

UNITED STATES PATENT OFFICE

2,409,799

LUBRICANT

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This invention relates to improvements in oils particularly to hydrocarbon oils such as mineral oils which are non-corrosive and resistant to oxidation. More particularly the present invention is directed to lubricants which are resistant to the formation of gums, resinous and varnish-like materials, and which are non-corrosive particularly to alloy bearings.

Many oils are not well suited as lubricants for use in internal combustion engines, particularly of the type operating under severe operating conditions, since under such severe operating conditions they are susceptible to deterioration resulting in the development of carbonaceous and/or resinous or similar varnish-like deposits in the engine and on and about the valves and rings of the engine. Furthermore, such lubricants are often corrosive particularly to the alloy bearings in such engines.

It is an object of the present invention to provide a combination of additives for oils, particularly hydrocarbon oils such as mineral oils which will stabilize such oils against oxidative deterioration and which will render the oils non-corrosive. It is another object of the present invention to provide lubricants for internal combustion engines which do not form carbonaceous deposits or resinous varnish-like materials on and about the valves, pistons and rings of such engines. Another object of the invention is to provide a combination of additives for lubricating oils which will materially inhibit the formation of carbonaceous deposits and/or resinous varnish-like materials and which will render the lubricants non-corrosive particularly to metals of the hard alloy type.

In accordance with the present invention the foregoing objects can be attained by adding to oils such as hydrocarbon oils, for example, mineral lubricating oils, small amounts of the neutralized reaction product of a hydrocarbon and a phosphorus sulfide in combination with a small amount of an oil-soluble organic amino compound having metal deactivating and/or corrosion inhibiting properties. Examples of the organic amino compounds suited for this purpose are polyamino poly-aryl methanes, particularly the aliphatic polyamino substituted poly-aryl methane compounds, such as the aliphatic diamino substituted diaryl methane compounds; for example aminomethyl aminodiphenyl methane, tetramethyl diamino-diphenyl methane, di(methylamino) dinaphthyl methane and derivatives of the same. Suitable derivatives are the reaction products of tetramethyl diamino-diphenyl methane and sulfur, sulfur chloride or sulfur dichloride; the reaction products of tetramethyl diamino diphenyl methane and an aldehyde such as aliphatic aldehydes, for example heptaldehyde, aromatic aldehydes, such as benzaldehyde, para-

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dimethyl amino benzaldehyde, etc. and ketones such as benzophenone or substituted ketones such as Michler's ketones or the sulfurized reaction products of the foregoing. Other suitable amino compounds are the reaction products of tetramethyl diamino diphenyl methane and nitroso compounds such as nitrosobenzene, nitrosonaphthalene, phenyl nitrosoamines, etc. Other products which may be used are the reaction products of aryl amines and a diazonium compound such as diazotized aniline or naphthylamine, a diazotized aminophenol, a diazotized primary amine, a diazotized nitrosoamine, diazotized diamines and the like.

Other suitable organic amino compounds suitable for the herein described purpose are the reaction products of aromatic ortho hydroxy aldehydes such as 2-hydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde, etc., or ketones with alkyl amines, particularly polyamines such methylenediamine, ethylene diamine, diethylenetriamine, 1:10-decylenediamine, triethylenetetramine, propylene diamine, etc. Examples of such reaction products are disalicylal ethylene diamine, salicylal ethylene amine, di(2-hydroxy-3-methoxy-benzol)-propylene diamine. The present invention contemplates also the use of other organic amino compounds such as aliphatic amines, aromatic amines, etc. The improvement obtained and the degree of improvement effected may vary to some extent with the type of amino compound employed.

As was aforesaid, one of the components of the improved lubricant is the neutralized reaction product of a hydrocarbon with a phosphorus sulfide such as P_2S_3 , P_4S_3 , P_4S_7 or other phosphorus sulfides and preferably phosphorus pentasulfide, P_2S_5 . The hydrocarbon constituent of this reaction is preferably a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefinic hydrocarbons or isomono-olefinic hydrocarbons such as propylenes, butylenes, and amylenes or the copolymers obtained by the polymerization of hydrocarbon mixtures containing isomono-olefins and mono-olefins of less than 6 carbon atoms. The polymers may be obtained by the polymerization of these olefins or mixtures of olefins in the presence of a catalyst such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and isomono-olefin polymers having molecular weights ranging from about 150 to about 50,000 or more, and preferably from about 500 to about 10,000. Such polymers can be obtained, for example, by the polymerization in the liquid

phase of a hydrocarbon mixture containing mono-olefins and isomono-olefins such as butylene and isobutylene 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, for example, boron fluoride, aluminum chloride and the like. In the preparation of these polymers we may employ, for example, a hydrocarbon mixture containing isobutylene, butylenes and butanes recovered from petroleum gases especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline.

A suitable polymer for the reaction with phosphorus sulfide is the product obtained by polymerizing in the liquid phase a hydrocarbon mixture containing butylenes and isobutylenes together with butanes and some C_3 and C_5 hydrocarbons at a temperature between about 0°F. and 30°F. in the presence of aluminum chloride. A suitable method for carrying out the polymerization is to introduce the aluminum chloride into the reactor and introduce the hydrocarbon mixture cooled to a temperature of about 0°F. into the bottom of the reactor and passing it upwardly through the catalyst layer while regulating the temperature within the reactor so that the polymer product leaving the top of the reactor is at a temperature of about 30°F. After separating the polymer from the catalyst sludge and unreacted hydrocarbons, the polymer is fractionated to obtain a fraction of the desired viscosity such as, for example, from about 80 seconds to about 2000 seconds Saybolt Universal at 210°F.

Another suitable polymer is that obtained by polymerizing in the liquid phase a hydrocarbon mixture comprising substantially C_3 hydrocarbons in the presence of an aluminum chloride complex catalyst. The catalyst is preferably prepared by heating aluminum chloride with isooctane. The temperature in the reactor is controlled within the range of about 50°F. to about 110°F. The hydrocarbon mixture is introduced into the bottom of the reactor and passed upwardly through the catalyst layer. The propane and other saturated gases pass through the catalyst while the propylene is polymerized under these conditions. The molecular weight of the propylene polymer is about 500 to about 1000.

Other suitable polymers can be obtained by polymerizing a hydrocarbon mixture containing about 10% to about 25% isobutylene at a temperature of from about 0°F. to about 100°F. and preferably 0°F. to about 32°F. in the presence of boron fluoride. 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 and the unreacted hydrocarbons subsequently separated from the polymers by distillation. The polymer mixture so obtained depending upon the temperature of reaction, varies in consistency from a light liquid to viscous, oily material and contains polymers having molecular weights ranging from about 100 to about 2000 or higher. The polymers so obtained may be used as such, or the polymer may be fractionated under reduced pressure into fractions of increasing molecular weights, and suitable fractions obtained reacted with the phosphorus sulfide to obtain the desired reaction products. The bottoms resulting from the fractionation of the polymer which may have Saybolt Universal viscosities at 210°F. ranging from about 50 seconds to about 10,000 seconds, are well suited for the purpose of the present invention.

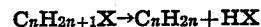
Another source of an olefinic polymer suitable for the herein intended purpose is a fraction of the polymer obtained in the treatment of a gaseous hydrocarbon mixture containing isobutylene and normal butylenes in the presence of a phosphoric acid catalyst in the synthesis of isooctane. The polymer may be obtained by subjecting a gas mixture comprising less than C_5 hydrocarbons and containing C_4 olefins and paraffins to temperatures of about 270°F. to about 430°F. and preferably at about 300°F. to about 330°F. at pressures of from about 500 pounds per square inch to 750 pounds per square inch in the presence of a catalyst such as phosphoric acid. The mixed polymer obtained comprises essentially a dimer but contains in addition about 5-10% of heavy polymers comprising trimers, tetramers and still higher polymers. This heavy polymer fraction may be fractionated to give about a 10-15% bottoms which comprises essentially a tetramer fraction bottom boiling about 400°F. to 520°F.

Essentially paraffinic hydrocarbons such as bright stock residuums, lubricating oil distillates, petrolatums, or paraffin waxes may be used. There can also be employed the condensation products of any of the foregoing hydrocarbons, usually through first halogenating the hydrocarbons, with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride and the like.

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

Other preferred olefins suitable for the preparation of the herein-described phosphorus sulfide reaction products are olefins having at least 20 carbon atoms in the molecule of which from about 13 carbon atoms to about 18 carbon atoms, and preferably at least 15 carbon atoms, are in a long chain. Such olefins can be obtained 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.

The olefins obtained by dehalogenation of long chain alkyl halides are preferably those obtained by dehalogenation of monohalogenated waxes, such as, for example, those obtained by dechlorination of monochlor paraffin wax. The alkyl halides are decomposed to yield olefins according to the reaction



in which n is a whole number, preferably 20 or more, and X is a halogen. It is preferred to employ paraffin waxes having at least about 20 carbon atoms per molecule, and melting points upwards from about 90°F. to about 140°F.

To obtain the halogenated paraffin wax, for example, chlorinated paraffin wax, chlorine is introduced 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

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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.

As a starting material there can be used 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 this invention is the treatment with phosphorus sulfide of the polymers resulting from the volatilization of hydrocarbons as described, for example, in United States Patents Nos. 2,197,768 and 2,191,787.

Also contemplated within the scope of the present invention are the 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-hydrocarbon reaction product can be readily obtained by reacting a phosphorus sulphide, for example P_2S_5 with the hydrocarbon at a temperature of from about 200° F. to about 500° F. and preferably from about 200° F. to about 400° F., using from about 1% to about 50% and preferably from about 5% to about 25% of the phosphorus sulphide in the reaction. It is advantageous to maintain a non-oxidizing atmosphere such as, for example, an atmosphere of nitrogen above the reaction mixture. Usually it is preferable to use an amount of the phosphorus sulphide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess amount of phosphorus sulphide can be used and separated from the product by filtration or by dilution with a solvent such as hexane, filtering and subse-

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quently removing the solvent by suitable means such as by distillation. If desired the reaction product can be further treated with an agent having an active hydrogen atom such as steam at an elevated temperature of from about 100° F. to about 600° F.

The phosphorus sulfide-hydrocarbon reaction product normally shows a titratable acidity which is neutralized by treatment with a basic reagent. The phosphorus-sulfide-hydrocarbon reaction product when neutralized with a basic reagent containing a metal constituent is characterized by the presence or retention of the metal constituent of the basic reagent. Other metal constituents such as a heavy metal constituent can be introduced into the neutralized product by reacting the same with a salt of the desired heavy metal.

The term "neutralized phosphorus sulfide-hydrocarbon reaction product" as used herein means a phosphorus sulfide hydrocarbon reaction product having at least about 1% of its titratable acidity neutralized by the reaction with a basic reagent and includes the neutralized phosphorus sulfide-hydrocarbon reaction products containing a metal constituent resulting from said neutralization or resulting from the reaction of a heavy metal salt with the phosphorus sulfide-hydrocarbon reaction product treated with a basic reagent.

The neutralized phosphorus sulfide-hydrocarbon reaction product can be obtained by treating the reaction product with a suitable basic compound such as a hydroxide, carbonate or an oxide of an alkaline earth metal or an alkali metal such as, for example, potassium hydroxide or sodium hydroxide. Other basic reagents can be used such as, for example, ammonia or an alkyl or aryl substitute of ammonia such as amines. The neutralization of the phosphorus sulfide-hydrocarbon reaction product is carried out preferably in a non-oxidizing atmosphere by contacting the reaction product either as such or dissolved in a suitable solvent such as naphtha with a solution of the basic reagent, for example, potassium hydroxide or sodium hydroxide dissolved in alcohol. As an alternative method, the reaction product can be treated with solid alkaline compounds such as KOH, NaOH, Na_2CO_3 , $KHCO_3$, K_2CO_3 , CaO, and the like at an elevated temperature of from about 100° F. to about 600° F. As was aforesaid, when the phosphorus sulfide-hydrocarbon reaction product is neutralized with a basic reagent containing a metal constituent, the neutralized reaction product is characterized by the presence of the metal constituent of the basic reagent. Neutralized reaction products containing a heavy metal constituent such as, for example, tin, titanium, aluminum, chromium, cobalt, zinc, iron, and the like, can be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-hydrocarbon reaction product which has been treated with a basic reagent. It will be understood that when the neutralization is accomplished with a polyvalent basic material such as lime, a product having excess basicity may be obtained.

It has heretofore been discovered that the neutralized phosphorus sulfide-hydrocarbon reaction products when added to mineral oils in small amounts are effective in inhibiting the formation of varnish, sludge, carbon, and the like, and in general are effective in inhibiting corrosion to metal surfaces in contact with such oils. The varnish and/or sludge and/or carbon inhibiting

effect of the neutralized phosphorus sulfide-hydrocarbon reaction products is taught in U. S. Patents 2,316,080 and 2,316,082 issued April 6, 1943, to C. M. Loane and J. W. Gaynor. However, under certain conditions these neutralized reaction products do not inhibit the corrosion to the desired degree and in some cases may accelerate corrosion. In accordance with the present invention the neutralized phosphorus sulfide-hydrocarbon reaction products are employed in combination with small amounts of an organic amino compound, particularly those organic amino compounds of the type above described, which exhibit metal deactivating and/or corrosion inhibiting properties. The neutralized phosphorus sulfide hydrocarbon reaction product is employed in amounts within the range of from about 0.001% to about 10% and preferably from about 0.01% to about 3% and the organic amino compound is employed in concentrations of from about 0.001% to about 5% and preferably from about 0.01% to about 2%. In addition to the organic amino compound and the neutralized reaction product of a phosphorus sulfide and a hydrocarbon the composition may also contain small amounts, for example from about 0.001% to about 5% of an organic sulfur compound or elemental sulfur. Examples of suitable organic sulfur compounds are sulfurized mineral oils, sulfurized animal or vegetable oils, sulfurized sperm oil, sulfurized olefin polymers, such as sulfurized propene or butene polymers, etc.

The improvement obtained when a small amount of an amino-type corrosion inhibitor is used in combination with a neutralized phosphorus sulfide-hydrocarbon reaction product, is illustrated by the data presented in the following table. The data presented therein are those obtained by running a conventional six cylinder spark ignition internal combustion engine equipped with copper lead bearings at 3150 R. P. M. and at a temperature of 280 to 285° F. and determining the corrosion to the copper lead bearing at the end of 36 hours operation. The corrosion is expressed in grams per full bearing loss during the operating period. The following oils were tested by this method:

- A. A solvent refined M. C. motor oil.
- B. A solvent refined M. C. motor oil containing 1.5% of neutralized phosphorus pentasulfide-isobutylene polymer reaction product.
- C. A solvent refined M. C. motor oil containing 1½% of a neutralized phosphorus sulfide-isobutylene polymer reaction product and 0.25% of a sulfurized mineral oil.
- D. The oil of sample C+0.05% of tetramethyldiamino diphenyl methane.
- E. The oil of sample C+0.1% of tetramethyldiamino diphenyl methane.

Table I

Oil sample tested	Duration of test, hrs.	Copper lead bearing corrosion grams loss per whole bearing
A.	36	0.97
B.	36	1.82
C.	36	2.49
D.	36	0.58
E.	36	0.37

The above data show the marked decrease in corrosion obtained by the addition of small amounts of an amino compound to the oils under test. Although I have described my invention as applied to hydrocarbon lubricating oils, my in-

vention contemplates the use of organic amino compounds of the type described in combination with a neutralized reaction product of a phosphorus sulfide and a hydrocarbon in products other than hydrocarbon lubricating oils such as, for example, fuel oils, insulating oils, turbine oils, non-drying vegetable and animal oils, synthetic oils, greases and the like.

While I have described my invention by reference to various representative constituents and have illustrated the same by reference to specific examples thereof, the invention is not to be limited to the various representative compounds named or to the specific examples given but includes within its scope such modifications as come within the spirit of the appended claims.

I claim:

1. A lubricant composition containing an oil and in combination from about 0.001% to about 5% of a polyamino poly-aryl methane and from about 0.001% to about 10% of a neutralized phosphorus- and sulfur-containing reaction product of a phosphorus sulfide and a hydrocarbon.
2. A lubricant composition containing an oil and in combination from about 0.001% to about 5% of a polyamino poly-aryl methane and from about 0.001% to about 10% of a neutralized phosphorus- and sulfur-containing reaction product of a phosphorus sulfide and an olefin.
3. A lubricant composition as described in claim 2 in which the olefin is an olefin containing at least 20 carbon atoms in the molecule of which from about 12 carbon atoms to about 18 carbon atoms are in a long chain.
4. A lubricant composition containing an oil and in combination from about 0.001% to about 5% of a polyamino poly-aryl methane and from about 0.001% to about 10% of the neutralized phosphorus- and sulfur-containing reaction product of a phosphorus sulfide and an olefin polymer.
5. A lubricant composition as described in claim 4 in which the olefin polymer is an isobutylene polymer.
6. A lubricant composition as described in claim 4 in which the olefin polymer is a propylene polymer.
7. A lubricant composition containing an oil and in combination from about 0.001% to about 5% of a diamino polyaryl methane and from about 0.001% to about 10% of a neutralized phosphorus- and sulfur-containing reaction product of a phosphorus sulfide and an olefin polymer.
8. A lubricant composition as described in claim 7 in which the neutralized reaction product contains a metal constituent.
9. A lubricant composition as described in claim 7 in which the neutralized reaction product contains potassium.
10. A lubricant composition as described in claim 7 in which the neutralized reaction product contains sodium.
11. A lubricant composition as described in claim 7 in which the neutralized reaction product contains calcium.
12. A lubricant comprising a hydrocarbon oil and in combination therewith from about 0.001% to about 5% of an aliphatic polyamino substituted poly-aryl methane, an organic sulfur compound and from about 0.001% to about 10% of a neutralized phosphorus- and sulfur-containing reaction product of a phosphorus sulfide and a hydrocarbon.
13. A composition of matter containing a petroleum fraction and in combination from about

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0.001% to about 5% of tetramethyl diamino diphenyl methane and from about 0.001% to about 10% of a neutralized phosphorus- and sulfur-containing reaction product of a phosphorus sulfide and a hydrocarbon.

14. A composition of matter containing a petroleum fraction and in combination from about 0.001% to about 5% of a polyamino poly-aryl methane and from about 0.001% to about 10% of a neutralized phosphorus- and sulfur-contain- 10

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ing reaction product of a phosphorus sulfide and an olefin.

15. A composition as described in claim 14 in which the olefin is an olefin polymer.

16. A composition of matter as described in claim 14 in which the polyamino poly-aryl methane is an aliphatic polyamino substituted poly-aryl methane.

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