

UNITED STATES PATENT OFFICE

2,463,429

LUBRICANT

Edward N. Roberts, Hammond, Ind., assignor to
Standard Oil Company, Chicago, Ill., a corpora-
tion of Indiana

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This invention relates to improvements in lubricant compositions and more particularly to hydrocarbon oil compositions which are non-corrosive and resistant to oxidative deterioration. More particularly the present invention is directed to internal combustion engine lubricants which are resistant to the formation of gums, resinous and varnish-like materials and which are non-corrosive to metal surfaces, especially bearings of the hard metal alloy type.

Straight petroleum lubricants are effective within certain defined limits of engine operating conditions but when these limits are exceeded, such lubricants frequently fail to give the desired performance demanded of them. Since in modern engine design to give increased performance 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 corrosion of improved hard metal alloy bearings of the cadmium-silver and copper-lead type is encountered. In order to overcome some of these deficiencies in the properties of hydrocarbon oils, certain types of additives have been added to lubricant compositions to impart thereto properties such as resistance to oxidative deterioration and corrosion inhibiting properties. Many of these additives are capable of imparting all of these desirable properties to lubricants under certain normal conditions but frequently such additives fail to afford the desired protection in one or more respects.

It has heretofore been found that certain reaction products of a phosphorus sulfide and a hydrocarbon, particularly an olefin or an olefin polymer, when added in small amounts to a hydrocarbon oil such as a mineral oil in combination with small amounts of an organic sulfur compound or elemental sulfur, effectively inhibit the formation of sludge and/or varnish-like deposits and inhibit the corrosion to metal surfaces, particularly to the bearings of the hard metal alloy type. The use of small amounts of an organic sulfur compound or elemental sulfur in combination with the neutralized reaction products of a phosphorus sulfide and a hydrocarbon in lubricants is the subject matter of United States Patent 2,316,090, issued to C. D. Kelso and L. W. Mixon on April 6, 1943. While the organic sulfur

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compounds or elemental sulfur in combination with the neutralized reaction products of a phosphorus sulfide and a hydrocarbon are normally effective in inhibiting corrosion, under some conditions they frequently fail to afford the desired protection.

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 such oils non-corrosive. It is another object of the 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 and which are not corrosive to metals, particularly to hard alloy bearing metals of the copper-lead and cadmium-silver 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 a polyhydroxy aromatic compound in combination with a small amount of the neutralized reaction products of a phosphorus sulfide and a hydrocarbon. The polyhydroxy aromatic compound can be employed in amounts of from about 0.001% to about 2% and preferably from about 0.01% to about .5% and the neutralized phosphorus sulfide-hydrocarbon reaction products can be employed in amounts within the range of from about 0.001% to about 10% and preferably from about 0.01% to about 3%. In addition the lubricant composition may contain from about 0.001% to about 5% of elemental sulfur or other organic sulfur compounds such as sulfurized mineral oil, sulfurized olefin polymers, sulfurized terpenes and the like.

It is also within the contemplation of this invention to provide the combination of addition agents, herein-described, in the form of a concentrate in a suitable oil base, the concentrate containing more than 2% of the polyhydroxy aromatic compound and more than 10% of the neutralized phosphorus sulfide-hydrocarbon reaction product. Such concentrates are used for blending with the hydrocarbon oil or other oils in the proportions desired for the particular conditions of use.

The polyhydroxy aromatic compounds or their partially etherified or esterified derivatives employed in the herein-described invention are those having the general formula $R-Ar-(OR')_x$ in which R represents hydrogen, alkyl or aryl substituents, Ar represents a mono- or polycyclic aromatic nucleus such as, for example, benzene, naphthalene, anthracene, phenanthrene, etc., R' represents hydrogen, alkyl, aryl, alkanoyl or aroyl substituents at least one of which is hydrogen and x is an integer greater than 1. The aromatic nucleus may contain, in addition to alkyl or aryl substituents, groups such as nitro, aldehyde, keto, amino, alkoxy, carboxy, and other radicals. Examples of specific compounds falling in the above defined class are: catechol, hexylcatechol, octylcatechol, dodecylcatechol, pyrogallol, capryl pyrogallol, resorcinol, hexyl resorcinol, hydroquinone, phloroglucinol, hydroxyquinone, dihydroxynaphthaquinone, dihydroxyanthraquinone, trihydroxyanthraquinone, peri-dihydroxy-naphthalene, peri-dihydroxyanthracene, alkylated catechol, alkylated dihydroxynaphthaquinones, alkylated dihydroxyanthraquinone, alkylated trihydroxyanthraquinone, alkylated peri-dihydroxynaphthalene, alkylated peri-dihydroxyanthracene, 2,4-dihydroxybenzaldehyde; 2,3-dihydroxybenzaldehyde; 2-hydroxy-3-methoxybenzaldehyde; 2-hydroxy-4-methoxybenzaldehyde; 2,3-dihydroxybenzophenone; 2,4-dihydroxybenzophenone; 2-hydroxy-3-methoxybenzophenone; 2-hydroxy-4-methoxybenzophenone; 2,2'-dihydroxybenzophenone; 2,3-dihydroxyacetophenone; 2,5-dihydroxyacetophenone; 3,4-dihydroxyacetophenone; the monoalkyl and aryl ethers of these dihydroxyacetophenones; 3,4-dihydroxydiphenyl; dihydroxynaphthalenes and dihydroxyanthracene in which the two hydroxy groups are in adjacent positions; mono- and dialkyl (such as methyl, ethyl, propyl, isopropyl, butyl and amyl) esters of 3,4-dihydroxyphthalic acid and their monoalkyl and aryl ethers; alkyl (such as methyl, ethyl, propyl, butyl, amyl and cetyl) esters of 2,4-dihydroxybenzoic acid and their 4-alkyl ether derivatives, alkyl (such as propyl, isopropyl, butyl, isobutyl, amyl, octyl, nonyl, decyl, dodecyl, lauryl and cetyl) esters of gallic acid and digallic acid and their alkyl ethers; monomethyl and monoethyl ethers of capryl pyrogallol and alkylated pyrogallol.

The specific activity of the various polyhydroxy aromatic compounds varies to some extent, all of them, however, being effective to some degree as corrosion inhibitors. It is therefore not to be implied that all the polyhydroxy aromatic compounds of the classes herein-described are equivalents.

As aforesaid, one of the components of the improved lubricant is the neutralized reaction product of a hydrocarbon and 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 pass 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 hydrocarbon mixture is introduced into the bottom of the reactor and passed upwardly through the catalyst layer, while a temperature of from about 50° F. to about 110° F. is maintained in the reactor. The propane and other saturated gases pass through the catalyst, while the propylene is polymerized under these conditions. The propylene polymer can be fractionated to any desired molecular weight, preferably from about 500 to about 1000 or higher.

Other suitable polymers are those 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

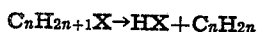
the polymer may be fractionated under reduced pressure into fractions of increasing molecular weights, and suitable fractions obtained reacted with the phosphorus sulfide to obtain the desired reaction products. The bottoms resulting from the fractionation of the polymer which may have Saybolt Universal viscosities at 210° F. ranging from about 50 seconds to about 10,000 seconds, are well suited for the purpose of the present invention.

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 (C₁₈), cerotene (C₂₆), melene (C₃₀) 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 carbons atoms to about 18 carbons atoms, and preferably at least 15 carbons 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 dehydrohalogenation of monohalogenated waxes, such as, for example, those obtained by dehydrochlorination of monochloroparaffin 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, monochlorowax and polychlorowax. This chlorinated product may be used as such, but it is advantageous to use the substantially monochlorowax fraction. The monochlorowax fraction can be segregated from the unchlorinated wax and the polychlorowax 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 monochlorowax, and the melting point of the latter is greater than that of the polychlorowax. Thus, the monochloroparaffin wax can be separated from the unchlorinated and the polychloroparaffin 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 monochloroparaffin wax by removing the chlorine from the latter as hydrogen chloride. The monochlorowax can be dehydrochlorinated by heating to a temperature of from about 200° F. to about 600° F. in the presence of a dehydrochlorinating 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 dehydrochlorinating agent.

After the dehydrohalogenation has been completed the olefin so obtained can be further purified by removing the dehydrohalogenating 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 adsorbents 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 sulfide, for example P₂S₅, 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 sulfide 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 sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess amount of phosphorus sulfide can be used and separated from the product by filtration or by dilution with a solvent such as hexane, filtering and subsequently 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.

ing 3 x 1 centimeter strips of lead and copper-lead alloy in 250 cc. of the lubricant which is maintained at a temperature of 280° F. and stirred at 1300 R. P. M. To accelerate the oxidation small amounts of naphthenic acid are added to the lubricant oil being tested. In one set of tests 0.10% naphthenic acid was employed while in another series 0.05% of the naphthenic acid was used. Periodically the test strips were removed from the lubricant oil bath and the loss in weight (expressed in mg.) was determined. In the table below the control lubricant oil was a solvent refined M. C. SAE 30 oil containing 1.5% of a KOH neutralized P_2S_5 -isobutylene polymer reaction product, and 0.16% sulfur added as sulfurized hydrocarbons. The catalyst A in the table denotes 0.1% naphthenic acid and the catalyst B was 0.05% naphthenic acid.

	Catalyst	Hours								
		3	5	10	15	20	30	40	50	60
Control Oil.....	A	70	100	164	225	---	---	---	---	---
Control+0.50% caprylpyrogallol.....	A	8	30	85	138	---	---	---	---	---
Control Oil.....	B	42	53	90	130	165	230	---	---	---
Control+0.5% hexylcatechol.....	B	0.0	0.5	1.0	1.5	1.6	---	2.0	---	2.7
Control+0.5% hexylcatechol.....	B	0.5	0.5	0.5	0.7	---	1.1	---	---	3.0
Control+0.1% hexylcatechol.....	B	0.5	1.0	1.0	2.0	---	4.5	---	---	10.7
Control+0.25% 2,4-dihydroxybenzaldehyde.....	B	0.8	0.8	0.8	---	---	0.8	---	0.8	3.0
Control+0.03% 2,4-dihydroxybenzaldehyde.....	B	0.0	0.0	0.0	0.3	---	---	---	---	3.0
Control+0.01% 2,4-dihydroxybenzaldehyde.....	B	7	13	---	39	---	---	---	---	78
Control+0.50% caprylpyrogallol.....	B	0.2	2	4.5	6.9	10	---	---	---	---

The neutralized phosphorus sulfide-hydrocarbon reaction product can be obtained by treating the acidic reaction product with a suitable basic compound such as hydroxide, carbonate, oxide or sulfide of an alkaline earth metal or an alkali metal such as, for example, potassium hydroxide, sodium hydroxide, sodium sulfide, etc. Other basic reagents can be used such as, for example, ammonia or an alkyl or aryl substituted 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 acidic 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 , K_2CO_3 , CaO, Na_2S , 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.

The effectiveness of the polyhydroxy aromatic compounds in inhibiting the corrosive action of lubricant compositions containing a small amount of a neutralized phosphorus sulfide-hydrocarbon reaction product is demonstrated by the following data. These data were obtained by suspend-

The above data clearly show the marked corrosion inhibiting property of polyhydroxy aromatic compounds of the type herein-described.

In addition to the foregoing additives, other additives such as oil-soluble organic amines (for example primary, secondary or tertiary aliphatic amines, aromatic amines, or tertiary aryl amines with nitrogen atoms in the aryl ring), pour point depressors, antioxidants, metal deactivators, anti-rust agents, corrosion inhibitors, V. I. improvers, extreme pressure agents, and the like may be present in the lubricant composition.

While I have described my invention as applied to lubricating oils, I contemplate the use of the combination of the herein-described additives in products other than lubricating oils, such as for example, fuel oils, insulating oils, waxes, greases, synthetic oils, non-drying animal and vegetable oils and the like.

While I have described my invention by reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto but includes within its scope such modifications as come within the spirit of the appended claims.

I claim:

1. A hydrocarbon oil containing in combination therewith from about 0.001% to about 2% of a polyhydroxy aromatic compound of the group consisting of a polyhydroxy aromatic alcohol and a polyhydroxy aromatic aldehyde 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.

2. A composition as described in claim 1 in which the olefin polymer is a polybutylene.

3. A composition as described in claim 1 in which the olefin polymer is a propylene polymer.

4. A composition as described in claim 1 in which the polyhydroxy aromatic alcohol is a polyhydroxy benzene.

5. A composition as described in claim 1 in

which the polyhydroxy aromatic alcohol is hexylcatechol.

6. A composition as described in claim 1 in which the polyhydroxy aromatic alcohol is capryl pyrogallol.

7. A composition as described in claim 1 in which the polyhydroxy aromatic aldehyde is 2,4-dihydroxy benzaldehyde.

8. A mineral lubricating oil containing in combination therewith from about 0.001% to about 2% of a polyhydroxy aromatic compound of the group consisting of a polyhydroxy aromatic alcohol and a polyhydroxy aromatic aldehyde and from about 0.001% to about 10% of a phosphorus-and sulfur-containing neutralized reaction product of a phosphorus sulfide and an olefin polymer.

EDWARD N. ROBERTS.

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