Patented June 12, 1945 2,377,955

UNITED STATES PATENT OFFICE

2,377,955

LUBRICANT

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No Drawing. Application September 30, 1942, Serial No. 460,282

14 Claims. (Cl. 252—48)

This invention relates to a new composition of matter suitable for use as a lubricant additive and more particularly suitable for use in lubricating oil compositions intended for use in internal combustion engines such as spark-ignition engines and compression-ignition engines under severe conditions wherein corrosion, piston ring-sticking, cylinder wear, carbon, and varnish formation may be encountered.

Straight petroleum lubricating oils are effective lubricants within certain defined limits of operating conditions, but when these limits are exceeded such lubricants frequently fail to give the desired performance demanded of them. Since in modern engines these limits are frequently exceeded, the use of straight mineral oils as lubricants produces undesirable conditions within the engine; thus varnish and carbon formation is excessive and serious corrosion problems are encountered.

It is an object of the present invention to provide a lubricant for internal combustion engines which will be effective in providing adequate lubrication for such engines. It is a further object of the invention to provide a lubricant additive which effectively inhibits the formation of varnish and/or carbon and/or corrosion in engines in which lubricants containing such additives are employed. Other objects and inventions mentioned will become apparent as the description thereof proceeds.

In copending applications of one of us, namely Serial No. 384,938 and No. 384,941 filed March 24, 1941, which issued respectively as Patents Nos. 2,316,080 and 2,316,082 on April 6, 1943, there are described certain types of lubricant additives resulting from the neutralization of the reaction products of phosphorus sulfides and certain hydrocarbons. The neutralization of the reaction product described in said applications is accomplished by means of basic reagents such as the hydroxides, oxides or carbonates of metals of the alkali metal group and the alkaline earth metal group. While these neutralized reaction products are very effective in inhibiting carbon and/or varnish formation, under certain conditions they sometimes do not exhibit the desired corrosion inhibiting effect.

We have now discovered that a product having the desired carbon and/or varnish formation inhibiting properties as well as much improved corrosion inhibiting properties, can be obtained by neutralizing or treating the reaction product of a phosphorus sulfide and a hydrocarbon with a basic metallic sulfide, preferably an alkali metal sulfide or an alkaline earth metal sulfide, such as, for example, sodium sulfide, sodium polysulfide, potassium sulfide, calcium sulfide, etc. Ammonium sulfide can also be used. These metallic sulfide treated reaction products can be used in lubricants alone or in combination with the alkali hydroxide-neutralized phosphorus sulfide-hydrocarbon reaction product. Improved lubricants are obtained by employing a small amount, for example, from about .001% to about 10% and preferably from about .5% to about 5% of the sulfide treated reaction product.

The phosphorus sulfide-hydrocarbon reaction products normally show a titratable acidity ranging from about 10 to about 50 milligrams KOH per gram of product. In accordance with the present invention these acidic products are treated with a metallic sulfide to effect the neutralization of at least about 1% of the titratable acidity. The term "neutralized" as used herein means a product having at least about 1% of its titratable acidity reduced by reaction or treatment with a metallic sulfide on the type described.

The hydrocarbon reactant is preferably a hydrocarbon compound having a molecular weight greater than about 150 and preferably a molecular weight greater than about 300. The hydrocarbons may be paraffins, olefins or olefin polymers, aromatics, or alkyl aromatics, cyclic aliphatics, petroleum fractions such as lubricating oil fractions, petrolatums, waxes, cracked cycle stocks, or condensation products of petroleum fractions, solvent extracts of petroleum fractions, etc.

While the basic metallic sulfide-treated phosphorus sulfide-hydrocarbon reaction products all impart to a definite degree improved and desired properties to mineral oils to which they are added, all are not necessarily exactly equivalent in their effectiveness. Most effective and therefore preferred are the basic metallic sulfide-treated reaction products of a phosphorus sulfide and an olefin having at least 20 carbon atoms in the molecule. Such olefins can be obtained by the polymerization of olefins, by the dehydrogenation of paraffins, such as by the cracking of paraffin waxes, or by the dehalogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

We prefer to employ as the hydrocarbon reactant olefin polymers, preferably mono-olefin polymers having molecular weights above 150 and preferably above 300. As starting materials for the production of suitable polymers as the hydrocarbon reactant, we can employ the individual olefins themselves, mixtures of olefins or mixtures of olefins and non-olefinic compounds. For example, the olefinic starting material can be propylene, butylenes, amylenes, refinery gases containing normally gaseous olefins and cracked distillates or other relatively low-boiling hydrocarbon mixtures containing normally liquid olefins and mixtures of normally liquid olefins, containing substantial amounts of dissolved normally gaseous olefins.

The polymers can be those obtained by polymerizing olefinic hydrocarbons in the presence of catalysts such as sulfuric acid, phosphoric acid, or aluminum chloride, zinc chloride, boron fluoride and other catalysts of the Friedel-Crafts type. For example, we may employ the polymers resulting from the treatment of mono-olefins, preferably iso-mono-olefins such as isobutylene and isoamylene, and/or the copolymers obtained by the polymerization of hydrocarbon mixtures containing low molecular weight iso-olefins and normal olefins, preferably those of less than six carbon atoms.

The polymers employed are preferably mono-olefin polymers, in which the molecular weight ranges from about 150 to about 50,000 or more, and preferably from about 500 to about 10,000. These polymers can be obtained, for example, by the polymerization in the liquid phase of an iso-olefin, such as isobutylene, or hydrocarbon mixtures containing the same at a temperature of from about —80° F. to about 100° F. in the presence of a metal halide catalyst of the Friedel-Crafts type, such as boron fluoride. In the preparation of these polymers we may employ, for example, liquid isobutylene or a hydrocarbon mixture containing isobutylene, butane, and butylene, recovered from petroleum gases, especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline. This light fraction may contain from about 10% to about 25% isobutylene, the remainder being principally butanes and normal butylene.

The preparation of low molecular weight polymers having molecular weight ranging from about 300 to about 2000 from the butane-butylene-isobutylene fraction may be carried out as follows: The hydrocarbon mixture containing 10% to 25% isobutylene is maintained under pressure sufficient to keep it in the liquid phase and cooled to a temperature of, for example, from about 0° F. to about 100° F., and preferably from about 0° F. to about 32° F., and from about 0.1% to about 2% boron fluoride, based upon the isobutylene content of the material treated, is added with vigorous agitation. Excessive rise in the temperature due to the heat of reaction may be avoided by efficient cooling. After the polymerization of the isobutylene together with a relatively minor amount of the normal olefins present, the reaction mass is neutralized, washed free of acidic substances arising from the catalyst, the oily layer separated, and the polymer subsequently separated from the unreacted hydrocarbons by distillation. The polymer mixture so obtained, depending upon the temperature of reaction, varies in consistency from a light liquid to a viscous oily material and contains polymers having molecular weights ranging from about 300 to 2000 or more. The polymers so obtained may be treated with a phosphorus sulfide or the polymer may be fractionated under reduced pressure into fractions of increasing molecular weights and the various fractions reacted with a phosphorus sulfide and the reaction product treated with the basic metallic sulfide.

Long chain olefines obtained by the dehalogenation of alkyl halides having at least about 20 carbon atoms in the molecule of which at least about 12 carbon atoms, and preferably at least about 15 carbon atoms are in a long chain are also suitable as hydrocarbon reactants. The alkyl halides are decomposed to yield olefins according to the reaction.

$$C_nH_{2n+1}X \rightarrow C_nH_{2n} + HX$$

in which n is a whole number, preferably 20 or more, and X is an halogen. We prefer to employ as the alkyl hydrocarbon to be halogenated paraffin waxes having at least about 20 carbon atoms per molecule, and melting points upwards from about 90° F. and preferably within the range of from about 120° F. to about 140° F.

To obtain the halogenated paraffin wax, for example, chlorinated paraffin wax, we introduce chlorine into the wax, maintained in a molten state, until the wax has a chlorine content of from about 8% to about 15%. The chlorinated wax product is a mixture of unchlorinated wax, monochlor wax and polychlor wax. This chlorinated product may be used as such, but it is advantageous to use the substantially monochlor wax fraction. The monochlor wax fraction can be segregated from the unchlorinated wax and the polychlor wax fractions by taking advantage of the differences in the melting points of the various fractions, since the melting point of the wax varies with the extent of chlorination; i. e. the melting point of the unchlorinated wax is greater than that of the monochlor wax, and the melting point of the latter is greater than that of the polychlor wax. Thus, the monochlor paraffin wax can be separated from the unchlorinated and the polychlor wax fractions by means such as sweating, fractional distillation, solvent extraction, solvent precipitation, and fractional crystallization.

The high molecular weight olefins are obtained by removing the halogen as hydrogen halide from the halogenated paraffin wax. For example, the corresponding olefin is obtained from the monochlor paraffin wax by removing the chlorine from the latter as hydrogen chloride. The monochlor wax can be dechlorinated by heating to a temperature of from about 200° F. to about 600° F. in the presence of a dechlorinating agent such as an alkali metal hydroxide or an alkaline earth metal hydroxide or oxide. Other alkaline inorganic or organic materials can also be used. The chlorine can also be removed from the chlorowax by heating the same for a prolonged period in the absence of any dechlorinating agent. After the dehalogenation has been completed the olefin so obtained can be further purified by removing the dehalogenating agent by means of filtration or by other suitable means.

Examples of other high molecular weight olefinic hydrocarbons which we may employ as reactants are cetene (C_{16}), cerotene (C_{26}), melene (C_{30}), and mixed high molecular weight alkenes obtained by cracking petroleum oils.

Although additives prepared with starting materials of the foregoing type are most effective, additives of different degrees of effectiveness are obtained by employing other hydrocarbons as starting materials. Thus we can employ as the starting material the polymer or synthetic lubricating oil obtained by polymerizing unsaturated hydrocarbons resulting from the vapor phase cracking of paraffin waxes in the presence of aluminum chloride which is fully described in United States Patents Nos. 1,995,260, 1,970,002, and 2,091,398. Still another type of olefin polymer which may be employed is the polymer resulting from the treatment of vapor phase cracked gasoline and/or gasoline fractions with sulfuric acid or solid absorbents such as fuller's earth whereby unsaturated polymerized hydrocarbons are removed. Also contemplated within the scope of our invention is the treatment with

phosphorus sulfide of the polymers resulting from the voltolization of hydrocarbons as described, for example, in United States Patents Nos. 2,197,768 and 2,191,787.

Another suitable polymer is a fraction of the polymer obtained in the treatment of a gaseous hydrocarbon mixture containing isobutylene and normal butylene in the presence of a phosphoric acid catalyst in the synthesis of isooctane.

Essentially paraffinic hydrocarbons such as bright stock residuums, lubricating oil distillates, petrolatums, or paraffin waxes may be used. We may also employ the condensation products of any of the foregoing hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride and the like.

Also contemplated within the scope of the present invention are the basic metallic sulfide-treated reaction products of a phosphorus sulfide with an aromatic hydrocarbon such as, for example, benzene, naphthalene, toluene, xylene, diphenyl and the like, or with an alkylated aromatic hydrocarbon, such as, for example, benzene having an alkyl substituent having at least four carbon atoms and preferably at least eight carbon atoms such as a long chain paraffin wax.

The phosphorus sulfide reaction product may be obtained by reacting a phosphorus sulfide such as P_2S_3, P_4S_7, P_4S_3, or preferably P_2S_5 with a hydrocarbon at a temperature of from about 200° F. to about 500° F., and preferably from about 300° F. to about 400° F. It is advantageous to maintain a non-oxidizing atmosphere, such as, for example, an atmosphere of nitrogen above the reaction mixture. From about 1% to about 50% and preferably from about 5% to about 25% of the phosphorus sulfide can be used. Any excess phosphorus sulfide can be separated from the reaction product after the reaction is completed by filtration or by diluting the reaction mixture with a suitable oil or with solvent, such as hexane, filtering, and subsequently distilling off the solvent. The reaction mixture can be further treated by blowing with nitrogen or other inert gases at an elevated temperature to improve the odor thereof.

The prosphorus sulfide-hydrocarbon reaction product obtained in the manner above described is then treated with a metallic sulfide such as an alkali metal sulfide or an alkali earth metal sulfide to effect the neutralization of the reaction product. From about 3% to about 15% of the metallic sulfide, based on the weight of the phosphorus sulfide-hydrocarbon reaction product, is slowly added to the reaction mixture maintained at a temperature of about 200° F. to about 500° F. Treatment with the metallic sulfide is preferably carried out in a diluted solution of the reaction product, thus the reaction product may be dissolved in a mineral lubricating oil or any other suitable solvent or diluent and the diluted product treated with the sulfide. Any solid particles remaining in the product after treatment with the sulfide are removed by filtering through a suitable filtering medium.

As a specific embodiment of our invention the following examples are given by way of illustration and are not intended as limitations thereof.

Example I

An isobutylene polymer having a Saybolt viscosity at 210° F. of 1000 seconds and an average molecular weight of about 1000 was treated at 400° F. with 10% by weight of P_2S_5. Two percent by weight of sulfur was added as a catalyst. The mixture was stirred and blown with inert gas at 400° F. for 3 hours. At the end of this time a clear homogenous product was obtained. This material was diluted with an S. A. E.-20 grade oil to a concentration of 65% additive and 35% oil. The mixture was then heated to 400° F. and 5.5% sodium sulfide (60–62%), based on the weight of the polymer-P_2S_5 reaction product, was added slowly over a period of about two hours. Considerable foaming and hydrogen sulfide evolution was obtained. A small amount of solid material (less than 1%) was removed by filtering the product through a mat of Celite 501.

Example II

The isobutylene polymer of Example I was treated at 400° F. with 25% P_2S_5 and 2% sulfur as in the preceding example. The product was diluted to 40% additive concentration with an S. A. E. 20 grade oil and neutralized with 14% sodium sulfide and finished as in Example I.

The effectiveness of our improved additive in inhibiting the corrosion to metals, particularly to alloy metals of the type of copper-lead alloy bearing metals, is illustrated by the data presented below, and obtained in the following tests. In this corrosion test about 250 cc. of the lubricant under test and containing 1% of powdered iron, 1% of lead oxide, 0.001% of soluble iron and 0.001% of soluble lead as catalysts, is maintained at a temperature of about 300° F. and stirred with a glass stirrer rotating at about 1300 R. P. M. A lead test strip and a copper-lead bearing test strip are suspended in the oil. At stated intervals the test strips are removed from the oil samples, cleaned, dried, and weighed to determine any loss in weight.

The following oils were subjected to the test above described:

Sample A.—A 20 S. A. E. high-grade motor oil.

Sample B.—Sample A plus 1½% of a P_2S_5-isobutylene polymer reaction product neutralized with KOH.

Sample C.—Sample A plus 1½% of the product obtained in Example I above.

Sample D.—Sample A plus 2% of the product obtained in Example I above.

Sample E.—Sample A plus 2½% of the product obtained in Example I above.

Sample F.—Sample A plus 3% of the product obtained in Example I above.

Sample G.—Sample A plus 1½% of the product obtained in Example II above.

Sample H.—Sample A plus 2% of the product obtained in Example II above.

Table I

	Lead loss, mg.				Cu-Pb loss, mg.		
	Hours				Hours		
	5	22	45	75	22	45	75
Sample A	82	469			52		
Sample B	166	603			38		
Sample C	0.0	321			22		
Sample D	0.0	240			8.1		
Sample E	0.0	0.0			0.0	36.4	
Sample F	0.0	0.3			0.0	9.0	
Sample G	0.0	0.0	2.5	75	0.0	0.0	0.0
Sample H	0.0	0.0	0.8	41	0.0	0.0	0.0

The corrosion inhibiting effectiveness of this present invention is well illustrated by the above data.

In another test the corrosion inhibiting property of an additive was determined in a standard

six cylinder spark ignition engine operated at an oil sump temperature of about 285° F. and the corrosion to copper lead alloy bearings determined. Samples B, C, and F were subjected to this test with the following results:

Table II

Sample	Hours for rapid corrosion to begin
B	0-10
C	10-30
F	36-60

The sludge and varnish inhibiting properties of our new additive are demonstrated by the data presented in Table III which were obtained in the following manner: About 250 cc. of the oil to be tested is heated at about 330 to 332° F. in a 500 cc. glass beaker in the presence of 5 sq. in. of copper at 10 sq. in. of iron. Four glass rods of about 6 millimeter diameter are suspended in each oil sample which is stirred at about 1300 R. P. M. with a glass stirrer having a 40 degree light pitch. At stated intervals samples of the oil are taken and sludge, acidity and viscosity values determined. The glass rods are also inspected for evidence of varnish formation thereon. Varnish values are based on a visual rating in which a glass rod, free of any varnish, is given a rating of 10, while a badly coated rod is given a rating of 1. Rods having appearances between these extremes are given intermediate values. The following samples were subjected to the foregoing tests and the data obtained as tabulated in Table III.

Sample 1.—S. A. E. 20 high grade motor oil.

Sample 2.—Sample 1+¾% P_2S_5-isobutylene polymer reaction product neutralized with KOH.

Sample 3.—Sample 1+¾% P_2S_5-isobutylene polymer reaction product neutralized with Na_2S.

Table III

Sample No.	Viscosity increase,[1] 48 hrs.	Sludge mg./10 g. oil		Acidity mg. KOH/g oil		Varnish [2]	
		24 hrs.	48 hrs.	24 hrs.	48 hrs.	24 hrs.	48 hrs.
1	1,158	350	975	9.9	16.6	4-5	1
2	114	6	23	1.5	2.4	10	10
3	35	20	19	1.0	1.7	10	10

[1] Saybolt Universal Viscosity at 100° F.
[2] Rating Scale—10=no deposit, 1=very heavy deposit.

The above data demonstrates that in addition to its corrosion inhibiting property, our improved additive is also effective in inhibiting oxidation, sludging, varnish formation and in general oil deterioration.

Concentrates of the basic metallic sulfide-treated reaction product of a phosporous sulfide and a hydrocarbon comprise a convenient method of handling these additives. The concentrates can then be added in small amounts to oils or other lubricants to give a finished product of the desired additive content. Thus a concentrate containing more than 10% by weight of the additive can be diluted with a mineral oil to give a product containing from about 0.01% to about 10% of the additive.

While we have described the use of our additives in lubricating oils, our invention is not limited to such use, since these reaction products may be employed in other petroleum products such as insulating oils, white oils, greases, waxes, and the like to increase the resistance thereof to oxidation, sludging and to inhibit the tendency thereof to corrode metals.

While we have described preferred embodiments of our invention, other modifications thereof may be made without departing from the scope and spirit of the invention, and we do not wish to limit our invention to the examples set forth herein except insofar as the same is defined by the following claims.

We claim:

1. As a new phosphorus- and sulfur-containing composition of matter the phosphorus sulfide-hydrocarbon reaction product reacted with a basic metallic sulfide.

2. As a new phosphorus- and sulfur-containing composition of matter the phosphorus sulfide-olefin reaction product reacted with a basic metallic sulfide.

3. As a new phosphorus- and sulfur-containing composition of matter the phosphorus sulfide-olefin polymer reaction product reacted with a basic metallic sulfide.

4. As a new phosphorus- and sulfur-containing composition of matter the phosphorus sulfide-mono-olefin polymer reaction product reacted with a basic metallic sulfide.

5. A new composition of matter as described in claim 4 in which the basic metallic sulfide is an alkali metal sulfide.

6. A new composition of matter as described in claim 4 in which the basic metallic sulfide is an alkaline earth metal sulfide.

7. An improved lubricant comprising a lubricating oil and a small amount of the phosphorus- and sulfur-containing phosphorus sulfide-hydrocarbon reaction product reacted with a basic metallic sulfide.

8. An improved lubricant comprising a lubricating oil and a small amount of the phosphorus- and sulfur-containing phosphorus sulfide-olefin reaction product reacted with a basic metallic sulfide.

9. An improved lubricant comprising a lubricating oil and a small amount of the phosphorus- and sulfur-containing phosphorus sulfide-olefin polymer reaction product reacted with a metallic sulfide selected from the class consisting of alkali metal sulfides and alkaline earth metal sulfides.

10. An improved composition of matter comprising mineral oil and a small amount of the phosphorus- and sulfur-containing phosphorus sulfide-mono-olefin polymer reaction product reacted with a metallic sulfide selected from the class consisting of alkali metal sulfides and alkaline earth metal sulfides.

11. A new composition of matter as described in claim 9 in which the metal sulfide is sodium sulfide.

12. A new composition of matter as described in claim 9 in which the metal sulfide is potassium sulfide.

13. An improved composition comprising a mineral oil and a minor amount of a basic metallic sulfide-neutralized reaction product of a phosphorus sulfide and an olefin hydrocarbon having at least about 20 carbon atoms in the molecule, said basic metallic sulfide neutralized reaction product containing phosphorus and sulfur.

14. An addition agent for mineral oils com-

prising a concentrated solution in a mineral oil of a phosphorus- and sulfur-containing basic metallic sulfide-neutralized reaction product of a phosphorus sulfide and a hydrocarbon, said concentrated solution containing more than about 10% by weight based on the oil of said neutralized reaction product, said solution being capable of dilution with a mineral oil to form a homogeneous mixture containing from about 0.01% to about 10% by weight of said basic metallic sulfide-neutralized reaction product of a phosphorus sulfide and a hydrocarbon.

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