Patented Sept. 4, 1951 2,566,398

UNITED STATES PATENT OFFICE

2,566,398

LUBRICANTS AND LUBRICANT ADDITIVES

John D. Bartleson, East Cleveland, and Herman P. Lankelma, Shaker Heights, Ohio, assignors to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application June 7, 1947, Serial No. 753,364

2 Claims. (Cl. 252—46.6)

1

This invention relates to lubricants and lubricant additives comprising a reaction product of an alcohol with a preformed reaction product of an olefin with a phosphorus sulfide.

Lubricants made in accordance with the invention are relatively non-corrosive and non-lacquer forming. They 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.

The art appreciates that many diverse factors are involved in attaining a single lubricating oil addition agent which imparts to the oil little or no lacquer formation and also shows little or no deterioration or corrosion of metals, especially bearing metals with which the lubricant comes in contact, as well as low oxidative deterioration, as indicated by low viscosity increase, sludge formation, etc. It is very difficult to produce a single addition agent which is nearly optimum for all these factors, especially at a commercially interesting cost.

The art is confronted with the problem of producing a low cost additive for lubricating oils and greases, and one approach to this problem is to prepare the desired composition from low cost raw material.

In accordance with the invention, it has been found that the reaction product of an olefin with a phosphorus sulfide may be further reacted with an alcohol, and the resulting reaction product is an excellent lubricant or additive for lubricants. These reaction products have good solubility in oils and greases, and improve the corrosion, lacquer, sludge, viscosity increase, and the like characteristics thereof.

The objects achieved in accordance with the invention include the provision of an agent which may be useful itself as a lubricant, and which when added to lubricants will markedly inhibit the very objectionable deposition of lacquer, and, at the same time, inhibit acid and sludge formation, corrosion and other types of deterioration occurring under operating conditions; the provision of lubricating oils containing an ash-free addition agent; and other objects which will be apparent as embodiments of the invention are disclosed hereinafter.

The primary phosphorus sulfide-olefin reaction product may be made with direct admixture of the reactants, or, if desired, by their admixture in the presence of a diluent which may or may not be subsequently removed. A heavy oil such as white oil, or a lubricating oil having about the same properties as that to which the new composition is to be added may be used as a diluent. The reaction is usually complete in about 10 hours or less time. The reaction time is not critical and is a function of the temperature, the amount of the sulfide that is to react, the subdivision of the reactants, the rate of stirring, etc., as will be understood in the art.

2

The olefin or mixture of olefin may be reacted with the phosphorus sulfide or a mixture of phosphorus sulfides in mol ratios from 1 to 3 mols of mono-olefin per mol of the phosphorus sulfide, preferably 2 mols of mono-olefin per mol of phosphorus sulfide; if a di-olefin is used, the amount of di-olefin would be half of the above; if a tri-olefin, one third of the above, and so on. An excess of either reactant may be used if desired, e. g., for commercial reasons.

Phosphorus pentasulfide is preferred although other phosphorus sulfides or mixtures of sulfides may be employed. Phosphorus pentasulfide is most economic and readily available and for this reason is used in the illustrative examples. Under suitable conditions sulfides of arsenic or antimony may be similarly employed.

In general, olefins having at least about 4 to 6 carbon atoms in the molecule are suitable. As an upper limit, the high molecular weight olefin polymers are also suitable. These olefin polymers may be prepared by the polymerization of low molecular weight olefins, as is known to the art. Their molecular weight generally ranges above about 60, preferably about 125 to 300 and such polymers are known which have a molecular weight in the range of about 3,000 to about 50,000.

The advantages of the invention are particularly apparent in the case of products obtained from olefins having from about 6 to about 25 carbon atoms in the molecule. A commercially desirable olefin is so-called "motor polymer" or "reduced motor polymer." Motor polymer is usually made from C_3 and C_4 olefins by non-selective polymerization, e. g., with a phosphorus acid type catalyst. Motor polymer boils in the range of 80° to 500° F. with a major portion in the range of 120° to 400° F. A polymer gasoline fraction may be removed therefrom by fractional distillation to the 250° F. cut point, or thereabouts, and this reduced form motor polymer is particularly useful. Its average molecular weight is about 145 and it preferably contains a major amount of highly branched olefins boiling below 600° F. The olefins used should be of a sufficiently high or suitable molecular weight to give a final product having the desired oil dispersibility.

The reaction 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 generated when the reaction is carried out in a closed vessel.

A reaction temperature in the range of 200° to 500° F. is suitable, although a higher temperature which is below that at which the reaction product would be decomposed could be used. A temperature in the range of 300° to 400° F. is preferred.

If desired the primary reaction product may be filtered but generally a sludge is not formed. If one is formed it may be removed by centrifuging or filtration or may remain and be removed after the next step.

The primary phosphorus sulfide-olefin reaction product is then treated with one or more alcohols, or mixtures thereof, i. e., aliphatic, aromatic, cycloaliphatic, alkyl, and heterocyclic compounds containing at least one alcoholic group, and preferably one to twelve carbon atoms per molecule. Hydrocarbon alcohols are preferred, such as aliphatic, alicyclic, aromatic, aryl-alkyl, etc., alcohols. These alcohols may be illustrated by the following: methanol, ethanol, isopropanol, normal propanol, a butanol, a pentanol, an isopentanol, a cyclohexanol, a benzyl alcohol, phenyl ethyl alcohol, phenol, a methyl phenol, a polyalkyl phenol, ethyl phenol, diethyl phenol, alkoxy phenols, methoxy phenol, alkoxy aliphatic alcohols, such as methoxy ethyl alcohol and phenoxy ethyl alcohol (such as those sold as "Cellosolves"), polyhydric alcohols, ethylene glycol, diethylene glycol, propylene glycol, glycerine, resorcinol, and (ring) alkyl substituted recorcinol, phloroglucinol, and the like alcohols. The word "alcohol" is used in its generic sense to include any of the above types om compounds, and corresponding compounds containing substituents which are inert under the conditions of the reaction with the sulfide-olefin reaction product. The alcohol used in forming the final reaction product should be selected with reference to the use of the final composition and the properties desired in it, e. g., oil solubility or dispersibility.

The reaction of forming the final reaction products may be carried out at the same temperature range discussed above for the primary reaction step. This reaction is usually completed in about 10 hours or less time, and the same factors as to reaction time are involved as discussed hereinabove. The second reaction step may be started under reflux conditions, the reflux temperature rising as the reaction proceeds, and then under pressure in order to carry the reaction to final completion.

The amount of the alcohol used is not critical. Even small amounts show a significant improvement. An excess of a volatile alcohol may be removed after formation of the secondary reaction product. A suitable amount of alcohol is that stoichiometrically equivalent to the saponification number of the primary reaction product, although an excess which is removed or which remains is generally not harmful.

The final reaction mass is preferably centrifuged or filtered to remove sludge, which is formed as a by-product. Any excess of a volatile reactant, or a volatile diluent, may be removed by vacuum distillation. If desired, the resulting product may be further refined by solvent extraction, e. g., with liquid propane, or with isopropyl alcohol.

The amount of the final reaction product, i. e., the additive, to be incorporated in an oil or grease will depend upon the characteristics of the oil or grease and the intended use. Some oils have more of a tendency to corrode metals, or to form acids, sludges and lacquer deposits than others, and such oils require larger quantities of the addition agent. Also, oils that are intended for higher temperature require larger amounts of the additive. In general, the range is from about 1 to about 10%; under some circumstances, amounts as low as about 0.01% show a significant improvement. Since the secondary reaction product is a lubricant, there is no upper limit. However, it may be uneconomical to include in the lubricant more of the secondary reaction product than is necessary to impart the desired properties.

The following working examples illustrate the scope of the invention:

A conventional petroleum base lubricating oil containing 0.1 to 10% of any one of the following compositions (all parts or percentages are by weight unless otherwise indicated herein)

1. Reaction product of 1 to 10 parts of cyclohexanol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of motor polymer, all reacted at a temperature in the range of 250° to 500° F.

2. Reaction product of 1 to 10 parts of glycerol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of cetene-1, all reacted at a temperature in the range of 250° to 500° F.

3. Reaction product of 1 to 10 parts of pentaerythritol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of octene-2, all reacted at a temperature in the range of 250° to 500° F.

4. Reaction product of 1 to 10 parts of n-cetyl alcohol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of pentadecene-3, all reacted at a temperature in the range of 250° to 500° F.

5. Reaction product of 1 to 10 parts of resorcinol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of heptadecene-5, all reacted at a temperature in the range of 250° to 500° F.

6. Reaction product of 1 to 10 parts of phenyl ethyl alcohol with one part of the reaction product of 1 mol of P_2S_5 with 0.5 to 1.5 mols of decadiene-2,8, all reacted at a temperature in the range of 250° to 500° F.

7. Reaction product of 1 to 10 parts of ethoxy phenol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of dodecene-4, all reacted at a temperature in the range of 250° to 500° F.

8. Reaction product of 1 to 10 parts of p-(n-amyl)-phenol with one part of the reaction product of 1 mol of P_4S_7 with 1 to 3 mols of n-butyl-cyclohexene, all reacted at a temperature in the range of 250° to 500° F.

9. Reaction product of 1 to 10 parts of benzyl alcohol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of motor polymer, all reacted at a temperature in the range of 250° to 500° F.

10. Reaction product of 1 to 10 parts of n-butanol with one part of the reaction product of 1 mol of P_2S_5 with 1 to 3 mols of decene-2, all reacted at a temperature in the range of 250° to 500° F.

The following specific embodiments and tests further illustrate the invention:

38 parts of P_2S_5 are mixed with 62 parts of reduced motor polymer, and agitated for 8 hours at 350° F. in a pressure reaction vessel, at a pressure of about 100 pounds per square inch. Some gas is vented during the reaction, depending upon the free space in the vessel, in order to maintain this pressure. No sludge is formed, but it is preferred to filter the resulting primary phosphorus sulfide-olefin reaction product. Volatile material can be distilled off if desired.

EXAMPLE I

200 grams of the above sulfide-olefin reaction product is mixed with 80.7 grams of n-octyl alcohol and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. A 74.7% yield of reaction product is obtained. The sludge amounts to 10.7%. The product analyzes 21.32% S and 7.96% P; and its molecular weight is 347 (determined by the cryoscopic method). This product is referred to as additive I hereinafter.

EXAMPLE II (*a*)

600 grams of the above sulfide-olefin reaction product is mixed with 60 grams of methyl alcohol and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. A 77.9% yield of reaction product is obtained. The sludge amounts to 9.5%. The product analyzes 7.18% S and 5.04% P; and its molecular weight is 276. This product is referred to as additive II (*a*) hereinafter.

EXAMPLE II (*b*)

Another preparation was made following the above II (*a*) procedure, but using only 54 grams of methanol. This product is referred to as additive II (*b*) hereinafter.

EXAMPLE II (*c*)

A further preparation was made following the above II (*a*) procedure, but using 66 grams of methanol. This product is referred to as additive II (*c*) hereinafter.

EXAMPLE III

200 grams of the above sulfide-olefin reaction product is mixed with 37.2 grams of n-propyl alcohol and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. An 85.2% yield of reaction product is obtained. The sludge amounts to 11.8%. The molecular weight of the product is 244. This product is referred to as additive III hereinafter.

EXAMPLE IV

400 grams of the above sulfide-olefin reaction product is mixed with 74 grams of iso-propyl alcohol and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. A 76.8% yield of reaction product is obtained. The sludge amounts to 10.4%. This product is referred to as additive IV hereinafter.

EXAMPLE V

400 grams of the above sulfide-olefin reaction product is mixed with 38.5 grams of ethylene glycol and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. An 80.2% yield of reaction product is obtained. The sludge amounts to 18.5%. The molecular weight of the product is 278. This product is referred to as additive V hereinafter.

EXAMPLE VI

600 grams of the above sulfide-olefin reaction product is mixed with 164 grams of commercial amyl alcohol and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. An 84.3% yield of reaction product is obtained. The sludge amounts to 11.8%. The molecular weight of the product is 257. This product is referred to as additive VI hereinafter.

EXAMPLE VII

400 grams of the above sulfide-olefin reaction product is mixed with 116 grams of phenol and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. A 98.5% yield of reaction product is obtained, with no sludge. The molecular weight of the product is 352. This product is referred to as additive VII hereinafter.

EXAMPLE VIII

400 grams of the above sulfide-olefin reaction product is mixed with 180 grams of reduced motor polymer and 22 grams of water (which potentially can react to give the corresponding alcohol) and agitated for 8 hours at 350° F. in a closed reaction vessel, at a pressure of 100 pounds per square inch. Depending upon the free space in the vessel, some vapor is vented during the course of the reaction, in order to maintain this pressure. The reaction product is filtered hot. A 78.15% yield of reaction product is obtained. The sludge amounts to 9.55%. This product is referred to as additive VIII hereinafter.

In testing oils containing addition agents the so-called standardized "Chevrolet Engine Test" is used. In this test, new piston rings and two new copper-lead bearing inserts are installed in the motor prior to each test. The engine is a conventional Chevrolet engine with 216.5 cu. in. piston displacement and a compression ratio of 6.5 to 1. The engine is operated at 3150 R. P. M. with a load of 30 B. H. P. and at a temperature at the jacket outlet of 200° F. The lubricating oil temperature is maintained at 265° F. for an SAE 10 grade oil, and at 280° F. for oils of SAE 30 to 50 grades. The fuel used contains from 2.5 to 3.0 ml. tetraethyl lead per gallon. Besides the weight loss of the test bearings, deposits in the

power section, and properties of the used oil, sampled near the middle and also at the end of the test, are examined.

A conventional acid treated Mid-Continent lubricating oil base stock and blended compositions of this oil made in accordance with the invention were submitted to 36-hour tests in accordance with the above Chevrolet engine procedure. The results given in the following table are typical.

TABLE A

Additive of Example No.	II (*b*)	II (*c*)
Concentration of Additive, in Per Cent by Weight	1.5	3.0
Piston Skirt Rating	6.0	6.50
Varnish Rating	41.25	45.25
Sludge Rating	39.50	41.50
Overall Rating	80.75	86.75
Corrosion of Cu-Pb bearing metal (in mgms. weight loss per bearing half-shell)	4	28
Viscosity Increase	123	79
Pentane Insolubles (mgms.)	1.83	1.25
Acid Number	1.74	0.70

The oil alone does not run 36 hours in the Chevrolet engine. Note particularly the low corrosion characteristic of the oil with 1.5% of the II (*b*) additive.

A conventional solvent extracted lubricating oil base stock (SAE 30) and blended compositions of this oil made in accordance with the invention were submitted to 36-hour tests in accordance with the above Chevrolet engine procedure. The results in the following table are typical.

TABLE B

Additive of Example No.	None	VIII
Concentration of Additive, in per cent by weight	0	1.5
Piston Skirt Rating	9.50	7.00
Overall Rating	92.00	90.50
Corrosion of Cu-Pb bearing metal (in mgms. weight loss per bearing half-shell)	1,428	12.5
Acid Number	2.4	1.6

Note especially the phenomenal decrease (over 100-fold) in corrosion characteristic imparted to the oil by 1.5% of additive VIII. The oil alone, and also the above blend, are generally very satisfactory as to the other characteristics.

Lubricating oils containing representative additives, prepared in accordance with the invention, were also laboratory tested by the Sohio test procedure described in U. S. Patent No. 2,403,474 except that the amount of the iron salt is increased to 0.05% under the "Iron Tolerance" conditions.

"Iron Tolerance" tests were made on a conventional medium duty acid-treated Mid-Continent lubricating oil base stock (SAE30) and compositions of this oil with additives, prepared in accordance with the invention. The results given in the following tables are representative:

TABLE C

Additive of Example No.	None	I	II	III	IV
Concentration of Additive, in Per Cent by weight		3	3	3	3
Corrosion (in milligrams weight loss) of Cu-Pb	9.2	6.2	−0.4	−1.1	−0.9
Viscosity Increase (S. U. S.)	1,540	160	69	69	57
Sludge (Pentane Insolubles) in weight Per Cent	6.87	0.73	0.69	0.70	0.47
Acid Number	7.8	1.6	2.0	2.1	1.7
Lacquer Deposit (mgms.)	12.1	1.2	0.8	1.2	0.5

TABLE D

Additive of Example No.	V	VI	VII	VIII
Concentration of Additive, in Per Cent by weight	3	3	3	4
Corrosion (in milligrams weight loss) of Cu-Pb	−0.5	−3.0	−6.8	−1.4
Viscosity Increase (S. U. S.)	75	71	88	53
Sludge (Pentane Insolubles), in weight Per Cent	0.73	0.64	1.11	0.14
Acid Number	1.6	2.1	1.5	2.0
Lacquer Deposit (mgms.)	0.6	1.0	1.6	0.5

The above tables C and D illustrate the marked improvements imparted to the lubricating oil by the additives of the invention, especially as to the viscosity increase characteristic, and also corrosion, lacquer and sludge characteristics.

The additives of the invention may be used in combination with other additives.

The above working examples and specific embodiments are for illustrative purposes only and are not intended as limitations of the invention. In view of the foregoing disclosures, the art will clearly understand the invention in its broad aspects, including variations and modifications thereof.

In some instances, it is desirable to include in a lubricating oil containing the additive an agent for improving the clarity of the oil, e. g., lecithin, lauryl alcohol, and the like, which agents are known to the art. In order to prevent foaming of the oil containing a small proportion of the additive, it is desirable in some cases to add a very small amount of tetra-amyl silicate, alkyl ortho carbonate, ortho formate or ortho acetate, or a polyalkylsilicone oil, for preventing foaming upon bubbling of air through oil containing a few per cent of the additive.

It is intended to claim the invention broadly, except as limited by the following claims.

We claim:

1. An oil-dispersible product of the reaction at 350° F. for eight hours of 1.15 moles ethyl alcohol to each mole of a reaction product of 1 mole of phosphorus pentasulfide and 1.5 moles of "reduced motor polymer" reacted together at 350° F. for eight hours to produce an oil-dispersible material suitable for improving the characteristics of a mineral lubricating oil.

2. A lubricant comprising a mineral lubricating oil and an amount sufficient to inhibit the oxidative deterioration in use of the oil of an oil-dispersible product of the reaction at 350° F. for eight hours of 1.15 moles ethyl alcohol to each mole of a reaction product of 1 mole of phosphorus pentasulfide and 1.5 moles of "reduced motor polymer" reacted together at 350° F. for eight hours to produce an oil-dispersible material suitable for improving the characteristics of a mineral lubricating oil.

JOHN D. BARTLESON.
HERMAN P. LANKELMA.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,063,629	Salzberg	Dec. 8, 1936
2,316,082	Loane	Apr. 6, 1943
2,365,938	Cook	Dec. 26, 1944
2,373,094	Berger	Apr. 10, 1945
2,411,153	Fuller	Nov. 19, 1946
2,415,837	Musselman	Feb. 18, 1947
2,461,961	Buckmann	Feb. 15, 1949