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The Origin of Oil-Shales.

P. N. Kogerman.

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Introduction.

The increasing demand for liquid fuels and the fact that the supply of well petroleum is not inexhaustible have caused serious concern in the minds of chemists and technologists, interested in oil. With appreciation of these facts comes the demand that technologists open up new fields of petroleum or seek possible substitutes for petroleum products. The possible sources of substitutes (for petroleum oils) are: (i) vegetable oils; (ii) low temperature coal tars; (iii) synthetic fuels, like synthol[1]) etc. and (iv) oil-shales (with some other low grade fuels). Of the above mentioned sources the reserves of oil-shales stand out as most important[2;3]). It is therefore natural, that the Oil-Shale Industry has made good progress in many countries and will be developed in the near future on much broader lines.

As a true oil-shale is practically insoluble in ordinary solvents[4;5]), the only way to produce an oil from it is by thermal decomposition of the organic matter of the shale. The yield of oil and its character are of primary importance for the development of the Shale-oil Industry; the character of liquid distillates is not only dependent on the temperature and manner of distillation but to a great extent on the chemical nature of the kerogen of the shale.

The present researches have for object to investigate as far as possible the chemical nature of the Estonian Oil-Shale, known as "kukersite"*), and the character of products obtained from it.

*) By the name of a village "Kukruse", Viru district, Eesti.

The chemistry of oil-shales is a fairly new subject and it is sometimes wrongly regarded by chemists as a "more industrial" branch of chemistry, but the organic chemists familiar with the subject know that the chemistry of oil-shales, like the chemistry of coal or petroleum, is one of the most difficult chapters of organic chemistry and from a scientific point of view is as much industrial as the chemistry of proteins, fats, etc.

There are two ways of solving the problem of chemical constitution of an oil-shale: (i) direct analysis (supported if possible by synthesis) and (ii) indirect, by way of analogy *i. e.* taking into consideration the origin of the substance, the possible changes in the original substances etc.

In this case the second way is very unsafe and full of pitfalls, although it has been used with certain success in the case of coal [6]) and some oil-shales [7]).

The Oil-shale. The Estonian Oil-shale is one of the oldest and richest oil-shales in the world. The oil-shale deposits occur in the Middle-Ordovician strata, the whole formation attaining a total average thickness of 2,2 meters, over an area of about 2,400 sq. kilometers [8]).

The colour of kukersite varies from greenish-yellow to reddish-brown. The freshly mined material is hard, the weathered is soft and brittle.

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

Table I.

Proximate analysis of the oil-shale.

Kukersite	Water per cent.	Ash per cent	CO_2 per cent	Ash+CO_2 per cent.	Organic matter per cent	Calorific value cals/kilogr.
Freshly mined	18.2	30.0	7.9	37.9	43.4	3000—3500
Air dry	1.5	36.1	9.5	45.6	52.9	4200—4500

The composition of the organic matter (kerogen) varies in the following limits: —

C = 71.1—72.4 per cent; H = 8.0—9.0 per cent; N = 0.2—0.5 per cent; S = 1.5—2.0 per cent and O_2 (by diff.) = 16.0—20.0 per cent; this nearly corresponds to an empirical formula $(C_6H_8O)_n$.

The composition of kerogen of Scottish Shales corresponds to an empirical formula ($C_6H_{10}O)_n$ [9]), so that Estonian oil-shale contains less hydrogen (is less saturated) than Scottish. The same general formula (as kerogen of kukersite) have some derivatives of hydroaromatic compounds, resins, unsaturated aldehydes etc.

PART I.

Origin of oil-shales.

Some neglected factors: biological & limnogeological.

Up to recently the classification of oil-shales has received very little attention. The well-known classification of coals and the scheme of their formation outlined by H. Potonié [10]) includes also oil-shales, but the scheme is very theoretical and the author (H. P.) seems not to be familiar with the chemistry of oil-shales. His son, R. Potonié, in a recently issued book on the petrography of coal [11]), devotes few lines only to oil-shales (p. 46): —

"Als Ölschiefer (Oil Shale) bezeichnen die Engländer gewisse, viel Öl liefernde Sapropelkohlen und -Schiefer".

More attention is given by American geologists to the study of oil-shales.

R. D. George [2]) classifies oil-shale deposits as follows: —

1. Shales partially or completely saturated with oil from an outside source. Evaporation and other changes may have converted the oil into a bituminous or carbonaceous residue.
2. Lignitic or coaly shales.
3. Torbanites, including Boghead coal, kerosene shale, cannel coal.
4. True oil shales.

"From groupes 2, 3 and 4 oil or other bituminous matter is obtained in commercial quantity only by destructive distillation. They are largely or wholly pyrobituminous . . . In the fourth group are shales in which organic matter was intimately mingled with inorganic matter at the time of deposition and subsequently became altered (bituminized) in such a way as to yield petroleum by destructive distillation".

"The general similarity of the geology of oil shales to that of coals suggests that the geological conditions and processes favorable for the making of the one were also those required for the making of the other. Both were formed in swamps, lagoons, deltas,

estuaries and lakes . . . A few coal and a few oil shale deposits were probably formed largely or wholly under marine conditions".

"It would seem probable that both plant and animal remains may contribute to bituminous matter, but the weight of evidence favors plant remains as the important source of the hydrocarbons".

Professor David [2; 12]) in discussing the kerosene shales of New South Wales says: "Examined under the microscope by transmitted light, the small spherical resinous-like bodies of which the shale is chiefly composed are seen to possess a decided organic structure. At all events, in the present state of our knowledge, it may be asserted that kerosene shale was probably formed in lakes, and that it was formed from minute plant bodies, probably either sporangia or algae".

Further, J. W. Dawson, White, Davis and some others assume that oil-shales were deposited in lakes or lagoons, and the impalpable mud was mixed with a large quantity of vegetable and partly of animal matter.

Generally speaking, all these views are similar to the view of H. Potonié on the origin of coals and oil-shales.

A diametrically opposite view is taken by E. H. Cunningham-Craig, which will be referred to below in connection with the origin of kukersite.

As regards the origin of kukersite two widely different theories have been advanced so far.

One was put forward by palaeobotanist M. Zalessky [13]), who examined microscopically a large number of sections of kukersite. He found that the pure organic substance consists of an accumulation of a colonial cyanophycean alga, very similar to the present form of *Gloeocapsa*. He recognised the colonies as small yellow particles of homogeneous substance. Amongst some extremely altered colonies were found other colonies of an alga the cells of which are observable as nearly spherical brown corpuscles.

Zalessky called the alga "*Gloeocapsamorpha prisca*", to indicate its morphological resemblance to *Gloeocapsa* and the mineral (according to Potonié's classification) "*saprocoll of silurian age*".

The observations of Zalessky have been recently repeated by three investigators independantly: H. A. R. Lindenbein, H. Winkler [14]) and H. Bekker [8]). H. A. R. Lindenbein [15]) says: "Chimiquement la kuckersite est donc à placer dans la classe des sapropèles. Géologiquement elle a aussi droit à cette désignation,

étant une accumulation d'algues, mais d'origine pélagochtone et non pas, comme la plupart des sapropèles, déposé dans une eau chargée de produits humiques". Although on the same page he states: "Si l'on considère les différents caractères de la kuckersite, il est difficile de placer ce sédiment dans l'une des classes de Potonié" *).

The same author after a careful examination of thin sections of kukersite came to the conclusion that the *Gloeocapsamorpha prisca Zalessky*, does not belong to the genera of *Gloeocapsa*. He says [16]) . . . "l'algue en question *Gloeocapsamorpha prisca Zalessky* ne peut être homologuée ni aux *Gloeocapsa* ni aux *Batryococcus*. Nous nous sommes demandé au cours de ces recherches, si ces corpuscules cérébriformes ne seraient pas uniquement des corpuscules organiques secrétés par des organismes d'animaux et dont matière colloïdale serait divisée irrégulierment à la façon d'un savon ou d'une grossière émulsion, mélange d'eau et d'un substratum visqueux qui lui donne l'apperence réticulaire". Nevertheless the author rejects this possibility on the basis of some regularities found in the form or structure of these corpuscles and finally, after consulting the botanist, Prof. Chodat, puts forward a view, that in this case we have to deal with a new form of algua, which he called the *Protophycéae* "pour indiquer et l'ancienneté et le rapport qui peut exister entre les Cyanophycées d'une part et les Rhodophycées d'autre part".

E. H. Cunningham-Craig, who visited Estonia in 1921, does not depart from his general "adsorption theory" also in this case. In his paper [17]) (read before the Institution of Petroleum Technologists in London), he says, "we may dismiss von Winkler's theory, as we have so often to do with German theories, as an ingenious explanation that has little or no relation to the facts of the case . . . In fact, if we consider all possible modes of origin for the so called kerogen we find that no other material but inspissated petroleum adsorbed by colloidal inorganic matter can give, even theoretically, the yield of oil that a rich oilshale gives under distillation".

Cunningham-Craig's theory was critisized some years ago by late Dr. H. Bekker [18]), who wrote as follows:

"Supposing that the oilshale was formed by impregnation, we must have a deposit (usually clay) which could be impregnated.

*) Italics are ours.

The only material in the kukersite which possibly could inspissate petroleum is $SiO_2, Al_2O_3, Na_2O, K_2O$ — derived from Felspar rocks. But the percentage of these particles in the kukersite is very unimportant. The CaO in the kukersite beds is mainly due to the calcareous skeletons of different fossils; studying thin sections of these, we see that only the cavities and hollows are filled with kukersite; the calcareous layers and tissues of the fossils are unable to inspissate oil. The % of the clayey material is nearly the same in the "Building limestone" VIII and kukersite bed V. This bed (V), 0.5—0.7 m. thick, contains clayey material 12.70%. The imagination must work greatly to thicken a thin clay deposit of a few centim. to the thickness of 0.7 m. by impregnation of petroleum.

"These chemical considerations make us still believe that the kukersite is mainly an algal deposit, as have shown by the microscopical studies of Fokin, Zalessky, Bekker, Lindenbein".

The quotations given above show the wide divergence in the opinions of different observers regarding the origin of oil-shales.

The divergence in opinion may be due largely to the method of investigation used by geologists, *i. e.* the microscopic examination of thin sections. Practically all that is recognised under a microscope is the shape and colour of particles; the few reagents employed in microchemical analysis cannot reveal the mystery of the internal structure or composition of these particles. Therefore, what appears to one investigator to be an alga, to another is only a globule of petroleum or resin *)

On the basis of his chemical examinations described further below, supported by geological and limnological evidence the (present) author is also inclined to believe, that the kukersite is a marine deposit. Now, what was really deposited and under what conditions?

If the development of deposits in early geological periods has proceeded on parallel lines to the formation of recent deposits (and so far we have no evidence for accepting a contrary view), we have to consider first of all the biological and biochemical factors in a lake or lagoon, leading to a mud formation or deposition.

The organisms. In the above given quotations "the weight of evidence favors plant remains as the important source of the

*) A. J. Franks and B. D. Goodier [7]) have arrived at the same conclusion; they say: "Microscopic investigations have shed almost no light on our problem (origin of oil shales P. K.), which is a very complicated one".

hydrocarbons". The rôle of algae (micro-algae) in formation of kukersite and other oil-shales seems to be very widely recognized [19]).

It is worthy of mention here, that kukersite represents an extreme case of mud deposition, where (according to Lindenbein): "il n'y a de plus aucune trace de spores ou de vegetaux terrestres: ces derniers apparaissent d'ailleurs seulement au Devonien inferieur"; so that the presence of remains of any land vegetation is very doubtful in such an old deposit [20; 21]).

At present very little is known of the chemical composition of these algae. Czapek in his well-known book "Biochemie der Pflanzen" [22]) (p. 640) states "the presence of cellulose in Cyanophycean algae is quite uncertain". Lemain assumes, that the jelly of *Gloeocapsa* consists of pectinic bodies. Anyhow the presence of lignin, which is usually regarded as a source of phenols in shale oils and coal tars [23]) seems to be out of the question in kukersite. Probably some resinic bodies, might be in this case the source of phenols, found to a considerable amount in kukersite oil [24]).

Very valuable information regarding the chemical composition of plankton was published recently by E. A. Birge and C. Juday in the Wisconsin Geological and Natural History Survey [25]). The following quotations give an idea of the proximate composition of plankton in Lake Monona.

"The mean quantity of (dry) organic matter in the total plankton of Lake Monona is 3,163 milligrams per cubic meter of water, of which 9.21 per cent consists of nitrogen (57.56 per cent of crude protein), 5.36 per cent of ether extract, 4.74 per cent of pentosans, and 4.35 per cent of crude fiber. The crude protein and three non-nitrogenous substances that were determined make up 72·01 per cent of organic matter while the remainder consists of undetermined nitrogen free extract". Chemical analyses of various organisms are also given (chapter VIII), but in this case we need only refer to the analyses of Myxophyceae or blue-green algae (Microcystis, Anabaena, Coelosphaerium, Aphanizomenon and Lyngbya). The following table shows the results of chemical analyses of more typical samples (compiled on the basis of table 49, p. 215).

The percentage of nitrogen (and correspondingly amount of crude protein) is very high and does not differ much from the average percentage of nitrogen in the total plankton. The percentage of ether extract (fat-content) is somewhat lower than in the average sample of total plankton and much lower than the corres-

Table II.

Lake.	Organism.	Ash	Ash free substance (% of dry weight).					
		% of dry weight	Nitrogen	Crude Protein	Ether Extract	Pento-sans	Crude Fiber	Nitrogen free extract
Monona	Microcystis	4.31	9.68	60.55	2.79	5.19	0.27	36.39
Mendota	Anabaena	7.17	8.91	55.68	1.20	5.18	0.68	42.44
Mendota	Aphanizomenon	7.51	10.05	62.83	4.02	2.20	0.57	32.58
Monona	Lyngbya	5.67	9.73	60.81	2.50	5.56	3.63	33.06
—	—	—	—	—	—	—	—	—
Mendota	Diaptomus & Cyclops	5.58	10.45	65.31	18.72	—	5.91	10.06

ponding figures obtained from the analyses of plankton animals (see Diaptomus & Cyclops in the table). The percentage of crude fiber is very low too. The composition of nitrogen free extract was not determined, but the extract supposed to contain carbohydrates (other than pentosans).

The above given figures show the proximate composition of the raw material, from which the oil yielding deposits are supposed to be formed.

Biochemical changes of raw material in "pre-deposition" period.

The recent limnological and limnogeological investigations state, that the plankton organisms, especially algae, are extensively consumed as food by various organisms. The calculations of E. A. Birge and C. Juday illustrate the magnitude of such consumption*): "Disregarding temperature and assuming that one cubic centimeter of water weighs one gram, the above organisms (*i. e.* Asplanchna, Cyclops, Diaptomus and adult *Daphnia hyalina*) would have to filter about 600.000 times their own dry weight of water in order to secure their own weight of dry organic matter in the form of nannoplankton. These animals may also feed upon some of the organisms in the net plankton and thereby reduce the above quantities of water proportionately".

And further . . . "Part of the plankton sinks to the bottom of the lake and this constitutes a source of food for the insect larvae,

*) loc. cit p. 155.

mollusks and worms which dwell upon the bottom; this material is especially important for the bottom dwellers which are found in the deeper portions of the lake".

The analyses of bottom sediments, carried out in Finland and Russia, confirm the observations of the above mentioned American limnologists. According to Tribom[26]) the mud of lakes in Finland (in pelagic part, not in litoral or sublitoral) contains 5 per cent of undigested vegetable remains, 5 per cent of animal remains, 15 per cent of inorganic matter and 75 per cent of excrements. A large percentage of excrements is found also in bottom sediments of Russian lakes[27]). The mud of Mid-Russian lakes contains as an average: C — 50 to 60 per cent, H — 7 to 9 per cent, ratio of C to H equals 8 to 5.5. This ratio is not far removed from the C/H ratio of kukersite.

In any case as limnologists state, the greater portion of the organic matter of the plankton organisms is already decomposed (digested) before sinking to the bottom of lakes or gulfs. In the sediments we shall find therefore mainly indigestable organic compounds, *i. e.* partly "crude fiber", waxes and resins with of course some inorganic matter.

But the "crude fiber" or (at least) the cellulose when subjected to the action of anaerobic bacteria on the bottom of a gulf or lake is slowly decomposed. As a result of such decomposition the fatty acids are formed, according to Omelianski, up to 50% in weight with butyric acid as the main constituent[28]). In the highly reducing medium, existing on the bottom of a quiet lagoon or in deeper parts of a sea charged with basic calcium compounds (this is the case of kukersite formation) some of the acids might probably be reduced to aldehydes and form aldehyde resins the greater portion of course forming calcium (or magnium) salts. The soluble salts might disappear, but a part might be retained by protective colloids or adsorption.

Even the waxes and gums could be decomposed by diastases formed in the digestive canal of animals. The main results obtained recently by Voskressensky[29]) are summarised as follows:

1. "Que le gomme peut être dédoublée par plusieur diastases dont quelques-unes se trouvent dans le tube digestif des animaux;
2. "Que ce dédoublement est assez faible;
3. "Que les animaux peuvent supporter sans grand inconvénient

pour la santé la nourriture demi-gommeuse, mais ne peuvent pas vivre exclusivement de gomme".

The substances most resistant to putrefaction and decomposition are the resins[30]).

The Nature of bottom sediments.

These theoretical considerations help to form an hypothesis regarding the nature of raw materials, which later formed the kerogen of kukersite. The main points are as follows:

1) The original organic matter of microscopic algae and other plankton organisms seems to be highly altered. The chief constituents of these organisms, the proteins, have totally disappeared, the percentage of N_2 in kukersite being practically nil (0·2%).

2) In the formation of kukersite have participated compounds, which are the most resistant to decomposition ("digested") *i. e.* waxes and resins, with decomposition products of proteins and cellulose on the one side, and putrefaction products of undigested organisms on the other, but the first groop of substances seems to predominate; the mineral or part of its organic matter might be regarded from genetic points of view as a coprogeneous substance. The so called "alguae", as recognised under the microscope at present might well be "synthetic" formations as has been shown by Stach[31]) in many cases ("pollen-like bodies in coal formed from bitumen and lime").

3) The nature of the kerogen of kukersite should be therefore resinous or "gummified".

In this case probably the aldehyde group and unsaturated linkings (more than one in a molecule) might be regarded as "resinophoric groups"[32]).

To prove this hypothesis some experiments were carried out which are described in the "Experimental Part".

PART II.

Experimental.

Bromination and chlorination of kukersite,

A. Procedure. Samples of dried oil-shale from different seams were finely ground and sieved through 1 cm²/5000 mesh-sieve. As a typical case, the shale from seam V is here referred to. The shale powder was suspended in pure CCl_4 and a known amount of Br_2 in CCl_4 was then added:

1 g. of shale powder was put into a 120 cc. glass bottle with a glass stopper, then 100 cc. of bromine solution in CCl_4 was added. A blanc experiment was carried out every time. The suspensions of kukersite in CCl_4 were shaken for 24 (resp. 36, 48 and 60 hrs.) in a shaking apparatus. Half an hour before the titration the shaking was stopped. From the clear solution three samples were taken for titration.

[$T_J = 0.014668$ and $T_{Na_2S_2O_3} - 0.018623$. Weight of Br_2 in 100 cc. — ca. 1.62 g.]

Table III shows the results of bromination: —

Table III.
Bromination of kukersite.

Hours	Weight of shale taken	Weight of Br_2 in 100cc of Soln.	Weight of Br_2 absorbed	Average % % of weight of Br_2 absorbed calcul. on dry kukersite.	Average % % of Bromine absorbed calc. on pure kerogen.
24	1.0112 (1.0090)	1.1359	0.4933	48.65	—
36	1.0081 (1.0005)	1.0868	0.5396	53.35	—
48	0.9995 (1.0141)	1.0716	0.5510	54.96	106.3
60	1.0102 (1.0401)	1.0613	0.5604	55.34	107.0

For control the bromination tests were repeated with the shale ash; the amount of bromine absorbed by inorganic substance was 0.37% only.

Chlorination. For chlorination about 10 g. of pulverized kukersite was suspended in pure CCl_4 (250 cc). The chlorine was bubbled through the suspension at the rate of 110—120 bubbles per. min. Duration of chlorination was 24—36 hours. The results of chlorination are given below (Table IV): —

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

Extraction of halogenated kukersite with absolute alcohol.

The samples of kukersite after chlorination and bromination were extracted with absolute alcohol. Untreated shale powder

Table IV.

Chlorination of kukersite.

Hours	Duration of drying of chlorinated shale in hrs.	Weight of kukersite g.	Weight of chlorinated kukersite g.	Average % % of increase in weight of kukersite on chlorination	
				calc. 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 „

yields about 0.31 per cent of extract on extraction with absolute alcohol or 0.60% calculated on pure kerogen. Halogenated shale powder shows a marked solubility in absolute alcohol.

The shale powder was extracted for 36 hrs. in a Soxhlet apparatus (as in previous experiment with untreated shale); 10 g. being taken, 350 g. of alcohol was used. The colour of the alcohol syphoned in the beginning was yellow; but it turned dark-brown after 36 hrs. of extraction.

The extracted shale was dried under 40 mm pressure at 70° C till constant weight was obtained, (usually 8—12 hrs.). The colour of the extracted chlorinated shale was yellow. The yield of extract reached up to 26.84% of the weight of dry shale.

The amount of Cl_2 was determined in chlorinated shale and in the residue after extraction. The Schiff's method [33]) was applied to the determination of chlorine.

The results were as follows: —

Average %% of chlorine in chlorinated shale 17.69; Average %% of chlorine in the residue 10.65

The analysis shows that a greater portion of chlorine remained in the residue.

In preliminary experiments trials were made to separate the extract from alcohol by diluting the latter with water: a brown precipitate was found, which on standing settled at the bottom of the flask, but partly remained in colloidal state in the solution. It was very difficult to separate the precipitate from the solution by filtration, and decantation only was applicable. The precipitation

with water was not complete, therefore the alcohol was removed from the extract by evaporation (under 40 mm, at 70° C). After evaporation a syrupy orange-yellow substance was obtained, which on drying turned to a dark-brown, and finally to a greenish solid, resinous body.

Further efforts to identify the extract have been unsuccessful so far, but research in this field is still in progress.

From above given data one might draw the conclusion, that the action of bromine is more effective, than that of chlorine, but considering the differences in the methods and the mol. weights, it follows that the halogenation proceeds nearly equally in both cases.

According to the researches of McKee *) a sample of Colorado shale yielded 6.23 per cent of extract (from the chlorinated shale) with absolute alcohol. Shale from Jone, California, yielded in the same conditions 41.3% of extract, after being chlorinated (the untreated shale yielded 6.9% of extract).

In addition to absolute alcohol other organic solvents were applied, namely $CHCl_3$, CS_2 and turpentine; all these liquids proved to be good solvents for chlorinated shale, especially turpentine.

Fusion with KOH. The temperature of fusion has a great effect upon the decomposition of the kerogen of shale: at 230—240° C the shale yielded only about 3—4 per cent of water soluble extract, at 260—280° C over 8 per cent, but above this temperature the decomposition was very marked, and the eliminating gases had a strong small of kerosine. The extract was partly neutralised with sulphuric acid and finally with hydrochloric acid to prevent the precipitation of calcium and barium sulphates: a blackish-brown precipitate was formed. The precipitate was washed with very dilute acid, with some water and dried, it formed about 6 per cent of the weight of dry shale. A qualitative analysis showed that the extract contained but little of „humic acids", and more of aromatic and probably some fatty acids.

The acid filtrate which had still an orange colour was shaken with ether many times; after the evaporation of the ether an orange semi-solid mass of acids was obtained with a very distinct smell of butyric acid.

Fusion with sulphur. Samples of powdred shale were heated with sulphur in sealed tubes at 180—200° C for two hours;

*) loc cit.

during the heating considerable pressure was developed and one tube „exploded". On opening a strong smell of H_2S was noticed; the shale treated in this way was extracted with various solvents, toluene, benzene and pyridine, but 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 pyridine-extract was concentrated by evaporation in vacuo and extracted with alcohol. The alcohol extract also ruby-red left on evaporation a sticky reddish mass, about 1 per cent of the weight of the fused mass. When the alcohol extract was poured into water, gray globules of soft rubber (with a smell of freshly vulcanised rubber) were precipitated. In this short paper it is impossible to describe in detail the numerous experiments in which the methods of attacking the resins and rubber were applied to the study of the shale, they will form the subject of another paper.

Finally the behaviour of the kukersite on distillation should be mentioned here.

On broad lines the character of the distillates, obtained on distillation in vacuo (5—20 mm Hg) and ordinary pressure brings to the mind the products of thermal decomposition of rubber [34]) and resins under the same conditions: *i. e.* the product of a vacuum-distillation is more viscous and heavier than the oil obtained on distillation under ordinary pressure; in the case of coal we observe the contrary [35;36]).

Lindenbein describes the vacuum oil of kukersite as a very viscous liquid, with a green fluorescence and characteristic smell of isoprene.

The water obtained on distillation of kukersite shows an acid reaction.

The kukersite oil, obtained on distillation in an internally heated retort (producer) at 500—600° C containes about 25—28 per cent of phenolic bodies, of which about 12 per cent are phenolic ethers (like quaiacol), about 3—4 per cent of saturated and nonsaturated (chiefly fatty) acids, and about 70 per cent of hydrocarbons. The light oil is rich in saturated hydrocarbons and hydroaromatic compounds, and the middle fractions contain in addition aldehydic and ketonic bodies.

Summary and conclusions.

1. The empirical formula of the kerogen of kukersite, $(C_6H_8O)_n$, recalls the formulae of hydroaromatic compounds, of certain aldehyde resins and oxygen-containing cyclic-compounds.

2. The mineral is a colloid of „irreversible coagulum“ type.

3. In nearly all theories dealing with the origin of oil-shales the biochemical changes in raw material in the „pre-deposition“ period, based on the recent limnological investigations, are usually neglected.

4. The so-called “algae“ might be synthetic formations.

5. The investigation of chlorinated and brominated shale powder shows, that the portion soluble in organic solvents is mostly resinic in nature.

6. The fusions with KOH and sulphur (and the action of solvents) show that the kerogen of kukersite is very resistant to the action of reagents and seems to be highly polymerised.

7. On broad lines the character of distillates, obtained on thermal decomposition of the shale brings to mind the character of distillation products of resins and rubber.

8. The organic matter of kukersite might be regarded as a highly polymerised, “resinic body“, containing many double bonds; it is insoluble in all ordinary organic solvents and could be depolymerised by the action of halogens and heat only.

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