation of the shale, and (iii) heating of the shale under nitrogen pressure. [37; 38]

An apparatus of the type described by Dr. F. Fischer in his book *The Conversion of Coal into Oils* (English edition, p. 152) was used for the experiments.

The main conclusions of Kopwillem's work, which agree with the results obtained by the present writer, are as follows: —

"1. The heating of kukersite or its crude oil at temperatures 400—410° C. under 250 kg. / cm^2-pressure favours the formation of oils with lower boiling points.

2. Heating under high pressure favours the formation of paraffin-, and naphthene-hydrocarbons. The oils obtained on hydrogenation are more saturated and contain less phenols than those obtained from the crude by distillation under atmospheric pressure.

3. On hydrogenation, under the same conditions, the shale and the crude oil yield oils, of which the lower boiling fractions are almost identical.

4. On hydrogenation of kukersite an absorption of hydrogen is observed, but the amount of the hydrogen is not sufficient to saturate all the liquid products of decomposition (cp. Fig. 19).

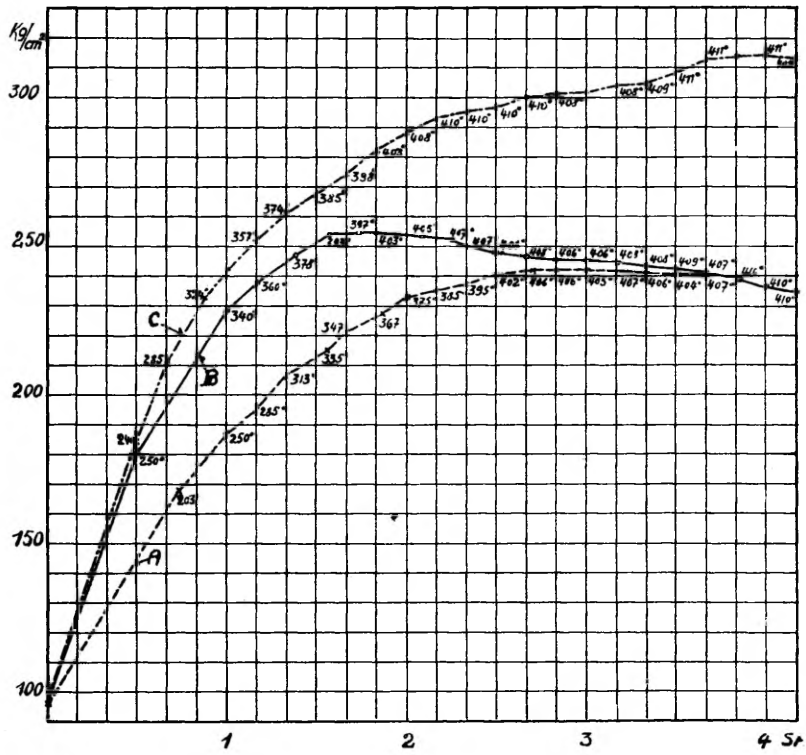


Fig. 19. Pressure-decomposition curves: A — blank experiment; B — under hydrogen pressure; C — under nitrogen pressure.

5. The corresponding lower boiling fractions of hydrogenated kukersite and of kukersite treated under nitrogen pressure are identical in regard to sp. gravities, refractive indices, content of phenols, and solubility in fuming sulphuric acid.

6. The amount (percentage) of kerogen liquefied on hydrogenation does not exceed to any considerable extent the amount of liquid products obtained by ordinary distillation."

The fact that the light oils, obtained on hydrogenation of the shale oil, are identical with the oils obtained by distillation of kukersite seems to support the present writer's hypothesis that the shale may be regarded as a "polygum" or a "polymerised resin".

When the shale is heated, only the surface of a big molecule or a section of a large chain is attacked, leaving unaltered the greater portion of the molecule; on hydrogenation of the heavy oil, the next surface layer of the molecule or next section is broken, yielding the low boiling products, identical with those obtained by direct distillation. When the oil is cracked at higher temperatures (700°), the secondary reactions mask the course of these reactions and the dehydrogenation, polymerisation, and other reactions take place.

II. — Comparing the chemical properties of kukersite with those of bituminous coal and lignite, we see a marked difference between these three kinds of minerals: —

(i) The shale is not soluble in organic solvents.

(ii) It is not affected to any considerable extent by strong solutions of potassium or sodium hydroxides.

(iii) Its thermal decomposition proceeds on different lines.

On the other hand, the crude shale oil contains many constituents, which are also found in the low-temperature coal tars, *viz.* cresols, saturated and unsaturated hydrocarbons, etc. But in addition to this, the shale oil contains many constituents, which so far have not been found in low-temperature coal tars, *viz.* phenolic esters, polyphenols, naphthenes, fatty acids, etc.

The majority of the compounds found in kukersite oil have been isolated also from well-petroleum. The neutral compounds of kukersite oil correspond closely to the neutral constituents of well-petroleum, especially to those found in asphalt-base oils.

The similarity in the composition of shale oils and petroleum may be ascribed to their common origin; there is no difficulty in explaining the origin of petroleum from the oil shales, neither from the chemical nor from the geological points of view.

It is regrettable that Engler's hypothesis of the origin of petroleum is still held by the majority of geologists, although it has but little chemical and geological evidence in its favour.

The biological and limnological processes do not favour any deposition of large amounts of animal remains (unaltered).

The optical activity of petroleum may be traced back to the resinous constituents of shale oils, and there are known some optically-active lignite oils. That the derivatives of resins may be the cause of the optical activity of petroleum was pointed out by W a l d e n [61] many years ago.

At present we do not know of any process in nature which might suggest the "hydrogenation of fish oils" or the "synthol"-like production of oils.

The *rôle* of micro-algae in the formation of oil shales and petroleum seems to be gaining wider recognition in recent works on geo-chemistry.

GENERAL SUMMARY AND CONCLUSIONS.

The results obtained in the preceding experiments allow us to draw some general conclusions regarding the chemical nature of kukersite, and to show its relation to coals and well-petroleum.

1. The empirical formula of the kerogen of kukersite recalls the formulas of hydro-aromatic compounds or certain aldehyde resins, and of certain oxygenated cyclic compounds.

2. On the basis of geological and limnological evidence, supported by chemical examinations, a new theory of the origin of oil shales, particularly of kukersite, has been proposed.

According to this, the organic matter of oil shales is chiefly formed from plankton organisms, and in the formation of oil shales the compounds of this raw material have participated which are most resistant to decomposition, *viz.* waxes and resins, with decomposition products of proteins and cellulose on one side, and putrefaction products of undigested organisms on the other; the first group of substances seems to predominate.

3. A part of the kerogen might be regarded from the genetic point of view as a "coprogenous substance". From the colloid chemical point of view the mineral is of the "irreversible coagulum" type.

4. The so-called "algae" as recognised under the microscope might well be synthetic formations.

5. The organic matter of kukersite might be regarded as a highly polymerised "resinic substance" mixed with calcium salts of fatty acids. It is insoluble in all ordinary organic solvents and can be depolymerised (and decomposed) only by the action of heat and conc. nitric acid.

6. On broad lines, the character of the products obtained on thermal decomposition of the shale (under ordinary and reduced pressures) recalls the character of distillation products of resins and gums:

(i) The gaseous products of the kukersite pyrolysis resemble those obtained by the distillation of fossil resins and amber.

(ii) The solubility of kukersite in organic solvents is increased by heating up to 200° C (below the decomposition point). The oxides of carbon are given off on heating below the decomposition point of the kukersite.

(iii) The crude oil and some of its fractions are capable of polymerisation and oxidation.

7. The four main groups of organic substances, which occur in coal tars and petroleum, *viz.* phenols, acids, bases, and neutral substances, were separated from the kukersite oil.

8. Some of the phenols of kukersite oil correspond to those found in low-temperature coal tars, for instance, *o*-, *m*-, and *p*-cresols, which have been determined quantitatively; 1 : 4 : 5-, 1 : 2 : 4-, and 1 : 3 : 4-xylenols have been determined only qualitatively. In addition to this, resorcinol and phenol-esters were found in the kukersite oil; the latter compounds are constituents of lignite tars and resin oils.

9. The disinfecting power of shale phenols was determined and compared with that of coal tar and other disinfectants.

10. The acid content of kukersite oil is one of its characteristic features; the acids are mainly fatty acids.

11. The chemical properties of the shale oil bases differ from the properties of the bases of low-temperature coal tars. The bases belong to the derivatives of pyridine and quinoline.

12. From the light shale oil a number of saturated hydrocarbons were isolated; in the light oil the normal paraffins predominate.

13. The portion of the light oil soluble in liquid sulphur dioxide probably contains diolefines, which undergo rapid autoxidation; it also contains naphthenes.

14. The gum formation in the light oil was studied, and for the first time the formation of crystalline oxidation products was observed.

15. The presence of ketones in the shale oil was proved qualitatively.

16. The higher fractions of neutral oil proved to have good lubricating properties.

17. The fact that the light oils obtained on the hydrogenation of the kukersite oil are identical with the oils obtained by the direct distillation of kukersite seems to suggest that the greater part of the molecules of kerogen of kukersite are built up either of concentric layers or of long spiral chains.

18. The majority of the compounds found in kukersite oil have also been isolated from well-petroleum.

19. The similarity in the composition of the shale oils and petroleum may be explained by their common origin: the well oils are formed from oil shales by pressure and mild heat. The same variety in composition and qualities is observed in the case of shale oils, ranging from "paraffin-base oils" to "asphalt-base oils", as in the case of petroleum.

20. The *rôle* of plankton organisms in the formation of oil shale deposits, of natural asphalt, and petroleum is of paramount importance, but up to recently, this fact has been neglected.

APPENDIX.

Physical Properties of Estonian Shale Oils.

To supplement the chemical researches on Estonian shale oils, the following physical properties of some crude shale oils and their fractions are given in this appendix: —

(1) Specific gravities of the Kohtla crude oil and its five fractions; (2) coefficients of expansion; (3) specific heats; (4) heats of vaporisation; (5) surface tensions at various temperatures, and (6) viscosities (K o g e r m a n and K õ l l [31]). Further (7) dielectric constants, (8) electrical conductivities of neutral shale oils (V. K o e r n [18]), and (9) fluorescence of some shale oils have been determined (W i t t l i c h [71]).

1. S p e c i f i c g r a v i t i e s of shale oils at various temperatures are given in Table XLIII and Fig. 20.

Specific gravities were determined by means of a pyknometer and a M o h r's balance .

T a b l e XLIII.

Specific Gravities at Various Temperatures.

Temperature °C	Specific gravities of fractions							Crude oils	
	Up to 150°	150° — 175°	175° — 200°	200° — 225°	225° — 250°	250° — 275°	275° — 300°	From Kohtla retort	From Davidson retort
20	0.8204	0.8375	0.8459	0.8582	0.8770	0.8977	0.9257	0.9915	0.9376
30	0.8126	0.8298	0.8382	0.8507	0.8694	0.8905	0.9187	0.9844	0.9288
40	0·8049	0.8220	0.8303	0.8430	0.8620	0.8830	0.9116	0.9776	0.9218
50	0.7968	0.8139	0.8230	0.8356	0.8548	0.8758	0.9047	0.9706	0.9148
60	0.7896	0.8066	0.8149	0.8280	0.8480	0·8694	0.8980	0.9627	0.9061
70	—	0.7987	0.8074	0.8212	0.8403	0.8620	0.8910	0.9555	0.8993

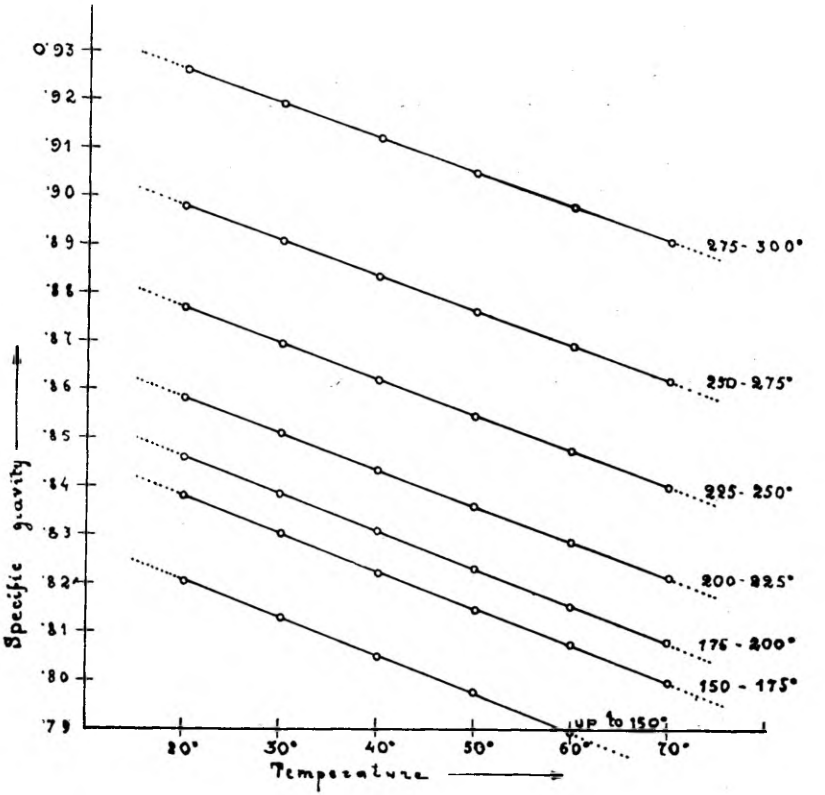


Figure 20. Specific gravities of shale oils at various temperatures.

2. The coefficients of expansion were calculated from the equation

$$a = \frac{a - b}{b(t' - t)}$$

where a and b are sp. gravities corresponding to temperatures t and t'; the calculated mean values are given in Table XLIV, which contains the values for heats of vaporisation and surface tensions as well.

3. The determination of specific heats was carried out in a Dewar flask, provided with a heating coil, a stirrer, and a thermometer, graduated with an accuracy to $^1/_{10}$ degree C. The current for the heating coil was supplied by a lead storage battery consisting of 20 cells.

Table XLIV.

Coeffs. of Expansion, Specific Heats, Latent Heats of Vaporisation and Surface Tensions of Shale Oils.

Fractions	Mean coeff. of expansion	Sp. heat at 20° C	Latent heat of vaporisation cals.	Surfare tension σ_{20} mg/.mm
Up to 150°	0.0009712	0.552	70.8	2.802
150°—175°	0.0009523	0.548	69.0	2.824
175°—200°	0.0009393		69.8	2.818
200°—225°	0.0009027	0.504	68.4	2.876
225°—250°	0.0008677	0.507	60.4	2.931
250°—275°	0.0008226	0.500	60.2	2.899
275°—300°	0.0007716	0.502	56.4	2.868
Kohtla crude oil	—	0.504	—	3.38
Davidson „ „	—	—	—	2.88

200 g. of oil was used for each experiment; the duration of heating was 2 mins. Pure distilled water was used for standardisation.

4. The heats of vaporisation were calculated by means of Trouton's rule, using a value of 20 for the constant.

5. The surface tensions of the crude shale oils were determined by means of Traube's stalagmometer, but the values for surface tensions of the fractions were calculated by means of the formula:

$$\sigma_{20} = 7.30\, d\, \frac{Aw}{A_0},$$

where σ_{20} is surface tension in mg/mm, d — specific gravity of oil at 20°, Aw — number of drops of pure water, and Ao — number of drops of the oil.

Table XLV.

Viscosities (η) at Various Temperatures.

Temperat. °C	Up to 150°	150—175°	175—200°	200—225°	225—250°	250—275°	275—300°
20	0.010011	0.011300	0.013013	0.015960	0.02263	0.03799	0.08741
30	0.008681	0.009889	0.011033	0.013310	0.01826	0.02924	0.06091
40	0·007624	0.008557	0.009461	0.011360	0.01506	0.02303	0.04426
50	0.006857	0.007545	0.008343	0.009770	0.01272	0.01853	0.03341
60	0.006092	0.006798	0.007332	0.008560	0.01097	0.01554	0.02638
70	—	0.005973	0.006517	0.007554	0.00943	0.01320	0.02109

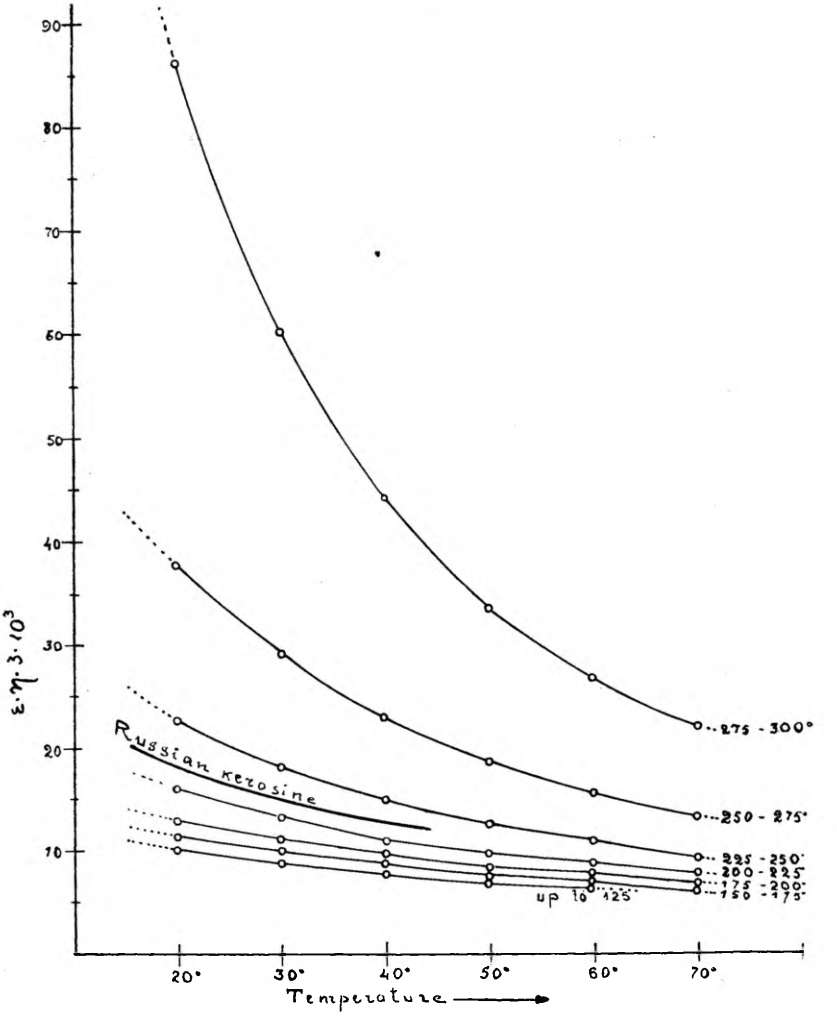


Figure 21. Viscosity-temperature curves of shale oils.

6. For the measurement of viscosities the viscometer of Ostwald was used. The values for η were calculated by means of the equation $\eta : \eta_0 = \frac{st}{s_0 t_0}$, η_0, s_0 and t_0 being values of water.

7. For the determination of dielectric constants a specially designed apparatus was used *). Nine fractions of the

*) This type of apparatus was described by Prof. Dr. J. Wilip in *Z. f. phys. u. chem. Unterricht*, III, 117, 1927.

Kohtla crude oil were treated with 10 per cent solution of KOH to remove the phenols and acids, then with conc. H_2SO_4 and again with the solution of potassium hydroxide; finally the oils were repeatedly washed with distilled water and dried over $CaCl_2$. Before the measurements each fraction was redistilled under 20 mm Hg pressure. Three series of measurements were carried out with each fraction. Table XLVI contains the values for dielectric constants and conductivities only of the first series of experiments.

Table XLVI.

Densities, Dielectric Constants, and Conductivities of Neutral Shale Oils.

Fractions °C	Temperatures at which the densities were determined	Densities	Electrical conduct. $\lambda . 10^{10}$ *)	Dielectric Const. **)	Temperatures at which the dielectric constants and conductivities were determined
Up to 250	22.5	0.8538	1.053	3.114	22.1
250—275	22.3	0.8698	0.775	2.989	21.6
275—300	23.2	0.8722	0.680	2.840	22.2
300—325	23.0	0.8815	1.482	2.817	21.3
325—350	23.3	0.8933	2.523	2.783	22.7
350—375	23.3	0.9130	3.905	2.817	23.0
375—400	23.0	0.9274	1.333	3.327	22.9
400—425	23.4	0.9423	0.926	3.609	22.9
425—450	23.3	0.0559	1.381	3.561	23.0

All temperatures in Table XLVI are reduced to atmospheric pressure.

The values of the dielectric constants found for shale oils are slightly higher than the figures usually given for petroleum products (about 2.1), and higher than the value for pure benzene (2.28) ***).

*) Specific conductivity was calculated by means of the formula:

$$\lambda = \frac{1}{\varrho} = 1{,}77.10^{-10}$$

**) Accuracy about 2 per cent.

***) See: International Critical Tables, Vol. VI, p. 90.

The values of the dielectric constants of the freshly distilled shale oils are changing with time: the minimum value is reached after standing for about 40 days.

8. The electrical conductivity of neutral shale oils is very low. The higher fractions of the neutral oil may be used as transformer or switch oils.

9. The Estonian shale oil, dissolved in pure benzine was analysed with a quartz lamp (type "Analysen-Quarzlampe Hanau 1926"), and it showed the following spectrum of fluorescence: —

bluish green — mixed shades of violet — blue to light blue — which resembles the spectrum of fluorescence of benzidine and other cyclic compounds.

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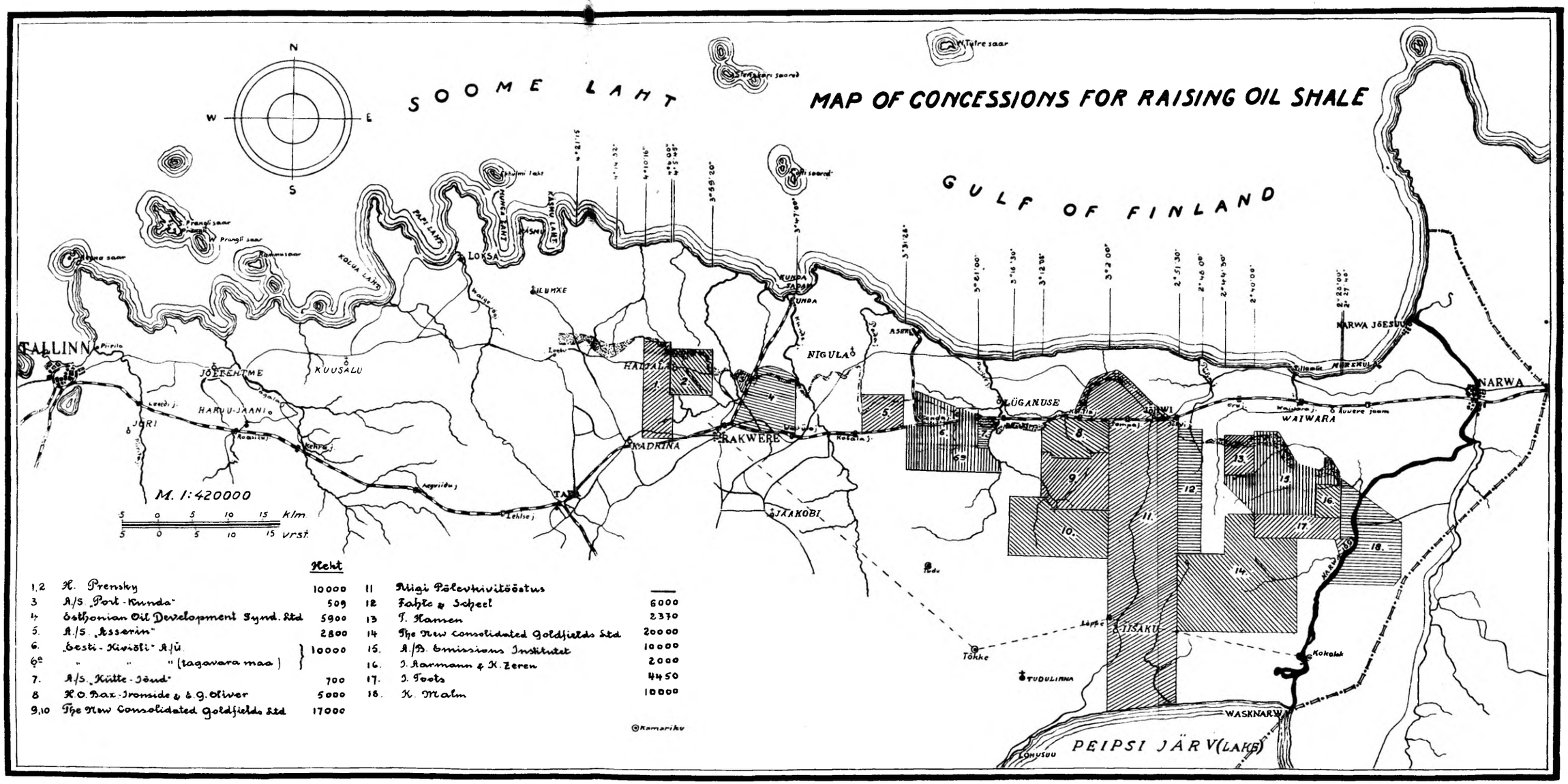

		Hekt			Hekt
1,2	H. Prensky	10000	11	Riigi Põlevkivitööstus	—
3	A/S „Port-Kunda"	509	12	Fahle & Scheel	6000
4	Esthonian Oil Development Synd. Ltd	5900	13	T. Hansen	2370
5.	A/S „Asserin"	2800	14	The New Consolidated Goldfields Ltd	20000
6.	„Eesti-Kiviõli" A/Ü.	10000	15.	A/B. Emissions Institutet	10000
6a	" " " (tagawara maa)		16.	J. Aarmann & K. Zeren	2000
7.	A/S. „Kütte-Jõud"	700	17.	J. Toots	4450
8	H.O. Bax-Ironside & E.G. Oliver	5000	18.	K. Malm	10000
9,10	The New Consolidated Goldfields Ltd	17000			

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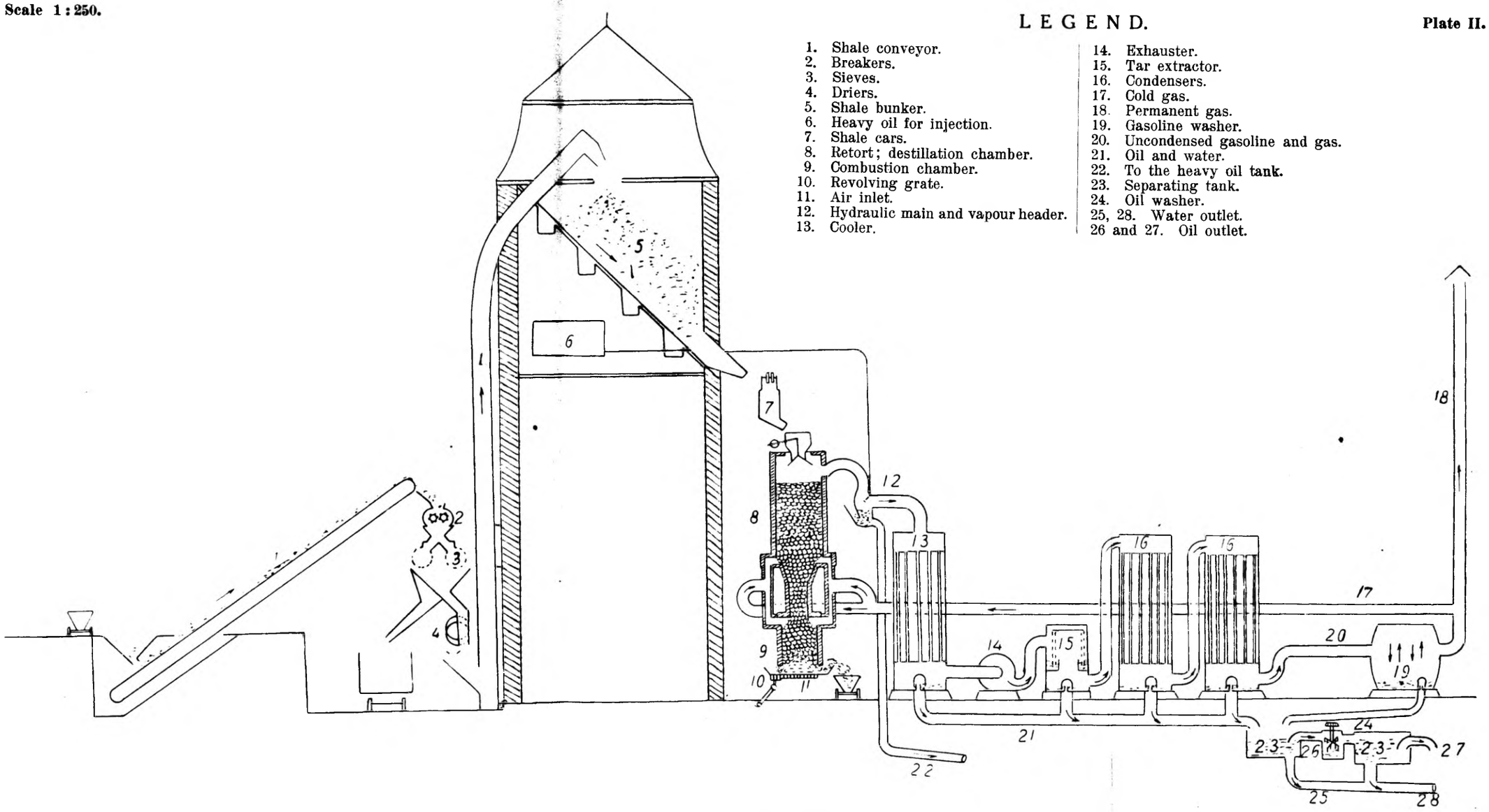
Area for possible open quarries ------ Limits (southern) of the investigated area. ⊙ borehole.

Scale 1 : 250.

Plate II.

LEGEND.

1. Shale conveyor.
2. Breakers.
3. Sieves.
4. Driers.
5. Shale bunker.
6. Heavy oil for injection.
7. Shale cars.
8. Retort; destillation chamber.
9. Combustion chamber.
10. Revolving grate.
11. Air inlet.
12. Hydraulic main and vapour header.
13. Cooler.
14. Exhauster.
15. Tar extractor.
16. Condensers.
17. Cold gas.
18. Permanent gas.
19. Gasoline washer.
20. Uncondensed gasoline and gas.
21. Oil and water.
22. To the heavy oil tank.
23. Separating tank.
24. Oil washer.
25, 28. Water outlet.
26 and 27. Oil outlet.



Kohtla retorting plant.