

UNITED STATES PATENT OFFICE

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LUBRICANT

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The present invention relates to a method of improving the lubricating qualities of lubricating oils and particularly to a method of improving the viscosity index characteristic and the non-ring sticking tendency of a lubricating oil and to a new lubricating oil additive capable of imparting the desired properties to a lubricating oil.

It is known that the viscosity of certain types of lubricating oils is greatly affected by temperature changes, and the viscosity-temperature relationship of an oil is therefore a highly specific characteristic. Highly paraffinic oils do not decrease in viscosity with increase in temperature as rapidly as do naphthenic oils. This viscosity-temperature relationship is measured by the viscosity index (V. I.) of the oil. Where wide variations in operation conditions are encountered, as with automobile and aircraft engine lubrication, the viscosity-temperature coefficient of the lubricant is of great importance and oils which show a minimum change in viscosity under these conditions are highly desired.

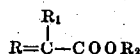
It is known that many types of lubricating oils usually used in internal combustion engines of the spark-ignition and compression-ignition types have a tendency to form carbon and/or varnish-like deposits on and about the pistons and piston rings etc. of such engines, causing the piston rings to become stuck in their slots, thus reducing the efficiency of the engine.

Lubricating oil additives have been developed to inhibit the formation of such carbon and/or varnish-like deposits in internal combustion engines during use. Other additives have been developed to enhance the viscosity index of lubricating oils. The various types of lubricating oil additives which have been developed to impart to lubricating oils certain desired properties are specific to their particular purpose and hence it has been necessary to employ several types of additives to impart to a lubricating oil all of the desired characteristics.

It is an object of the present invention to provide a lubricating oil additive which is capable of imparting to the oil improved viscosity index characteristics and non-ring sticking properties. It is another object of the present invention to provide a mineral lubricating oil composition having improved viscosity index character-

istics and which forms substantially no carbon and/or varnish-like deposits in internal combustion engines during use.

It is known that the viscosity index of an oil can be increased by adding thereto certain high molecular weight organic compounds having molecular weights of from about 800 to about 100,000 and higher, and preferably from about 2,000 to about 50,000. Organic compounds which can suitably be employed are rubber, hydrogenated natural or synthetic rubber, natural or synthetic rubber, high molecular weight polymers of olefinic hydrocarbons such as high molecular weight isobutylene and isobutylene-normal butylene polymers, and hydrogenated high molecular weight polymers of olefinic hydrocarbons. The synthetic rubbers referred to include butadiene, isoprene and chlorprene polymers and/or copolymers. Other types of additives which have been employed for this purpose are oil-soluble polymers of compounds having the general formula

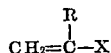


in which R is an alkylene radical, R₁ is a hydrogen atom, an alkyl, aryl or other hydrocarbon group and R₂ is a monovalent hydrocarbon radical or an amino substituted aliphatic radical derived from an amino alcohol or a long-chain fatty acid salt thereof. Compounds of this type are described in United States Patent Nos. 2,091,627 and 2,104,796.

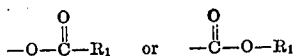
In accordance with the present invention the high molecular weight organic compounds as exemplified by the above classes of compounds are modified to impart still other properties to lubricants to which they are added. Particularly, compounds of the types above described, are modified to inhibit carbon and/or varnish-like formations on and about pistons, piston rings and the like of internal combustion engines when added to lubricating oils normally susceptible to form such carbon and/or varnish-like deposits, as well as improving the viscosity index of such lubricating oils. The improved additive of the present invention is obtained by treating a high molecular weight organic compound, capable of increasing the viscosity index of an

oil, with a phosphorus sulfide such as P_2S_3 , P_2S_4 , P_4S_7 , P_4S_{10} , or preferably, P_2S_5 .

Suitable starting materials are the oil-soluble high molecular weight polymerization products of esters having the vinyl or substituted vinyl group of the type described in United States Patent No. 2,091,627. Esters of the type therein described have the general formula

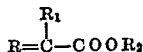


in which R is a hydrogen atom, an alkyl, aryl or other hydrocarbon group and X is



in which R_1 is a monovalent hydrocarbon radical having more than four carbon atoms or an ether derivative thereof. Especially suitable as starting materials are the polymerized esters of acrylic acid or of its alpha-alkyl or alpha-aryl substitution products and monhydric alcohols of more than four carbon atoms. These polymers can be prepared by heating the esters at a temperature of from about $158^\circ F.$ to about $212^\circ F.$ in the presence of a catalyst such as peroxide, ozonide, or other catalyst such as the anhydrous halides of polyvalent or amphoteric metals.

Other high molecular weight organic compounds which can be used as the starting materials are the high molecular weight, preferably those above about 2,000, oil-soluble polymerized acrylic and alpha-substituted acrylic acid esters of amino alcohols or the long-chain fatty acid salts of such alcohols. These compounds of the types described in United States Patent No. 2,104,796 may be represented by the formula



wherein R represents an alkylene radical, R_1 represents hydrogen or an alkyl radical and R_2 an amino substituted aliphatic radical derived from an amino alcohol or its salt. Preferably, the amino alcohol contains a tertiary nitrogen atom in which the substituents attached to the nitrogen are aliphatic hydrocarbon radicals. The polymeric esters derived from N substituted amino alcohols in which the substituents are aliphatic hydrocarbon radicals of at least four carbon atoms will, in general, be found to be sufficiently soluble in the oil. The polymeric esters derived from amino alcohols containing a lesser number of carbon atoms will be less soluble in the oils and it will generally be necessary to employ these polymers in the form of long-chain fatty acid salts in order to render them sufficiently soluble to enable the desired amount to be added and retained in the oil.

High molecular weight compounds which are suitable starting materials are high molecular weight volatilized fatty oils and/or mineral oils. Compounds of the type of polystyrene and polyindene can also be employed. Other high molecular weight organic compounds having V. I. imparting properties which can be used as starting materials in the preparation of the improved multifunctional additive are the high molecular weight polymers having molecular weights higher than about 2,000, resulting from the low temperature polymerization of olefinic hydrocarbons in the presence of a catalyst of the Friedel-Crafts type such as boron fluoride or aluminum chloride.

The high molecular weight olefin polymer may be a polymer resulting from the polymerization of a low molecular weight iso-mono-olefin such

as isobutylene or isoamylene and/or the copolymers obtained by the polymerization of hydrocarbon mixtures containing low molecular weight iso-mono-olefins and normal mono-olefins such as those having less than six carbon atoms and preferably those of four carbon atoms. These high molecular weight polymers can be obtained, for example, by the polymerization in the liquid phase of an iso-olefin such as isobutylene or a hydrocarbon mixture containing isobutylene at a temperature of from about $0^\circ F.$ to about $-150^\circ F.$, for example $-80^\circ F.$, in the presence of a catalyst such as boron fluoride. For example, a hydrocarbon mixture containing from about 10% to about 25% isobutylene is maintained under pressure sufficient to keep it in the liquid phase and cooled to a temperature of about $-80^\circ F.$ and from about 0.01% to about 2% boron fluoride, based upon the isobutylene content of the material treated, added with vigorous agitation. Excessive rise in temperature due to the heat of the reaction is 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 and washed free of acidic substances arising from the catalyst. The oily layer is separated and the polymer subsequently separated from the unreacted hydrocarbon by distillation. The polymer so obtained has a molecular weight of from about 3,000 to about 50,000 and is an effective additive for increasing the viscosity index characteristics of a lubricating oil normally having a relatively poor viscosity-temperature coefficient.

The multifunctional additive of the present invention is prepared by reacting a phosphorus sulfide, preferably phosphorus pentasulfide, with a high molecular weight organic compound of the hereindescribed type, having the property of improving the viscosity index characteristics of a lubricating oil. Thus, the new additive of the present invention can be prepared by reacting phosphorus pentasulfide with a high molecular weight organic compound selected from the class of compounds above described, capable of imparting improved V. I. properties to a lubricating oil. The reaction is carried out at a temperature of from about $200^\circ F.$ to about $500^\circ F.$ and preferably from about $300^\circ F.$ to about $400^\circ F.$ while maintaining a non-oxidizing atmosphere, such as 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 should be used. It is preferable to use an amount that will react completely with the second reactant so that no further purification becomes necessary. However, if an excess amount of the phosphorus sulfide is used the unreacted phosphorus sulfide can be removed from the final product by filtration or by diluting the reaction product with a solvent, such as hexane, filtering and subsequently distilling and evaporating off the solvent. The final reaction product can be further refined by treating the same with a compound having an active hydrogen atom at a temperature of from about $100^\circ F.$ to $600^\circ F.$ and preferably by steam blowing the reaction product at a temperature of from about $200^\circ F.$ to about $600^\circ F.$ and preferably from about $300^\circ F.$ to $400^\circ F.$

The above reaction may be carried out by merely admixing the two reactants, or the high molecular weight organic compound may be dissolved in a suitable solvent, such as a lubricating

oil or other high-boiling hydrocarbon solvents, and the phosphorus sulfide added to the solution or the organic compound may be dispersed in a solvent and the phosphorus sulfide added to the dispersion. The mixture is then heated to a temperature within the above range to bring about a reaction between the phosphorus sulfide and the high molecular weight compound. If desired the solvent may be removed from the reaction product by distillation and reused or recycled.

The reaction product of a phosphorus sulfide and a high molecular weight organic compound of the class described herein normally shows a titratable acidity which is neutralized when the reaction product is treated with a basic reagent. The phosphorus sulfide-high molecular weight organic compound 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 may be introduced into the neutralized reaction products by reacting the same with a salt of the desired heavy metal.

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

The neutralized phosphorus sulfide-high molecular weight organic compound reaction product can be obtained by adding to the reaction product a suitable basic compound such as a hydroxide, a carbonate or an oxide of an alkaline earth metal or an alkali metal, preferably potassium hydroxide, sodium hydroxide or lime. Other basic reagents can be used such as, for example, ammonia or alkyl or aryl substituted ammonia such as amines.

As aforesaid, when the phosphorus sulfide-high molecular weight organic compound reaction product is neutralized with a basic reagent containing a metal constituent, the neutralized reaction product is characterized by the presence of a metal constituent of such basic reagent. Neutralized reaction products containing a heavy metal constituent such as, for example, tin, titanium, aluminum, chromium, cobalt, iron and the like may be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-high molecular weight organic compound 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 reaction product of a phosphorus sulfide and a high molecular weight organic compound of the class described when added to a lubricating oil in small amounts of from about 0.01% to about 20% and preferably from about 0.5% to about 5% is effective in increasing the viscosity index of the lubricating oil and also in inhibiting the formation and/or deposition of carbon and/or varnish-like deposits in internal combustion engines during the operation thereof. To

facilitate handling of these products, as much as 50% or more of the reaction product may be dissolved in a mineral oil to form a concentrate, which can be diluted with lubricating oils as required.

The following examples will serve to illustrate the hereindescribed invention.

Example I

10 Hydrogenated rubber is admixed with 10% of phosphorus pentasulfide and the mixture heated in an atmosphere of nitrogen at 380° F. for six hours. The reaction product is an effective V. I. improver and carbon and/or varnish inhibitor
15 when added in small amounts of the order of from 0.1% to 2% to a lubricating oil normally having a poor viscosity index and normally susceptible to form carbon and/or varnish-like deposits in an internal combustion engine during use.

Example II

The reaction product obtained by mixing an oil solution of octa-decyl-alpha methacrylate polymer with 10% phosphorus pentasulfide and heating the mixture at 380° F. for six hours in an atmosphere of nitrogen, when added to an SAE 20 lubricating oil in small amounts improves the viscosity-temperature coefficient of the oil and also inhibits the formation of varnish-like deposits in an internal combustion engine during operation.

Example III

An isobutylene polymer having a molecular weight of about 7500 was reacted with about 10% phosphorus pentasulfide at a temperature of about 380° F. for five hours in an atmosphere of nitrogen. The product was then diluted with hexane, filtered, and the hexane removed from the filtrate by distillation. The reaction product was then diluted with an equal volume of a motor oil and the mixture blown with steam at a temperature of about 300° F. until the product was substantially odorless.

Example IV

An isobutylene polymer having a molecular weight of about 7500 was treated with 10% by weight of phosphorus pentasulfide at a temperature of 180° F. for six hours in an atmosphere of nitrogen. The reaction product was then neutralized by treating the same with dry potassium hydroxide at a temperature of 340-350° F. for about five hours. The product was then diluted with hexane, filtered and the filtrate freed of the solvent by distillation.

It will be obvious to one skilled in the art that many modifications and variations of the above illustrative examples may be effected in the practice of the present invention, which, broadly includes within its scope any and all lubricating composition containing therein a reaction product of a phosphorus sulfide and a high molecular weight organic compound having the property of enhancing the V. I. of a lubricating oil.

We claim:

1. A lubricant comprising a lubricating oil and the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight organic compound having a molecular weight of at least about 2000 characterized by its ability to enhance the viscosity index of a lubricating oil, said reaction product being used in a small but sufficient amount to simultaneously increase the viscosity index of said lubricant and

to inhibit the formation of sludge and varnish-like materials in said lubricant.

2. A lubricant as described in claim 1 in which the phosphorus sulfide is phosphorus pentasulfide.

3. A lubricant comprising a lubricating oil and a phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight hydrocarbon having a molecular weight of at least about 2000 characterized by its ability to enhance the viscosity index of the lubricating oil, said reaction product being used in a small but sufficient amount to simultaneously increase the viscosity index of said lubricant and to inhibit the formation of sludge and varnish-like materials in said lubricant.

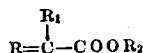
4. A lubricant as described in claim 3 in which the high molecular weight hydrocarbon is hydrogenated rubber.

5. A lubricant as described in claim 3 in which the high molecular weight hydrocarbon is a monoolefin polymer having a molecular weight above about 2,000.

6. A lubricant as described in claim 3 in which the high molecular weight hydrocarbon is an isomono-olefin polymer having a molecular weight above about 2,000.

7. A lubricant as described in claim 3 in which the high molecular weight hydrocarbon is an isobutylene polymer having a molecular weight above about 2,000.

8. A lubricant as described in claim 1 in which the high molecular weight organic compound is an oil-soluble polymer of a compound having the general formula



in which R is an alkylene radical, R₁ is a substituent selected from the group consisting of an hydrogen atom, and a hydrocarbon radical and R₂ is a substituent selected from the group consisting of a monovalent hydrocarbon radical, and an amino substituted aliphatic radical.

9. An oil of improved viscosity index and resistance to the formation of sludge and varnish-like materials comprising a lubricating oil of undesirably low viscosity index and normally susceptible to the formation of sludge and varnish-like materials and a small amount of the phosphorus and sulfur-containing reaction product of the phosphorus sulfide and a high molecular weight organic compound having a molecular weight of at least about 2000 characterized by its ability to increase the viscosity index of a lubricating oil, said reaction product being added in amounts sufficient to increase the viscosity index of said lubricating oil and to substantially inhibit the formation of sludge and varnish-like materials therein.

10. An oil of improved viscosity index and resistance to the formation of sludge and varnish-like materials comprising a lubricating oil having an undesirable low viscosity index and normally susceptible to the formation of sludge and varnish-like materials during use and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight hydrocarbon having a molecular weight of at least about 2000 characterized by its ability to increase the viscosity index of a lubricating oil, said reaction product being added in amounts sufficient to increase the viscosity index of said lubricating oil and to substantially inhibit

the formation of sludge and varnish-like materials therein.

11. An improved lubricating oil as described in claim 10 in which the high molecular weight organic compound is an isobutylene polymer having a molecular weight above about 2,000 and characterized by its ability to improve the viscosity index of a lubricating oil normally having poor viscosity index.

12. An improved lubricating oil as described in claim 9 in which the high molecular weight organic compound is an organic compound having a molecular weight of at least about 2,000, selected from the group consisting of oil-soluble polymerized acrylic acid esters of amino alcohols, alpha-alkyl substituted acrylic acid esters of amino alcohols, oil-soluble long-chain fatty acid salts of polymerized acrylic acid esters of amino alcohols, and alpha-alkyl substituted acrylic acid esters of amino alcohols, which polymerized esters are characterized by their ability to enhance the viscosity-temperature coefficient of a lubricating oil normally having a poor viscosity-temperature coefficient.

13. An addition agent for lubricating oils comprising a concentrated solution in a hydrocarbon oil of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight organic compound having a molecular weight of at least about 2000, characterized by its ability to increase the viscosity index of a lubricating oil, said reaction product being effective in increasing the viscosity index of a lubricating oil and to inhibit the formation of sludge and varnish-like materials therein, said concentrate being capable of dilution with a hydrocarbon lubricating oil to form an homogeneous mixture containing from about .01% to about 20% by weight of said reaction product based on the lubricating oil.

14. An addition agent for lubricating oils comprising a concentrated solution in a hydrocarbon oil of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight hydrocarbon compound having a molecular weight of at least about 2000 characterized by its ability to increase the viscosity index of a lubricating oil, said reaction product being effective in increasing the viscosity index of a lubricating oil and to inhibit the formation of sludge and varnish-like materials therein, said concentrate being capable of dilution with a hydrocarbon lubricating oil to form a homogeneous mixture containing from about .01% to about 20% by weight of said reaction product based on the lubricating oil.

15. An addition agent for lubricating oil comprising a concentrated solution in a hydrocarbon oil of the neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight organic compound having a molecular weight of at least about 2000 characterized by its ability to increase the viscosity index of a lubricating oil, said neutralized reaction product being effective in increasing the viscosity index of a lubricating oil and to inhibit the formation of sludge and varnish-like materials therein, said concentrate being capable of dilution with a hydrocarbon lubricating oil to form a homogeneous mixture containing from about .01% to about 20% by weight of said neutralized reaction product based on the lubricating oil.

16. An addition agent for lubricating oils comprising a concentrated solution in a hydrocarbon

oil of the neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight hydrocarbon compound having a molecular weight of at least about 2000 characterized by its ability to increase the viscosity index of a lubricating oil, said neutralized reaction product being effective in increasing the viscosity index of a lubricating oil and to inhibit the formation of sludge and varnish-like materials therein, said concentrate being capable of dilution with a hydrocarbon lubricating oil to form a homogenous mixture containing from about .01% to about 20% by weight of said neutralized reaction product based on the lubricating oil.

17. A lubricant comprising a lubricating oil and a neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a high molecular weight organic compound having a molecular weight of at least about 2000 characterized by its ability to enhance the viscosity index of a lubricating oil, said neutralized reaction product being used in a small but sufficient amount to simultaneously increase the viscosity index of said lubricant and to inhibit the formation of sludge and varnish-like materials in said lubricant.

18. A lubricant as described in claim 17 in which the neutralized reaction product contains a metal constituent.

19. A lubricant as described in claim 17 in

which the neutralized reaction product contains potassium.

20. A lubricant as described in claim 17 in which the neutralized reaction product contains sodium.

21. A lubricant as described in claim 17 in which the neutralized reaction product contains calcium.

22. A lubricant comprising a lubricating oil and a neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a mono-olefin polymer having a molecular weight above about 2000, said neutralized reaction product being used in a small but sufficient amount to simultaneously increase the viscosity index of said lubricant and to inhibit the formation of sludge and varnish-like materials in said lubricant.

23. A lubricant as described in claim 22 in which the neutralized reaction product contains a metal constituent.

24. A lubricant as described in claim 22 in which the neutralized reaction product contains potassium.

25. A lubricant as described in claim 22 in which the neutralized reaction product contains sodium.

26. A lubricant as described in claim 22 in which the neutralized reaction product contains calcium.

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