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METHOD OF PROCESSING LUBRICATING OIL BY SOLVENT-EXTRACTION AND TREATING WITH A PHOSPHORUS SULFIDE AND CLAY AND THE RESULTING PRODUCTS

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This invention relates to processes of improving hydrocarbon base lubricants, and more particularly to subjecting hydrocarbon lubricant stocks to a conventional solvent refining treatment, and then to the treatment of the solvent refined hydrocarbon with a small amount of a phosphorus sulfide. A clay treatment before and after the sulfide refining is included and the refined lubricants have improved properties, especially as to corrosion, lacquer, sludge, viscosity increase, and the like characteristics. It also relates to the resulting improved lubricants.

Many of the commercially used lubricants are based upon hydrocarbon stock, whch may be synthetically prepared or which may be derived from natural sources, such as petroleum. For many purposes so-called "additives" must be included with the hydrocarbon in order to provide a lubricant having particularly desirable characteristics. This is especially so in the case of solvent refined oils which are known to be corrosive. Generally, the addition of these additives is associated with a higher cost of the finished lubricant. The preparation of a finished lubricant directly from hydrocarbon stock by a chemical finishing or refining process at a commercially interesting cost has been an especially hard problem in this art.

In accordance with the invention, it has been found that hydrocarbon lubricating oil stock may be extracted with an aromatic removing solvent such as sulfur dioxide, furfural, phenol or the like, in the known manner, and the resulting solvent refined raffinate is treated with a small amount of a phosphorus sulfide. A clay treatment after or before and after the sulfide refining is included. The resulting refined oil is an improved lubricant; i. e., a chemically finished or refined lubricant. Such lubricants are suitable for use under various conditions, including high temperatures or high pressures or both; as, for instance, use in an internal combustion engine operating at high temperatures and in which the lubricant is in close contact with metallic surfaces, metal compounds and high temperature gases. They are also suitable for use in extreme pressure lubricants, e. g., in oils and greases containing them.

Treatment of the hydrocarbon oil with the solvent may be carried on in the conventional manner, e. g., in accordance with modern methods of refining lubricating oil. In general, the solvent tends to remove aromatic, unsaturated, and low viscosity index constitutents and these are separated from the oil. The step is well known in the art of solvent refining or solvent extraction and need not be further described here. The resulting solvent refined hydrocarbon oil is further refined with a phosphorus sulfide. This may be

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conducted with direct admixture, or, if desired, by their admixture in the presence of a diluent which may be subsequently removed. Generally, a diluent is not necessary. The sulfide treating step is usually complete in about 10 hours or less time, generally 1 to 2 hours. The treating time is a function of the temperature, the amount of sulfide that is to react, the subdivision of the reactants, the efficiency of mixing the reactants, and the like.

The solvent refined hydrocarbon lubricant stock is reacted with the phosphorus pentasulfide in a ratio of from about 0.1 to about 0.75% by weight, based on the weight of the hydrocarbon stock, desirably about 0.25 to about 0.6%. At least about 0.1% of the sulfide should be used to achieve the results desired on a commercial scale, although small amounts show improvement.

The treatment of the hydrocarbon with the phosphorus sulfide may be carried out in the presence or absence of air, or in an atmosphere of inert or non-deleterious gas, such as nitrogen or H_2S. It may also be carried out under pressure, e. g., pressure of the inert gas or that generated when the reaction is carried out in a closed vessel.

The sulfide treating temperature varies with the hydrocarbon lubricating stock. Generally, the temperature should be at least 275° F., but should be below the temperature at which the reaction product would be decomposed. A temperature in the range of about 300° to about 450° F. is preferred in many cases. The treated oil mass is preferably centrifuged or filtered to remove any by-products, sludge, or other by-product material. If a volatile diluent is used, it may be removed by evaporation.

The clay treatment, which is the third essential step of the process, is carried out after the sulfide treatment and is accomplished by treating the oil with 1 to 25 pounds of clay per barrel of oil. The temperature is usually in the range of 100 to 350° F. The clay is separated by filtration. The treatment may be before as well as after the sulfide refining.

The hydrocarbon lubricant stock to which the process is applied may be a raw oil, i. e., a fluid hydrocarbon having a viscosity at 100° F. of 10 to 500 centistokes, such as that used as the base for the S. A. E. 10 to 50 oils. It may be obtained as a distillate or from synthetic material, such as petroleum, and oils produced by cracking, polymerization, hydrogenation, and the like methods.

In order to illustrate and point out some of the advantages of the invention, but in no sense as a limitation thereof, the following specific embodiments are included.

In the following Examples 1 to 6 #300 Red Oil (a conventional Mid-Continent lubricating oil

base stock, of 20–30 S. A. E. viscosity) is used as the hydrocarbon oil stock. The raw oil is solvent refined with furfural in a conventional manner, using 50% to 1000% of solvent based on the oil, and the extract and solvent are separated. The solvent refined hydrocarbon oil is then mixed with the kind and amount of phosphorus sulfide indicated in the following table, agitated for 1 hour at 300° F., at atmospheric pressure. A good yield is obtained, based on the hydrocarbon lubricating oil, and no sludge is formed in the phosphorus sulfide treating step. However, it is preferred to filter the final reaction product. In some of the examples, the clay treatment is used before (column 2), as well as after (last column) the phosphorus sulfide treatment, using the amounts of clay as indicated in the following table. For comparison, samples A, B and C are included. The reaction product is identified hereinafter by the example number.

Example Number	Solvent Extraction	Clay in Lbs. per Barrel of Oil	Kind and Amount of Phosphorus Sulfide in Per Cent by Weight of Hydrocarbon Oil	Clay in Lbs. per Barrel of Oil
1	Yes	8	0.4% P_2S_5	5
2	Yes		0.2% P_4S_3	10
3	Yes		0.4% P_4S_3	10
4	Yes		0.2% P_4S_3	5
A	No	none	none	none
B	No	none	none	8
C	Yes	8	none	15

The "Sohio" corrosion test was used in evaluating lubricants made in accordance with the invention. This test is described in a co-pending application of E. C. Hughes, J. D. Bartleson, M. L. Sunday and M. M. Fink, which also correlates the results of the laboratory tests with a Chevrolet engine test.

Essentially the laboratory test equipment consists of a vertical thermostatically heated glass test tube (45 mm. outside diameter and 42 cm. long), into which is placed the corrosion test unit. An air inlet is provided for admitting air into the lower end of the corrosion unit in such a way that in rising the air will cause the oil and suspended material therein to circulate into the corrosion unit. The tube is filled with an amount of the oil to be tested which is at least sufficient to submerge the metals being tested.

The corrosion test unit essentially consists in a circular relatively fine grained copper-lead test piece of $\frac{3}{16}$'' O. D., which has a $\frac{1}{4}$'' diameter hole in its center (i. e., shaped like an ordinary washer). The test piece has an exposed copper-lead surface of 3.00 sq. cm. Of this surface area, 1.85 sq. cm. acts as a loaded bearing, and is contacted by a part of the cylindrical surface of a hardened steel drill rod (14'' diameter and $\frac{3}{32}$'' long, and of 51–57 Rockwell hardness).

The drill rod is held in a special holder, and the holder is rotated so that the surface of the drill rod which contacts the bearing sweeps the bearing surface (the drill rod is not rotated on its own axis and the surface of the drill rod which contacts the bearing is not changed).

The corrosion test unit means for holding the bearing and the drill rod is a steel tubing (15'' long and $1\frac{1}{32}$'' O. D.) which is attached to a support. A steel cup (1'' long, $1\frac{1}{32}$'' O. D. by $\frac{3}{16}$'' I. D.) is threaded into the steel tube, at the lower end. The cup has a $\frac{3}{8}$'' diameter hole in the bottom for admitting the oil into the corrosion chamber. The copper-lead test piece fits snugly into the steel cup and the hole in the test piece fits over the hole in the steel cup. A section of steel rod ($\frac{3}{8}$'' in diameter and 19'' long) serves as a shaft and is positioned by 2 bearings which are fixedly set in the outer steel tubing, one near the top and one near the lower (threaded) end thereof. Several holes are drilled just above and just below the lower bearing. The holes above the bearing facilitate cleaning the apparatus, while the holes below the bearing enable the circulation of oil through the corrosion chamber. The drill rod holder is connected to the shaft by a self-aligning yoke and pin coupling. This assures instantaneous and continuous alignment of the drill rod bearing member against the bearing surface at all times. A pulley is fitted to the top of the steel shaft and the shaft is connected therethrough to a power source. The shaft is rotated at about 675 R. P. M.; and the weight of the shaft and attached members is about 600 grams, which is the gravitational force which represents the thrust on the bearing. The air lift from the air inlet pumps the oil through the chamber containing the test piece and out through the holes in the steel tubing.

The ratios of surface active metals to the volume of oil in an internal combustion test engine are nearly quantitatively duplicated in the test equipment. The temperature used is approximately that of the bearing surface. The rate of air flow per volume of oil is adjusted to the same as the average for a test engine in operation. Of the catalytic effects, those due to soluble iron are the most important. They are empirically duplicated by the addition of a soluble iron salt. Those due to lead-bromide are duplicated by its addition.

The test was correlated with the L–4 Chevrolet test, and a slightly modified version thereof. The modified test comprised reducing the oil additions from the 4 quarts in the usual procedure to 2 quarts, by reducing the usual 1 pint oil additions which are made at 4 hour intervals to ½ pint additions. This modification increases the severity of the test in its corrosion and detergency components, particularly in the case of border line oils.

For each test, the glass parts are cleaned by the usual chromic acid method, rinsed and dried. The metal parts are washed with chloroform and carbon disulfide and polished with No. 925 emery cloth or steel wool. A new copper-lead test piece is used for every test. The test piece is polished before use, on a surface grinder to give it a smooth finish. The test piece is weighed before and after the test on an analytical balance to evaluate the corrosion. After placing the oil and corrosion test unit in the tube, and bringing the assembly up to temperature in the thermostat, soluble catalyst is added and the air flow is started. Lead-bromide catalyst is added immediately after starting the air, and timing of the test is begun.

The laboratory test conditions which were found to correlate with the Chevrolet procedure 36-hour test are shown in the following table:

Table A

Temperature—325° F.
Oil sample—107 cc.
Air flow rate—70 liters/hour
Time—10 hours
Catalysts—Steel; copper-lead bearing: 3 sq. cm. area of which 1.85 sq. cm. is a bearing surface;

ferric 2-ethyl hexoate: 0.05% as Fe_2O_3 in C. P. benzene; lead bromide: 0.1% as precipitated powder.

Bearing assembly:

Load	grams	600
Speed	R. P. M.	675

By extending the laboratory test to 20 hours, it was found that correlation with the Chevrolet 72-hour test could be obtained.

At the close of the test period, the extent of corrosion is determined by reweighing the corrosion test piece and determining the change in weight due to the test. An accurate evaluation of the lacquering properties of an oil is obtained by a visual rating system which is applied to the outer surface of the corrosion unit steel tube and metal cup in much the same way that the piston skirt, cylinder wall, etc., of an engine are rated for varnishes. The sludge rating of the engine is simulated by a visual rating of the insoluble materials and used oil which are coated on the glass test tube at the conclusion of the test. For both sludge and varnish rating a scale rating A (best) to F (worst) is used.

A sufficient volume of used oil is obtained from the test for determination of the usual used oil properties, such as pentane insoluble (sludge), viscosity increase, neutralization number and optical density.

The term "optical density," as used in the present disclosure, represents the standard logarithmic ratio of intensity of an incident ray falling on a transparent or translucent medium to the intensity of the transmitted ray for a sample length of one meter and light of wave length from 5100 to 5500 Angstroms.

The data in the following tables typify the results obtained in 20-hour "Sohio" corrosion tests on the hydrocarbon lubricating oil base stock, and the improved lubricants prepared therefrom in accordance with the invention.

Table I

Lubricant—Example No.	A	1	2	3	4
Corrosion of Cu-Pb (in mgms. weight loss of)	28.1	12.1	5.2	5.4	23.7
Viscosity Increase (SUS)	938	186	154	261	457
Pentane Insolubles (in mgm/10 g. of lubricant)	895	84.0	37.3	94.7	190.2
Acid Number	5.39	2.9	0.73	1.51	4.1
Sludge Rating	D−	A	A−	A−	A−
Lacquer Rating	E	B+	A−	A−	A−

Table II

Lubricant—Example No.	A	B	C
Corrosion of Cu-Pb (in mgms. weight loss of)	28.1	49.5	45.4
Viscosity Increase (SUS)	938	1,168	4,700
Pentane Insolubles (in mgm/10 g. of lubricant)	895	699	7.7
Acid Number	5.39	6.64	11.5
Sludge Rating	D−	E	E
Lacquer Rating	E	A+	A−

The above data clearly show that the reaction products of the invention are markedly superior to the blank oil as lubricants; especially as to corrosion, viscosity increase, and pentane insoluble characteristics. Examples 2, 3 and 4 show results with one clay treatment at the end.

In the clay treatment, generally the amount of clay is in the range of about 2 to about 10 lbs. per barrel of oil, preferably at least 5 lbs. If too large an amount of clay is used, the resulting product is less desirable, and may even be worse than the starting oil as to some characteristics.

Example B, in which raw oil is only clay treated, is inferior to the untreated oil in corrosion, viscosity increase and sludge rating. Example C, which is solvent extracted and given two clay treatments, shows abnormally high viscosity increase. This shows the beneficial effect of the sulfide refining in combination with the solvent refining and clay treatment in accordance with the invention.

By comparable procedures, using any known comparable phosphorus sulfide, or amount of phosphorus sulfide, or hydrocarbon lubricating oil stock, within the broad types and ranges as indicated hereinbefore, comparable improved lubricants are obtained.

If desired, the improved lubricants of the invention may be used in blends together with other lubricants or lubricant agents, e. g., with soap or the like in a grease. If desired, an agent for improving the clarity of the oil may be included, e. g., lecithin, lauryl alcohol, and the like. If desired, an agent for preventing foaming may be included, e. g., tetra-amyl silicate, an alkyl ortho-carbonate, ortho-formate or ortho-acetate, or a polyalkyl silicone oil.

In view of the foregoing disclosure, variations and modifications of the invention will be apparent to those skilled in the art, and it is intended to claim such variations and modifications broadly, except as do not come within the scope of the appended claims.

I claim:

1. A method of processing lubricating oil stock consisting essentially of hydrocarbon material to yield an oil having improved inhibition to oxidation in service, which method comprises solvent-refining said stock, treating the resulting solvent-refined hydrocarbon with an amount of a phosphorus sulfide in the range of about 0.1 to about 0.75% by weight at a temperature in the range of about 275° to 450° F., and then treating the resulting product with clay.

2. The method of claim 1 wherein the solvent-refined hydrocarbon is treated with phosphorus pentasulfide at a temperature in the range of about 300° to 450° F.

3. The method of claim 1 wherein the solvent-refined hydrocarbon is treated with phosphorus sesquisulfide at a temperature in the range of about 300° to 450° F.

4. The method of claim 2 wherein the solvent-refined hydrocarbon is treated with clay prior to the treatment with the phosphorus pentasulfide, and then again subsequent to said treatment with phosphorus pentasulfide.

5. The lubricating oil obtained by the process of claim 1.

6. The lubricating oil obtained by the process of claim 2.

7. The lubricating oil obtained by the process of claim 3.

8. The lubricating oil obtained by the process of claim 4.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,316,091	White	Apr. 6, 1943
2,393,335	Musselman	Jan. 22, 1946
2,398,429	Hughes	Apr. 16, 1946
2,419,584	Noland	Apr. 29, 1947