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Research work on the production of valuable lubricants from crude oil from home sources, carried out on behalf of the Ministry of Transport

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The problem is that of producing valuable lubricating oils from crude oil from home sources by means of selective solvents. In particular, an attempt was to be made to produce automobile lubricants whose viscosity is little affected by temperature and which possess good oxidation resistance.

Two typically German crude oils are available, viz. distillation residues (topped up to about 350°) from Nienhagen and from Wietz.

The first point mentioned in the detailed experimental programme was the setting up of an apparatus in which the asphalt could be precipitated from the above distillation residues by means of propane.

The actual apparatus (compare appended fig.1) consists of a pressure vessel withstanding up to 30 atm. A stirrer is mounted in the pressure vessel; this is driven by a motor by means of a pulley. At different heights in the pressure vessel, six observation windows are provided; pairs always being at the same height so that the inside can be surveyed at every height. At the top of the pressure vessel there is one inlet tube for oil and one for propane and also a safety and an outlet valve. In the lower part outlet valves have been provided at the lowest point and at the sides at slightly higher points.

When the asphalt has been precipitated with propane in the vessel, it is filtered off through a suction filter. An upright cone of wire gauze is placed on top of the filter disc which is covered with a filter cloth. This has the purpose of catching larger lumps of asphalt and thus extending the life of the filter disc.

The treated oil which still contains the propane was collected in a steel bomb from which the propane could be distilled off into the pressure vessel. Mainly Wietzer oil (which contains hardly any wax) was treated in this apparatus. In the Nienhagen oil, a large part of the wax is thrown out of solution together with the asphalt; a mixture of wax and asphalt is therefore collected on the filter. On the other hand the lubricating oil distillate of the Nienhagen oil was treated with propane in the same way; the result was that wax was collected in the suction filter.

The propane de-asphalted Wietz oil showed a somewhat greater viscosity than the lubricating oil distillate obtained from the same residue. Both these oils require, however, treatment with sulphuric acid and fuller's earth or selective solvents before they can be considered useful lubricants. This research is still proceeding and the report on the lubricating oil obtained in this way will be issued later.

In order to distil off the lubricating oil fractions from the available distillation residues an apparatus was designed which had the same characteristics as a large scale plant (see fig.2).

From the storage vessel the distillation residue flows past an observation window and into an electrical heating coil and thence into an evaporation chamber. There the vapours separate from the residue, and are cooled and collected in separate vessels. The apparatus can be evacuated so completely by a rotary oil pump that the distillation

can be carried out at about 400°C at a vacuum of 5 to 7 mm.

About 10 litres of distillation residue were worked in this plant per hour. Under these conditions a final residue was obtained from both distillation residues which is called a hard asphalt. This means that all the lubricating oils which it was possible to obtain from the distillation residue by distilling, have actually been obtained. The distillate from the Wietz oil is more fluid than that from the Nienhagen oil. Part, in any case, of the distillate of the Wietz oil was sent through the processes of the plant once more and a low-boiling fraction was separated; the remainder left after this stage had about the same viscosity as the distillate of the Nienhagen oil.

Since the distillate from the Nienhagen oil is very rich in paraffins it was generally freed from paraffins before any further processing. This was done by diluting with a mixture of benzene and acetone and cooling to about -20°C; the whole was then filtered in a refrigerator when the paraffin was retained. The benzene-acetone mixture was subsequently distilled off again.

In one case the distillates prepared in this way were treated with 5% concentration sulphuric acid at 50 to 60°C, acid resins were separated and the distillate then treated at 105° with 3% fuller's earth.

The distillates were treated with selective solvents in the following manner: generally the first step was that 1 litre of oil was shaken with 1 litre of the solvent in a separating funnel at room temperature. If two layers are formed on standing, the lower layer, the extract, is separated. The solvent was distilled off from the extract and also from the refined product. The refined product was subsequently treated with 3% sulphuric acid and 2% fuller's earth (temperatures as above). The following physical properties of the refined product were measured: specific gravity, viscosity at two temperatures, viscosity pole height and refractive index. The oxidation properties of many of the refined products were measured in the Indiana apparatus. Where necessary a different temperature was selected for solvent extraction of the oils. Further, many of the refined products were again treated with the same amount of solvent in the same manner.

If Furfurol is employed there is good separation of the extract from the refined product at room temperature. If the extraction is repeated the colour of the refined product becomes progressively lighter. The ageing properties also improve steadily. If one wants to work at higher temperatures one observes that in the first extraction one obtains a clean separation of the two layers only below 50°C. For the second and third extractions the temperatures may be allowed to exceed 50° and rise, say, to 100°C. This is advantageous because it further improves the ageing properties.

The viscosity pole height cannot or can hardly be improved by any further extractions. It can be seen from the accompanying table that only oils having viscosity pole heights slightly above 2.15 can be obtained by extraction from the Nienhagen distillate with furfurol. The ageing stability, i.e. the time in which 1% of asphalt has been formed, can be increased to 100 hours without the losses incurred in refining amounting to more than about 30%.

Furfurol is accordingly quite well suited for the production of lubricating oils (satisfying the conditions mentioned above) from the treated German crude oils. If, however, one requires the oils not to exceed the viscosity pole height of 2.0 this cannot probably be achieved with the use of furfurol.

Nitrobenzene is frequently employed in America; it failed, however with the oils available here. It was very difficult or impossible to distil off the nitrobenzene completely from the refined products which had been treated in the above manner. When the after-treatment with sulphuric acid was carried out the nitrobenzene changed into a semi-solid mass from which it was hardly possible to obtain any more oil by centrifuging. Difficulties with nitrobenzene were experienced during the extraction: the extract and the refined product did not separate at room temperature and when the whole was cooled the nitrobenzene crystallized out. The separation could however be effected by adding 10% methyl alcohol or similar substance.

In order to eliminate the nitrobenzene from the refined product one has to make a steam distillation! As the mixture of nitrobenzene and methanol did not yield a refined product the viscosity pole height of which was particularly good and as furthermore the yields were bad, the solvent was not used any further.

β-β-dichloro-diethyl ether, called "chlorex", on the other hand, is relatively well suited as a selective solvent even for the treated oils, i.e. the layers of refined product and of the extract give comparatively clean separations both at room temperatures and at higher temperatures. With this solvent it was also not possible to exceed a limiting value of 2.15 for the viscosity pole height of the Nienhagen oil; the oxidation stability could however still be increased by further extractions.

The properties of the oils treated with chlorex have been quoted in the accompanying table. The work on this solvent has not yet been concluded.

This solvent would not qualify for large scale production either because the yield becomes very bad in a very short time without the refined product improving very much.

It was also attempted to continue the treatment which had been begun with furfurol and nitrobenzene by extracting with chlorex. The nitrobenzene may quite well be used in this case. It was found however that no particular advantage is gained by this change of solvent: the lower limit of the viscosity pole height reached with furfurol again could not be exceeded.

Apart from the three solvents mentioned above a large number of tests were devoted to numerous other organic liquids in order to determine whether it would not be possible to attain a considerably lower viscosity pole height.

Both phenol and cresol are much used in America. They are not particularly suitable for the oils treated by us since in these oils also the separation of the layers leaves much to be desired. The properties of the refined products obtained with these solvents are not particularly good (see table).

Salicyl aldehyde proved to be the only solvent which allows one to obtain a viscosity pole height only slightly exceeding 2.0.

The so-called Duo-Sol method was applied in further experimental series, i.e. the oil was treated simultaneously with both propane and a mixture of tricresol and phenol. It appears that the viscosity pole height even of the Wietz oil may be reduced to 2.1 by means of this treatment.

In place of the mixture of phenol and cresol one may also use furfurol in conjunction with the propane; this has no advantage as compared to the use of furfurol alone, at any rate for working up the distillate. One can also use the Duo-Sol method for working the crude distillation residues. With, e.g. 100% furfurol and 150% propane one obtains a refined product with comparatively favorable properties. In the course of this process the hard asphalt separates in coarse lumps and it may therefore be filtered off easily. It seems that heavier and more viscous oils may be obtained by this method of working up the distillation residues than by further distillation.

The work on the Duo Sol method is still proceeding so that more will be reported on it later.

The experiments described so far were carried out with single or repeated extractions of the oil. In order to simulate the conditions of large scale operation an apparatus was constructed in which the oil penetrates through several layers of furfurol and each time separates from the extract.

The appended fig.3 shows the path of the oil which is being treated; from the dropping funnel at the left it enters at the bottom of the left tube, then rises and by passing through a connecting piece enters the second tube, etc., until it arrives in the collection vessel. The furfurol from the tube on the left is withdrawn from time to time, the furfurol of the consecutive tube, then goes back to the preceding one and the last tube is filled with fresh furfurol. Just as in the large scale contraflow apparatus the oil first comes into contact with furfurol which has already been used, i.e. an extract and only in the end passes through pure furfurol. In a large water-bath it is possible to raise the temperature of the extraction tubes up to 100°C.

The work on this apparatus is also still proceeding, so that later reports on the experiments will be issued.

NIENHAGEN OIL

Treatment	Spec. Grav.	Visc. cs in °E 20°C	168°C	100°	VPH	Refr. Index	Indiana time (h)	Setting Pt. °C	Yield
Refined product with 5% H_2SO_4 and fuller's earth	0.930	1068	3.98	2.55	2.35	1.5216	35.7		90%
Furfurol 100% 1st extract. 20°C	0.926	1000	3.77	2.5	2.4	1.5174	50	-10.5	82%
Furfurol 100% 2nd extract. 20°C	0.915	690	3.48	2.25	2.23	1.5100	83.8	-10.0	78.5%
Furfurol 100% 3rd extract. 20°C	0.913	703	3.48	2.25	2.24	1.5089	88.8	- 6.5	72%
Furfurol 100% 1st extract. 50°C	0.920	681	3.11	2.1	2.5	1.5151	-	-14.0	82%
Furfurol 100% 2nd extract. 50°C	0.911	524	3.2	2.07	2.2	1.5063	-	-11.5	78%
Furfurol 100% 3rd extract. 50°C	0.905	447	3.03	1.97	2.2	1.5030	-	-12.5	70%
Crude oil + 100% Furfurol + 100% Propane 3rd extr. 5% H_2SO_4	0.913	930	3.63	2.4	2.45	1.5122	-	-	ca 50%
Mix. of Nitrobenzene + 1 Methanol 2 : 3 oil	0.921	933	3.93	2.49	2.29	1.5138	-	-	60%
With Chlorex 100% (β-β-Dichlorethyl ether at 20° 2nd extraction	0.920	802	3.62	2.3	2.35	1.5159	-	-11.5	60%
100% Chlorex, 3rd extraction 20°C	0.905	520	3.51	2.18	2.15	1.5074	-		45%
100% Chlorex 3rd extraction @ 20°C	0.903	495	3.42	2.12	2.12	1.5070	-	-	25%
Phenol (100%) oil 1 : 1	0.919	996	3.90	2.50	2.33	1.5144	-	-	63%

WIETZER OIL

Treatment	Spec. Grav.	Visc. cs in °E 20°C	168°C	100°	VPH	Refr. Index	Indiana time (h)	Sett. Pt °C	Yield
Distillate with only 5% H_2SO_4 and fuller's earth	0.931	657.2	3.40	3.40	2.36	1.5200	31.5	-3.5	--
Crude oil + 200% Propane 1st extr. 5% H_2SO_4 + fuller's earth	0.929	1280	4.68	3.0	2.28	1.5175	-	-	--
Furfurol 100% 1st extr. at 20°C	0.915	357.2	2.72	1.83	2.2	1.5111	46.8	-3.0	90%
Furfurol 100% 2nd extr. at 20°C	0.911	327.4	2.72	1.82	2.2	1.5087	69.5	-2.0	83%
Furfurol 100% 3rd extr. at 20°C	0.910	242.0	2.49	1.70	2.06	1.5085	63.8	-2.0	80%
Furfurol 100% 1st extr. 20° 2nd 50°	0.980	602	3.77	2.3	2.0	1.5178	77.3	-2.0	75%
Furfurol 100% 1st extr. 20° 1st 35° 1st 45° 1st 55°	0.905	610	3.53	2.22	2.15	1.5151	88.2	-2.5	70%
Nitrobenzene + Methanol (4 : 1) 2nd extr.	0.908	182.5	2.23	1.65	2.1	1.5071	-	-	69%
Phenol (95%) 1 : 1 at 20° 1st extr.	0.923	858.0	3.52	2.3	2.5	1.5198	52.0	-1.5	80%
Phenol (95%) 1 : 1 at 20° 2nd extr.	0.918	791.1	3.83	2.3	2.2	1.5165	56.5	-1.0	75%
100% Tricresol:Phenol (1:1) + 100% Propane 1st extr.	0.910	590.1	3.48	2.2	2.12	1.5170	-	0	ca 60%
100% Furfurol + 100% Propane 1st extr.	0.925	679.3	3.30	2.2	2.4	1.5194	54.2	-1.0	85%
Crude oil + 100% Furfurol + 150% Propane 1st extr.	0.915	569.6	3.43	2.18	2.11	1.5190	-	-5.0	ca 40%