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LUBRICANT

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This invention relates to improvements in lubricant compositions and is more particularly related to lubricating oil compositions which have had one or more of its properties improved by the addition thereto of a new and novel addition agent.

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, i. e. a high viscosity index, are highly desired.

It is known that many types of lubricating oils usually used in internal combustion engines of both 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 characteristics and which forms substantially no carbon and/or varnish-like deposits in internal combustion engines during use.

A copending application of C. D. Kelso and L. W. Mixon Serial No. 384,945 discloses an improved lubricant composition containing the reaction product of a phosphorus sulfide and certain high molecular weight organic compounds such as synthetic rubbers obtained by the polymerization of butadiene, isoprene, and the like.

I have now discovered that improved lubricant additives are obtained by reacting a phosphorus sulfide with a high molecular weight copolymer of a low molecular weight mono-olefin and a more unsaturated olefin preferably a conjugated diolefin, the copolymer having a controlled degree of unsaturation. By reacting a phosphorus sulfide with the copolymer, having the desired degree of unsaturation, reaction products are obtained which have a higher phosphorus content than is otherwise obtainable, by reacting a phosphorus sulfide with a monoolefin polymer, and which are more stable than the reaction products of a phosphorus sulfide and a diolefin polymer.

The copolymer base is prepared by controlled copolymerization of a low molecular weight olefin and a non-aromatic hydrocarbon having the general formula C_nH_{2n-x}, in which x is 2 or a multiple of 2, in the presence of a catalyst of the Friedel-Crafts type. The low molecular weight olefin is preferably an isoolein or a tertiary base olefin preferably one having less than 7 carbon atoms per molecule. Examples of olefins which can be suitably employed are isobutylene, 2-methyl-butene-1,2-ethylbutene-1, secondary and tertiary base amylene, hexylenes and the like, isobutylene being preferred however. A "tertiary base" olefin is one related to a tertiary alcohol and corresponding to the formulas $R_2C{=}CH_2$, $R_2C{=}CHR$ and $R_2C{=}CH_2$ in which the R groups are alike or different.

Examples of the non-aromatic hydrocarbons having the above general formulas which can be used are the conjugated diolefins, such as butadiene, isoprene, cyclopentadiene, 2,3-dimethyl-butadiene-1,3, pentadiene-1,3, hexadiene-2,4 and the substituted diolefins such as chloroprene and the like. Diolefins such as dialkyls, for example, diisobutenyl, and the like, in which the double bond is not conjugated are also suitable. Other hydrocarbons falling within the class are the acetylenes such as acetylene, vinyl acetylene and the like. It is to be understood that the term "non-aromatic hydrocarbons having the general formula C_nH_{2n-x} in which x is the number 2 or a multiple of 2" embraces the substitution products of these hydrocarbons such as, for example, chloroprene.

The copolymerization is preferably carried out in the presence of aluminum chloride or boron fluoride, although other Friedel-Crafts type cat-

alyst such as aluminum bromide, zinc chloride, zirconium chloride and the like can be employed.

In the preparation of the copolymer base which preferably has a molecular weight of from about 1,000 to about 30,000, and preferably from about 2,000 to about 20,000, and contains from about 2% to about 20% butadiene, from about 20% to about 60% by weight of the diolefin, for example, is reacted with the olefin at a low temperature ranging from about 32° F. to about —150° F. and preferably from about 10° F. to about —130° F. The polymerization is conducted in the presence of a diluent and preferably a diluent which is capable of functioning also as a refrigerant such as a liquefied normally gaseous hydrocarbon such as for example liquefied ethylene, liquefied propane, liquefied butane and the like. Alkyl halides such as methyl chloride can also be used.

In carrying out the polymerization the reaction chamber is first cooled to the desired low temperature by adding a sufficient amount of the liquefied normally gaseous hydrocarbon. The diolefin is then added to the reactor followed by the addition of the isoolefin. After the isoolefin has been added the catalyst, preferably in solution in a suitable solvent such as for example, a low molecular weight alkyl halide, is then added to the mixture. It is highly desirable to provide for rapid mixing of the reaction mass to obtain a uniform product. The polymerization reaction is permitted to proceed to a polymer yield of from about 50% to about 90% in order to obtain polymers of the desired molecular weight and of the desired degree of unsaturation. The reaction can be stopped at the desired yield by adding to the reactor a material capable of quenching the reaction. Suitable quenching agents are alcohols, ethers, ketones and the like; ethyl alcohol is preferably employed for this purpose.

By conducting the polymerization reaction under the above controlled conditions copolymers of olefins and diolefins having the desired degree of unsaturation are obtained. Because of the unsaturation of these copolymers they are more receptive to the introduction of phosphorus into the molecule at the points of unsaturation, and hence products having a higher phosphorus content can be obtained. Products having a higher sulfur content may also be obtained.

Material which when reacted with the phosphorus and sulfur containing agent will produce a satisfactory V. I. improving agent, may be produced by depolymerizing natural and synthetic rubbers but such a product is undesirably unstable and thus the copolymer of this process is much preferred.

In accordance with the present invention the copolymers obtained by the above described method are reacted with a phosphorus sulfide such as P_2S_5, P_2S_3, P_3S_4, P_4S_7, P_4S_{10}: the phosphorus pentasulfide (P_2S_5) being preferably employed. The reaction is carried out at a temperature of from about 200° F. to about 500° F. and preferably from about 300° F. to about 400° F. while maintaining a non-oxidizing atmosphere, such as an atmosphere of nitrogen, above the reaction mixture. From about 1% to about 50%, by weight 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 phosphous 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 or 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° F. to 600° F. and preferably by steam blowing the reaction product at a temperature of from about 200° F. to about 600° F. and preferably from about 300° F. to 400° F.

The above reaction may be carried out by merely admixing the two reactants, or the copolymer may be dissolved in a suitable solvent, such as a lubricating oil or other high-boiling solvents, and the phosphorus sulfide added to the solution, or the copolymer 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 copolymer. 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 copolymer reaction product 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-copolymer 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-copolymer reaction product" as used herein means a phosphorus sulfide-copolymer reaction product having at least about 1% of its titratable acidity reduced by reaction with a basic reagent and includes a neutralized phosphorus sulfide-copolymer reaction product containing a metal constituent resulting from said neutralization or resulting from the reaction of a heavy metal salt with a phosphorus sulfide-copolymer reaction product treated with a basic reagent.

The neutralized phosphorus sulfide-copolymer 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-copolymer 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-copolymer 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 copolymer 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 above described invention may be illustrated by the following examples:

Example I

A mixture comprising about 40% butadiene and 60% isobutylene is dissolved in liquefied propane and cooled to a temperature of about —80° F. by the partial evaporation of the liquefied propane. A 0.5% solution of aluminum chloride in methyl chloride is cooled to approximately —80° F. and slowly added to the butadiene-isobutylene mixture, and the reaction permitted to proceed to a copolymer yield of 50–80%. The reaction is then stopped by introducing into the reactor sufficient ethyl alcohol to quench the reaction.

The above copolymer is reacted with about 10% phosphorus pentasulfide at a temperature of about 380° F. for five hours in an atmosphere of nitrogen. The product is then diluted with hexane and filtered. A lubricating oil is then added to the filtrate, the hexane removed from the filtrate by distillation, and the diluent-free mixture blown with steam at a temperature of about 300° F. until a substantially odorless product is obtained.

Example II

The P_2S_5-copolymer reaction product obtained in Example I is treated with 0.5% of dry KOH at a temperature of about 200° F. The temperature is then raised to 340–350° F. and maintained at this temperature for five hours.

Example III

A copolymer of isobutylene and isoprene is obtained by reacting 93 parts of isobutylene with 7 parts of isoprene at a temperature of about —80° F. with a ½% solution of aluminum chloride in methyl chloride as a catalyst.

The copolymer obtained is then taken up in a hexane solution, and treated with about 10% phosphorus pentasulfide at a temperature of about 380° F. for five hours in an atmosphere of nitrogen. The reaction product is then freed of hexane and taken up in an equal volume of a motor oil of about S. A. E. 20 grade.

Example IV

The phosphorus pentasulfide reaction product obtained in Example III is treated with about 3 volumes of a 5% solution of alcoholic KOH.

Example V

A mixture of 10 grams isoprene and 50 grams isobutylene in 100 cubic centimeters of hexane is chilled to —70° F. and an excess of BF_3 introduced into the mixture. Upon completion of the reaction the excess BF_3 is neutralized with caustic soda solution, and an oil layer separated from an aqueous layer. The oil layer is then stripped at about 200° F. to remove the light fractions. A yield of about 80% by weight of a copolymer having a molecular weight of about 1000 is obtained.

The above copolymer is treated with about 10% phosphorus pentasulfide at a temperature of about 380° F. for five hours in an atmosphere of nitrogen and the product then diluted with an equal volume of a light lubricating oil.

The reaction product is then neutralized with 0.5% of dry KOH at a temperature of about 200° F.

Example VI

A copolymer having a molecular weight of about 27,000, is obtained by reacting a mixture of isobutylene and acetylene in the weight proportions of 95% of the former and 5% of the latter, with about 0.1% BF_3 at about —100° F. This copolymer is treated with 10% phosphorus pentasulfide at a temperature of about 380° F. for about five hours. The reaction product is diluted with about an equal volume of a lubricating oil and the mixture steam blown at about 300° F. until a substantially odorless product is obtained.

The above steamed product is then treated with 0.5% dry KOH at a temperature of about 340–350° F. for about five hours.

The hereindescribed phosphorus sulfide-copolymer reaction products either neutralized or unneutralized when added in small amounts to motor oils are effective in inhibiting the formation of deposits such as sludge, carbon and varnish upon the pistons, piston rings, etc. of internal combustion engines. They are also effective in imparting to lubricating oils to which they are added improved viscosity index characteristics.

The compounds of the present invention may be added to products other than mineral lubricating oils, such as for example, fuel oils, non-drying vegetable and animal oils, insulating oils, synthetic oils, greases and the like.

The improved properties obtained and the degree of improvement effected in any particular property may vary with the degree of copolymerization and the olefin and diolefin employed, although they all exhibit a definite improvement in lubricating oil properties.

While I have described certain preferred procedures which may be followed in the preparation of the copolymer and in the preparation of the copolymer-phosphorus sulfide reaction products as additives for oil compositions contemplated by the present invention, and have named various representative constituents in the preparation of these additives, such procedures and examples have been used for illustrative purposes only. The invention is not to be limited to the 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 a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of a mono-olefin and a non-aromatic hydrocarbon having the general formula C_nH_{2n-x} in which x is a whole number selected from the group consisting of 2 and multiples of 2 said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

2. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of a mono-olefin and a polyolefin said copolymer being prepared in the

presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

3. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of an olefin and a conjugated polyolefin said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

4. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of an isoolefin and a conjugated diolefin said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

5. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of isobutylene and a butadiene said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

6. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of isobutylene and acetylene said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

7. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of an amylene and a butadiene said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

8. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of a butylene and butadiene said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

9. A lubricant composition containing an oil, and a small amount of the phosphorus and sulfur-containing reaction product of a phosphorus pentasulfide and a copolymer having a molecular weight of at least about 1000 to 30,000 of isobutylene and a conjugated diolefin, said copolymer being obtained by polymerizing the isobutylene and the conjugated diolefin at a temperature of 32° F. to —150° F. in the presente of a Friedel-Crafts type catalyst to obtain a copolymer yield of from about 50% to about 90%.

10. A lubricant composition containing a mineral oil and a minor amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing an isoolefin and a conjugated diolefin and subsequently reacting the copolymer with a phosphorus sulfide said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

11. A lubricant composition containing a mineral oil and a minor amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing an isobutylene and a conjugated diolefin and subsequently reacting the copolymer with a phosphorus sulfide said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

12. A lubricant composition containing a mineral oil and a minor amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing isobutylene and butadiene and subsequently reacting the copolymer with a phosphorus sulfide said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

13. A lubricant composition containing a mineral oil and a minor amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing isobutylene and a diolefin in the presence of a Friedel-Crafts type catalyst to obtain a copolymer having a molecular weight within the range of about 1,000 to 30,000 and containing from about 2% to about 10% butadiene and subsequently reacting said copolymer with a phosphorus sulfide.

14. A lubricant composition as described in claim 13 in which the diolefin is a conjugated diolefin.

15. A lubricant composition containing a mineral oil and a minor amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing isobutylene with from about 20% to about 60% by weight of a conjugated diolefin at a temperature within the range of from about 32° F. to about —150° F. in the presence of a Friedel-Crafts type catalyst to obtain a copolymer yield of 50 to 90% of a copolymer having a molecular weight of at least about 1000 to 30,000 and subsequently reacting the copolymer so obtained with a phosphorus sulfide.

16. A lubricant composition containing a mineral oil and a minor amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing isoolefin with a conjugated polyolefin, reacting the copolymer having a molecular weight of at least about 1000 to 30,0000 with a phosphorus sulfide and subsequently neutralizing the reaction product.

17. A lubricant composition containing a mineral oil and a small amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing isobutylene and a conjugated diolefin in the presence of a Friedel-Crafts type catalyst to obtain a copolymer having a molecular weight within the range of from about 1000 and about 30,000 reacting the copolymer with a phosphorus sulfide and subsequently neutralizing the reaction product.

18. A lubricant composition containing a mineral oil and a small amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing isobutylene and butadiene in the presence of a Friedel-Crafts type catalyst under conditions to obtain a copolymer having a molecular weight whithin the range of from about 1,000 to about 30,000 and containing from about 2% to about 10% butadiene, reacting said copolymer with phosphorus pentasulfide and subsequently neutralizing the reaction product so obtained with a basic reagent.

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

20. A lubricant composition as described in claim 18 in which the neutralized product contains sodium.

21. A lubricant composition as described in claim 18 in which the neutralized product contains potassium.

22. A lubricant composition as described in claim 18 in which the neutralized product contains calcium.

23. The method of inhibiting the formation of deposits of the type of sludge, carbon and varnish in an internal combustion engine during use comprising lubricating said engine with a lubricant comprising a lubricating oil normally susceptible to form sludge, carbon and varnish in an internal combustion engine during use and a small amount of the phosphorus and sulfur-containing product obtained by the process comprising copolymerizing an isoolefin and a conjugated diolefin at a temperature within the range of 32° F. to −150° F. in the presence of Friedel-Crafts type catalyst to obtain a polymer yield of from about 50% to 90% and subsequently reacting said copolymer having a molecular weight of at least about 1000 to 30,000 with a phosphorus sulfide.

24. A composition comprising an oil and the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a co-polymer of a mono-olefin and a non-aromatic hydrocarbon, said non-aromatic hydrocarbon having the general formula C_nH_{2n-x} in which x is a whole number selected from the group consisting of 2 and multiples of 2 said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

25. A composition comprising an oil and the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and copolymer of an olefin and a conjugated polyolefin said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

26. A composition comprising an oil and the phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of a butylene and butadiene said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

27. A composition comprising an oil and the neutralized phosphorus and sulfur-containing reaction product of a mono-olefin and a non-aromatic hydrocarbon having the general formula C_nH_{2n-x} in which x is a whole number selected from the group consisting of 2 and the multiples of 2 said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

28. A composition comprising an oil and the neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of an olefin and a conjugated polyolefin said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

29. A composition comprising an oil and the neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of a butylene and a butadiene said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

30. A composition comprising an oil and a metal-containing neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a copolymer of an olefin and a conjugated polyolefin said copolymer being prepared in the presence of a Friedel-Crafts type catalyst and having a molecular weight of at least about 1000 to 30,000.

31. A composition as described in claim 30 in which the metal is an alkali metal.

32. A composition as described in claim 30 in which the metal is potassium.

33. A composition as described in claim 30 in which the metal is sodium.

34. A composition as described in claim 30 in which the metal is an alkaline earth metal.

35. A composition as described in claim 30 in which the metal is calcium.

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