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DESULPHURISATION OF ESTONIAN SHALE OIL

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The problem of the removal of sulphur compounds from mineral oils is of great industrial and economic importance. The upper allowable limit of sulphur compounds regarded as deleterious (corrosive) to the engine, etc., are still open questions. The U.S. limit for sulphur compounds,* expressed in per cent. of the element (0.1), has undoubtedly been based on the sulphur content of "straight run" petrols, or gasolines, from paraffin-base oils, and must be regarded as very low in relation to petrols obtained from other sources. The increasing production of mixed-base and asphalt-base well oils (Californian, Mexican and other fields) is supplying the refineries with heavy oils containing high percentages of sulphur. The gasoline obtained on cracking these heavy oils also generally shows high content of sulphur. The usual refining methods adopted for treatment of "straight run" oils are not adequate to reduce the sulphur content of cracked distillates to the requirements of the specification. Consequently, drastic refining should be applied, which causes large refining losses.**

The Estonian crude shale oils belong to the asphalt-base type of oils. They contain about 1 per cent. of sulphur, whilst the raw shale contains about 2 per cent. of the element.

The yields of oil obtained on distillation of the shale, with and without steam, in the Fischer apparatus at about 520° C. are given in Table I.

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* United States Government Specification for Lubricants and Liquid Fuels, Bureau of Mines Tech. Paper 323a, Washington, 1924.

Estonian War Office New Specification for Liquid Fuels allows 0.5 per cent. of sulphur in shale petrols (benzines).

** For financial side of the question see: G. Egloff, C. D. Lowry, Jr., and P. Truesdell, *Petroleum*, Vol. xxvi. (1930), pp. 919—927.

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Particulars relating to the chemical composition of the shale, the yield of oil under various conditions, etc., have been published elsewhere. [*]

Table I.

Yields of Oil and Distribution of Sulphur in Products of Distillation.

	Products of Distillation of Shale without Steam			Products of Distillation of Shale with Steam		
	Oil	Coke	Gas	Oil	Coke	Gas
Yield per cent	33.23	52.52	14.25	35.77	50.85	13.38
Sp. gravity	0.9473	—	—	0.9557	—	—
Per cent. of sulphur based on total S. in Shale .	9.3	44.4	42.4	11.0	44.7	40.2

The distribution of sulphur compounds in fractions of a crude shale oil obtained on distillation in Fischer aluminium apparatus (in laboratory) was determined by M. Wittlich, [**] and the results are given in Table II.

The residue (pitch) left on fractionation of crude oil contained 4.0 per cent. of sulphur. (See Table II.)

The distribution of sulphur in the fractions of Estonian shale oils resembles on broad lines the distribution of sulphur in Kimmeridge Shale Oils (which, of course, are characterised by very high sulphur content), *i. e.*, the percentage of sulphur compounds is higher in the lower boiling fractions. [***]

The crude petrol produced on distillation on a large scale usually contains about 0.8 to 1.0 per cent. of sulphur. After alkali and sulphuric acid treatments (3 per cent. of H_2SO_4) the petrol still contains 0.6 per cent. of sulphur, although the "doctor" test is negative. By increasing the amount of

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[*] P. N. Kogerman: On the Chemistry of the Estonian Oil Shale "Kukersite." *Archiv für die Naturkunde Estlands*, I. S., X. Bd., 2 Lief, Tartu, 1931. *Abstract, Journ. Inst. Petr. Techn.*, vol. 17, No. 98, pp. 569—570a, 1931.

[**] M. Wittlich: „Einiges über den Schwefel im estländischen Ölschiefer (Kukersit) u. dessen Verschwelungsprodukten“, *Acta et Comment. Univers. Dorpat*, A. VIII., 6, Tartu, 1925.

[***] H. G. Shatwell, "The Hydrogenation and Desulphurisation of Norfolk Shale Oil." *Journ. Inst. Petr. Techn.*, vol. XI, p. 550 (1925).

Table II.
Distribution of Sulphur Compounds in Fractions of Crude Shale Oil.

Fractions °C	Oil Obtained on Distillation of Shale without Steam			Oil Obtained on Distillation of Shale with Steam		
	Percent by weight	Per cent S.	Sp. gravity	Percent by weight	Percent S.	Sp. gravity
Up to 175°	12.32	1.26	0.7557	11.74	1.20	0.7526
175—200°	2.49	1.11	0.8438	2.35	1.08	0.8022
200—225°	2.86	1.08	0.8808	3.84	1.02	0.8787
225—250°	5.04	0.97	0.9017	4.74	0.99	0.8989
250—275°	6.59	0.80	0.9224	4.55	0.87	0.9013
275—300°	8.13	0.74	0.9509	6.87	0.76	0.9428
300—325°	10.59	0.78	0.9589	13.87	0.92	0.9840
325—350°	12.28	0.99	0.9904	18.35	0.90	0.9935

sulphuric acid the sulphur content can be reduced, but at the same time the refining losses are increased. Therefore, other methods of treatment of shale petrols have been studied.

The distribution of sulphur compounds in the fractions of crude petrol is shown graphically in Fig. 1.

Properties of Crude Benzine or Petrol Used in the Experiments.

The crude petrol used in the experiments was of heavy type, obtained form a Swedish company Estländska Oljes-

Table III.
Engler Distillation of Crude Petrol.

Fractions °C.	Amount g.	Per cent. yield	n_{20}^{D}	d_{20}	Colour
Up to 100	10.63	13.06	1.4146	0.7322	Light yellow
100—150	32.48	39.89	1.4327	0.7696	Yellow
150—170	10.71	13.16	1.4501	0.8074	
170—200	16.70	20.51	1.4637	0.8356	
200—230	7.99	9.81	1.4854	0.8897	Brownish yellow
Residue	2.26	2.78	—	—	—
Total	80.77	99.21	—	—	86.62

kifferkonsortiet, operatning in Estonia:* Sp. gravity = 0.8035/20°C.; $n_{20}^{D} = 1.4486$. Distillation by Engler method gave the results shown in Table III.

81.4 gm. of petrol were taken for distillation.

Sulphur	1.48	per cent.
Soluble in 6 per cent. NaOH . . .	4.9	„
Soluble in 100 per cent. H_2SO_4 .	53.6	„
Unsaturated compounds	38.2	„
Aromatic compounds	10.5	„
Saturated compounds	46.4	„
Water	0.34	„

The distribution of the saturated, unsaturated and aromatic compounds is illustrated graphically in Fig. 2.

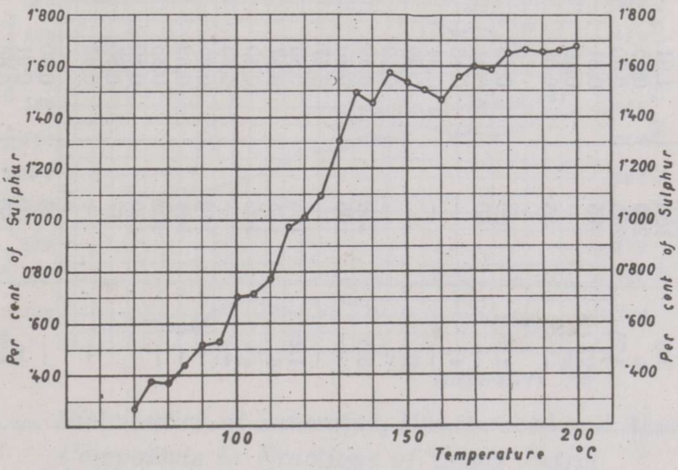

Fig. 1. — *Distribution of Sulphur Compounds in Fractions of Crude Petrol.*

I. Vapour-Phase Refining.

Dr. Rostin ** and others chaim that motor spirits can be desulphurised in the vapour-phase in the presence of certain catalysts. To prove this assumption a number of experiments

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* For types of retorts see P. N. Kogerman and John Roberts: "Progress in the Treatment of Estonian Oil Shale," *Trans. Second World Power Conference*, Vol. viii., pp. 110—125 (1930).

** G. P. 372,663; F. P. 613,101; E. P. 107,034, 286,255; U. S. P. 1,604,235 (by L. L. Odom) and many others.

Table IV.

No. of experiment	Catalyst	Amount of gas (litres)	Duration of experiment (hours)	Amount of petrol distilled	Per cent. of sulphur in the distillate	Remarks
1	CuO	27	3	150	0.91	Only a small amount of catalyst was used.
2	CuO	65	4	180	0.26	
3	CaO	38	3.5	200	0.58	
4	CaC_2	100	3.5	150	1.01	
5	NiO	73	4	200	0.75	
6	Zn	51	3.75	200	0.80	
7	Fe_2O_3	19	—	75	0.81	
8	„	—	—	—	0.40	
9	CuO from the exprts. Nos. 2 and 1	11.5	—	35	0.08	Blank experiment with normal benzine and amylene (1 : 1).
10	Minette	108	2.5	100	0.53	Minette — a German iron ore.
11	Minette	64	—	60	0.41	
12	Ni, colloid	60	4	—	0.13	
13	Minette+PbO+CuO	64.5	—	—	0.91	Temp. of reaction, 180^0—200^0.
14	„ „	—	—	—	0.89	Temp : 300^0—320^0, rapidly distilled.
15	„ „	—	—	—	0.59	Temp.: 300^0—320^0, slowly distilled.
16	Minette	18	3.5	250	0.89	
17	Minette+CuO+PbO	33	—	105	0.80	Ratio: 8 : 1,6 : 1.
19	Minette+MnO_2	—	—	—	0.67	Ratio: 3,3 : 1.
20	„ „	23	1.25	165	0.86	
21	Minette+MnO_2	28	6	185	0.87	Ratio: 1 : 1.
22	„ „	45	—	105	0.80	
23	Fe *a*	—	—	—	0.93	Temp.: 140^0—170^0.
24	Fe *b*	—	—	170	0.95	Temp.: 300^0—310^0.
25	Cu	24	—	104	0.66	Fraction up to 170^0.
26	„	—	—	100	0.83	Unrefined benzine.
27	CuO	—	—	125	0.80	
28	„	33	—	47	0.85	Fraction up to 170^0, in stream of H_2.
29	Al $(OH)_3$, Ca-Aluminate +PbO	38	—	—	0.93	In current of hydrogen.
30	ZnS	32.5	—	50	0.80	„ „
31	Activated charcoal	40	—	50	0.91	„ „
32	$PbCrO_4$	23	1.25	50	0.66	„ „
33	Pyrite	27	2.75	50	0.92	„ „
35	Ni	25.5	3.5	100	0.83	„ „
36	Mn	15	2	100	0.90	„ „
37	Bi	—	—	—	0.90	„ „
38	Cd	—	3.5	—	0.91	„ „

were carried out. For these experiments a specially designed copper column filled with copper sieves was used (Fig. 3).

Procedure. — A 250 cc. round bottom pyrex flask, provided with a dropping funnel, a thermometer, and gas inlet and outlet tubes, was used for evaporation of shale petrol. The flask was heated on a hot plate. From the dropping funnel the crude shale petrol or benzine was dropped into the hot flask. To sweep the oil vapours into the reaction column a stream of illuminating gas was passed into the flask. In some experiments hydrogen was used.

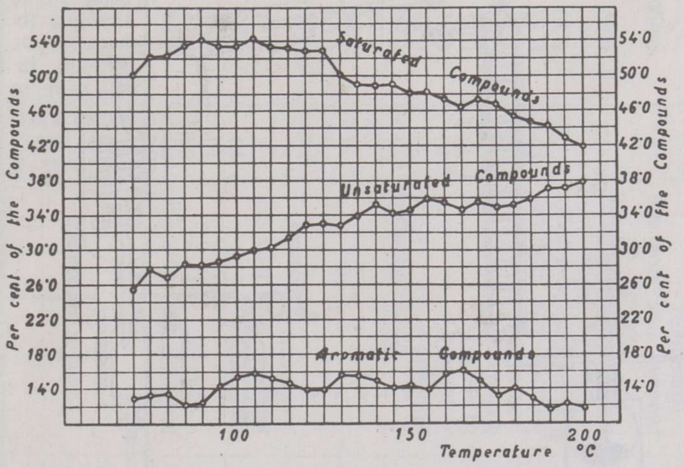

Fig. 2. — *Distribution of Saturated, Unsaturated and Aromatic Compounds in Fractions of Crude Petrol.*

As supporters of the catalysts, copper sieves were placed in the column. The column was electrically heated, the inner temperature varied from 280° to 310° C. The top of the column was connected with the condenser by means of a copper still-head. The receiver attached to the condenser was cooled in a freezing mixture.

Three groups of catalysts were used: metals, metallic oxides and salts. Some results of a great number of experiments are given in Table IV.

The experiments showed that the most active catalysts were copper and nickel; but even these catalysts lose their activity rapidly. After a few runs a certain state of equilibrium, or a "limit of saturation," between the catalyst and absorbed sulphur is reached; beyond this limit, during further runs, the catalyst begins to give off the sulphur. A blank experiment (No. 9) on a mixture of Kahlbaum's "normal benzine" and amylene confirmed this: on leading the vapour of the mixture (containing 0.06 per cent. of S) over a "saturated catalyst" the reaction product showed a much higher content of sulphur, *i. e.*, 0.08 per cent., and in another experiment a still higher percentage of sulphur.

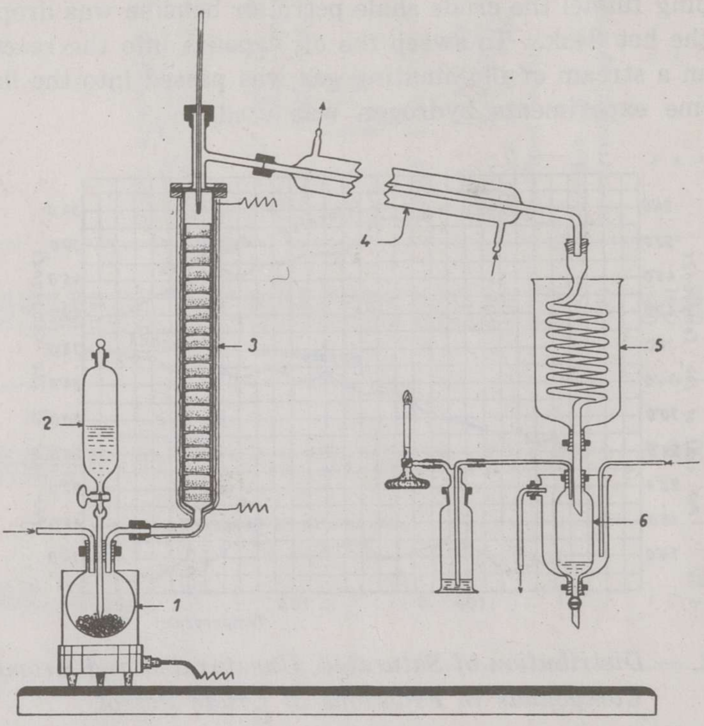

Fig. 3. — *Apparatus for Desulphurisation of Shale Petrols in Vapour-phase.* 1. *Flask.* 2. *Graduated cylinder.* 3. *Reaction column.* 4. *Condenser.* 5. *and* 6. *Receivers.*

The vapour-phase refining does not give satisfactory results from the economic point of view, because it is difficult to regenerate the catalyst.

Table V.

No. of experiment	Amount of petrol taken (c.c.)	Initial pressure in kg/cm^2	Highest pressure during the experiment kg/cm^2	Final pressure	Temp. of experiment (reaction temp.)	Duration (mins.)	Contact substance	Per cent. of the substance taken	Per cent. of sulphur in petrol after reaction in fract. up to 170^0	Per cent. of unsaturated comp.	Per cent. loss	Boiling up to 170^0	Residue boiling below 230^0	Sp. gravity of the petrol (refined)
16	300	0	74	0	390—400	120	reduced bog iron ore	10	0.84	23.4	16			0.7663
17	200	92	222	36	„ „	111	„ „	5.2	0.11	9.8		62.2	10.3	0.7566
18	300	30	104	0	„ „	105	„ „	10	0.24	16.2		57.3	14.3	0.7566
19	207	86	246	60	395—405	110	iron oxide	10	0.37	16.6	15	46.9	14.3	0.7606
20	200	50	139	16	390—400	105	reduced bog iron ore (Estonian)	4	0.31	19.0	13	60.6	15.7	0.7575
21	200	32	110	12	390—398	120	„ „	12	0.45	21.4	8.5	55.7	18.7	0.7594
22	200	89	224	49	390—400	„	„ „	5.5	0.09	14.0	7.5	59.7	17.9	0.7595
23	200	89	226	49	„ „	112	„ „	3.6	0.06	11.0	9.5	58.9	17.1	0.7562
24	199	91	218	42	„ „	110	„ „	2.5	0.20	11.2	7.5	63.4	12.2	0.7637
25	200	92	226	62	„ „	105	„ (from Finland)	9.5	0.35	19.0	14	57.5	20.3	0.7814
26	200	85	236	76	„ „	„	Silicogel	20	0.53	17.6		63.4	12.5	0.7655
27	100	75	182	58	370—390	75	Metallic Na	10	0.01	12.0	5	67.6	9.0	0.7623
28	206	92	210	39	390—400	„	Bi + W	5.3	0.11	10.2	9	65.3	9.6	0.7447
29	200	87	250	73	„ „	60	Metallic Na	1	0.58	19.0	10	57.4	19.4	
30	200	88	219	54	„ „	130	iron oxide	7	0.22	14.6	7	54.0	18.2	0.7373
31	300	86	218	12	„ „	„	reduced bog iron ore	10	0.13	11.2	8	58.5	15.0	0.7367
32	200	94	233		„ „	110	regenerated from Expt. No. 30	5.2	0.40	15.9	9.5	55.5	16.9	0.7497
33	400	60	177	4	380—390	120	regenerated from Expt. No. 31	7.2	0.49	16.8	7.2	51.2	24.4	0.7506
VI	300	88	202	4	„ „	220	reduced bog iron ore (Estonian)	9	0.006				12.8	

II. Desulphurisation of Shale Oils by Hydrogenation.

It has previously been observed that on hydrogenation the sulphur content of oils is reduced.* The object of the experiments described in this paper was to find the conditions for almost complete desulphurisation of shale oil under high hydrogen pressures. The temperature and pressure curves are shown in Fig. 4.

Table VI.

Properties of Crude and Hydrogenated Petrols.

	Colour	Odour	Sp. grav.	n_{20}^{D}	Per cent. of S	Unsatur. cmpds. Per cent.	Arom. cmpds. Per cent.
Hydrogenated b. up to 200^0	colourless	pleasant	0.7505	1.4314	0.000	4.0	10.0
Crude benzine b. up to 200^0	yellow	penetrating	0.7792	1.4386	1.09	35.5	11.0

Table VII.

Engler Distillation of Crude Petrol and of its Hydrogenation Product.

Fractions. ^{0}C.	Crude Benzine up to 200^0 C.				Hydrogenated Benzine up to 200^0 C.			
	Amount g.	Per cent. by weight.	n_{20}^{D}	d_{20}	Amount g.	Per cent. by weight	n_{20}^{D}	d_{20}
1. Up to 100	11.28	14.64	1.4171	0.7309	16.31	22.01	1.4037	0.7018
2. 100—150	39.97	51.86	1.4340	0.7697	37.18	50.18	1.4214	0.7438
3. 150—170	10.30	13.36	1.4484	0.8024	9.93	13.40	1.4370	0 7798
4. 170—200	12.34	16.01	1.4576	0.8194	9.14	12.33	1·4476	0.7980
Residue	2.90	3.76			1.45	1.96		
Total . . .	76.79	99.63			74.01	99.88		
Amount of petrol taken	77.01				74.10			

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* Compare H. G. Shatwell, *loc. cit.*; J. Kopwillem, „Beitrag zur Untersuchung der Estländischen Schieferöle“, Inaug. Dissertation, University of Zürich, 1927. Many patents have been taken out on this aspect.

The experiments were carried out in a revolving steel high-pressure autoclave of about 900 cc. capacity. The autoclave was heated by a gas flame. The particulars of the experiments, showing the effect of temperature, pressure, catalysts, and duration of heating on the sulphur contents in petrol are given in Table V.

From the data given in Table V. it is evident that on hydrogenation the percentage of sulphur in petrol is considerably reduced, and at the same time the "saturation" of the product is increased. The optimum temperature is about 390^{0} to 400^{0} C., and optimum pressure (initial) about 90 to 100 atmospheres. The initial pressure of 32 atm. used by Shatwell* in his experiments must be regarded as too low for a successful desulphurisation of shale oils. The most effective catalysts in our experiments were reduced iron ores (either alone or, even more effective, mixed with a small

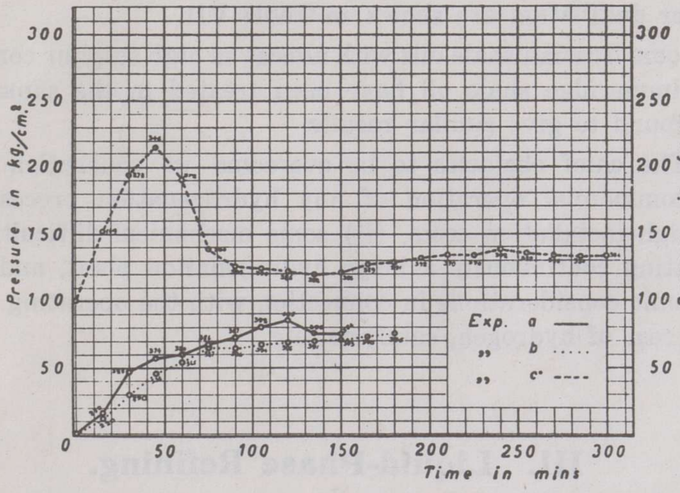

Fig. 4. — *Temperature-pressure Curves.* A. *Blank experiment without hydrogen pressure and without catalysts*; B. *Blank experiment with catalysts (minette not reduced)*; C. *Hydrogenation curve showing effect of time,* i. e., *duration of heating.*

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* *Loc. cit.*

amount of Ni or Cr). The losses caused by inefficient condensation of gases and adsorption on the catalysts undoubtedly could be reduced when working on a larger scale.

Properties of Petrol Obtained on Hydrogenation.

Crude benzine and its hydrogenation product were distilled up to 200° C., washed with 6 per cent. NaOH solution and water, and subjected to Engler distillation. The properties of these two petrols are given in Table VI., and the results of Engler distillation are shown in Table VII.

Some Russian shale oils with almost as high sulphur contents as Kimmeridge shale oil have been treated in the same way and found to give similar results.

The chief obstacles to be overcome in connection with the commercial operation of any hydrogenation process are (i) high installation costs, (ii) some mechanical difficulties in operating continuously a large hydrogenation plant, and (iii) economic considerations in connection with the operating costs, *e. g.*, cost of hydrogen, catalysts, etc.

III. Liquid-Phase Refining.

Comparing the properties of refined shale petrols obtained on usual chemical treatment of crude shale petrol, *i. e.*, alkali and sulphuric acid, clay and acid, hypochlorite, and treatment with certain reagents, it was found that by keeping the refining losses below 12 per cent. the refined product still contained about 0.3 per cent. of sulphur. The hypochlorite process and application of oxidisers gave, with certain shale petrols, fairly satisfactory results, and it seems to the author that investigation in this field might open new possibilities for treatment of shale petrols in liquid phase.

Summarising the expermimental results of all the processes investigated so far at the Oil Shale Research Laboratory, University of Tartu, one cannot fail to observe that the complete desulphurisation of shale petrols is achieved only on hydrogenation, using a large excess of hydrogen, and fairly high initial pressures.

In conclusion, the author desires to record his thanks to Mr. J. Usk, M. Chem., and Dr. J. Kopwillem for experimental assistance, and to the New Consolidated Gold Fields, Limited, London, for financial support.