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METAL SALTS OF SULFONATED ACRYLIC ESTER POLYMERS AND LUBRICATING OILS CONTAINING THE SAME

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This invention relates to a lubricating oil additive composition which when incorporated in mineral lubricating oil imparts improved detergency, viscosity index and pour point characteristics. The invention relates particularly to oil-soluble metal salts of sulfonated polymerization products of esters containing a vinyl or substituted vinyl group and to lubricating oils containing these metal salts.

It is known that metal sulfonates, particularly those derived by sulfonating mineral oil fractions, impart good detergent properties to mineral lubricating oils. However, it is found that in order to impart satisfactory detergency characteristics, relatively large proportions of the metal petroleum sulfonates must be employed and because of the high ratio of metal to sulfonic acid group in such sulfonates, the amount of metal added to mineral lubricating oils in order to obtain the desired detergency, is objectionably high, running as high as 2% by weight or more in some mineral lubricating oils available on the market. The high metal content is objectionable because it has the effect of increasing engine deposits, particularly in the combustion chambers of the engine. Thus an engine operating with an oil having a high metal content is found to have an objectionable octane requirement increase during a relatively short period of operation, resulting primarily from the increased amount of deposits in the combustion chamber.

Moreover, it is known that by adding polymerization products of various types to mineral lubricating oils it is possible to increase the viscosity index of the oil and to reduce the pour point of the oil and in order to meet requirements of engine lubricants it is often necessary not only to add materials which improve the detergency of the mineral lubricating oil but secondary additives designed to improve the viscosity index and pour point characteristics.

acteristics.

The object of this invention is to provide an oil-soluble, stable, additive material, which when added to mineral lubricating oil will improve the detergency characteristics of the oil, raise the viscosity index of the oil and reduce the pour point of the oil, which additive material contains a relatively small amount of metal and 55 thus, when employed in amounts necessary to impart the desired characteristics to the oil, imparts only a very small metal content to the finished oil.

A further object of the invention is to prepare mineral lubricating oils suitable for use in internal combustion engines, which oils contain the mentioned additive material, and have the desired properties of low metal content, high detergency, improved V. I. and reduced pour point.

Another object of this invention is to produce an additive material which when added to mineral lubricating oil produces a multi-grade lubricating oil, i. e., one suitable for use, particularly in automotive engines, under widely varying conditions of temperature, such oils being referred to as SAE 5W-20 or 10-30 grade lubricating oils.

The above objects are accomplished by sulfonating the oil-soluble polymerization products of esters containing

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an acrylic acid or substituted acrylic acid group, which esters have the general formula

where R is hydrogen or an alkyl or aryl radical containing between 1 and about 9 and preferably between 1 and about 6 carbon atoms and R' is a monovalent hydrocarbon radical containing more than 4 carbon atoms or an ether radical containing more than 4 carbon atoms and converting the resulting sulfonated polymers into their metal salts. The resulting metal salts when added to mineral lubricating oils impart the desirable characteristics referred to hereinabove. The metal salts may be further reacted with a basically reacting metal compound and the resulting complex or modified sulfonate used as the oil addition agent with the same or improved results.

Compounds which are suitable for sulfonating and which fall within the definition above given include polymerized esters of acrylic acid or alkyl or alpha aryl substituted acrylic acids and monohydric alcohols containing more than about 4 carbon atoms. The esters which when polymerized are useful in preparing the additive compounds include the amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, myricyl, acetyl and octadecyl esters of acrylic acid, alpha methacrylic acid, alpha phenylacrylic acid and other alpha substituted homologs of these acids. The esters may be those prepared from normal, saturated aliphatic alcohols, although the corresponding iso and branched chain alcohols may be employed. Moreover, ether alcohols may be substituted for the monohydric alcohols in preparing the esters. Thus, the benzyloxyethyl, cyclohexoxyethyl, amylphenoxyethyl, butoxyethyl esters may be polymerized and sulfonated in the same manner as those produced from the alcohols mentioned and the resulting sulfonic acids converted to sulfonates or complex sulfonates which are useful according to this

The polymers are prepared from the monomeric esters by processes well known in the art, as for example, by heating the monomeric esters at elevated temperatures, as for example, in the range of 175° F. to 215° F., in the presence of polymerization catalysts, such as peroxides. The method of preparing the polymers is disclosed in U. S. Patent No. 2,091,627. Generally, polymerization is continued until the average molecular weight of the polymer is within the range of about 5000 to 30,000 and preferably unpolymerized monomer is removed from the resulting polymer prior to sulfonation. The polymerization may be carried out on the ester itself or the ester can be polymerized in the presence of about 1 to 3 parts of mineral lubricating oil per part of ester. In the latter case the polymer is obtained in oil solution.

Molecular weights shown herein are those determined following the method outlined in an article "Intrinsic Viscosity-Molecular Weight Relationship for Polystyrene," by A. I. Goldberg et al., Journal of Polymer Science, volume 2, page 503, 1947.

In preparing the additive of this invention the ester polymer is sulfonated and the resulting sulfonic acid is converted into the desired metal salt. The metal salt may be used per se or it may be further treated with a basically reacting metal compound of the same or different metal under conditions to produce a sulfonate complex as will be described hereinbelow. Because of the fact that the ester polymers are viscous liquids or plastic solids, the polymer is dissolved in a solvent prior to sulfonation. The solvent is preferably a relatively low boiling aliphatic hydrocarbon or hydrocarbon fraction, as for example, a paraffinic solvent having a boiling point range between about 140° F. and about 170° F. In place of the paraffinic solvent any solvent which is

not affected by sulfuric acid during sulfonation may be employed. In the following description the method of sulfonation will be described in connection with the sulfonation of polylauryl methacrylate, however, the same conditions are applicable to the sulfonation of the other polyesters described hereinabove. One part by weight of lauryl methacrylate was dissolved in two parts by weight of a paraffinic solvent boiling between 140° F. and 170° F. This solution was heated to 100° F. and 0.3 parts by weight of 15% fuming sulfuric acid was added slowly, with stirring, over a period of approximately 30 minutes, and stirring was continued for an additional 15 minutes to insure completion of the sulfonation reaction. The sulfonated product was then neutralized with an aqueous ratio of water to isopropanol was 1 to 1, and the neutralized product permitted to separate. This product separated into three phases, a water phase, an alcohol phase and a solvent phase. The water and alcohol phases were discarded and the sodium sulfonate which remained in the paraffinic solvent phase was recovered by evaporation of the solvent. The resulting sodium salt is useful per se as the detergent additive and may be added to lubricating oils to impart detergency, increase viscosity index and lower the pour point of the oil.

By the term "15% fuming sulfuric acid" as used herein is meant 100% sulfuric acid containing 15% by weight of dissolved SO<sub>3</sub>.

The sodium salt produced as above may be converted into a complex or modified sulfonate by treatment with 30 aqueous sodium hydroxide or other basically reacting metal inorganic compound at elevated temperatures. Preferably the aqueous solution of basic compound will be added slowly over a period of 30 minutes or more to a solvent or lubricating oil solution of the sulfonate at a temperature of about 150-350° F. When the complexing is effected in the presence of solvent a reflux system is arranged so that water being vaporized with the solvent is removed by means of a water trap in the reflux line. Heating is then continued until all the water has been removed. Following removal of the water, the solvent solution is filtered and then evaporated to remove solvent.

In case it is desired to produce other metal salts of the sulfonated polyesters, as for example, the calcium salt, the solvent solution of sodium sulfonate before evaporation of solvent is metathesized with a water-soluble calcium salt, as for example, calcium chloride. Following phase separation and removal of aqueous phase, the solvent phase may then be evaporated to obtain the calcium sulfonate or, as described above in connection with the sodium salt, the calcium salt in solvent solution may be complexed with additional calcium oxide or hydroxide or other basically reacting metal inorganic compound to produce the complexed or modified calcium sulfonate.

In order to clarify the disclosure herein, the terms acrylic acid and acrylic acid esters are used in their broad 55 sense to designate the unsubstituted as well as the various hydrocarbon substituted acrylic acids and acrylic acid esters described.

Methacrylate type polymers and various polyesters of the type described herein are available commercially in 60 the form of an oil solution containing from about 1 to 3 parts of a neutral oil per part of polymer. It is found that these oil solutions of polymer may be sulfonated in the same manner and under the same conditions described above for the polymer itself and with substantially the 65 same results. Moreover, the resulting sulfonic acids may be converted into their metal salts and these may be further converted into complex metal sulfonate in the manner described for those produced directly from the polvesters.

Metals which may be employed to produce the metal sulfonates of this invention are preferably the alkaline earth metals, calcium, magnesium, strontium and barium; the alkali metals, sodium, lithium and potassium; and lead, although other metals are useful. Such other metals in- 75 60 are advantageously employed because the additives of

clude copper, nickel, cobalt, iron, manganese and the like. The alkali metal sulfonates are preferably produced by direct neutralization of the sulfonated polyesters with the corresponding alkali metal hydroxide, as for example, sodium hydroxide, potassium hydroxide or lithium hydroxide. The polyvalent metal salts may be produced by direct neutralization of the sulfonated polyesters, however, they are preferably produced by metathesis following the procedure outlined above in connection with the 10 preparation of the calcium sulfonate.

The preparation of the complex or modified sulfonates described hereinabove is simplified if the metal sulfonate is recovered from its solvent solution and dissolved in mineral lubricating oil prior to the complexing. Thus, the alcoholic solution of sodium hydroxide, in which the 15 metal salt of the sulfonated polyester dissolved in approximately 3 parts of oil may be readily complexed by heating the oil solution of metal sulfonate to a temperature preferably above the boiling point of water, as for example, 220-300° F. and while agitating the oil solution, adding an aqueous solution or slurry of the basically reacting metal compound which is to be used for complexing. The aqueous solution or slurry is added slowly over a period of at least about 30 minutes and heating continued for an additional 15 to 20 minutes or longer to effect the removal of water and complexing. During this period the water is expelled, leaving a modified sulfonate containing excess basically reacting inorganic compound in the form of a complex or stable dispersion in the oil solution. Methods of preparing complexes of sulfonic acids which are applicable to sulfonic acids of this invention are described in U. S. Patent No. 2,501,732.

Basically reacting metal compounds which may be employed include the oxides, hydroxides, carbonates and bicarbonates of the metals disclosed above as being useful in the preparation of sulfonates. Generally it is desirable that the metal of the basically reacting metal compound be the same as the metal of the sulfonate, although the metals may be different. For example, a barium sulfonate may be complexed with strontium hydroxide.

The complex or modified sulfonates described herein appear to be and may be defined as permanent dispersions of basically reacting metal inorganic compound with sufficient sulfonate to serve as dispersing agent for the basic compound.

Generally in preparing the complex sulfonates of this invention between about 0.2 and 2 equivalents of the basically reacting metal inorganic compound per equivalent of metal sulfonate will be employed and in most cases all or nearly all of the basic compound will be complexed thus giving complex or modified sulfonates in which the ratio of total metal to metal of the metal sulfonate will be between about 1.2 and 3 to 1.

Lubricating oils are prepared from the sulfonates and complex sulfonates described herein by dissolving between about 0.2% and 7% by weight of the sulfonate or complex sulfonate in mineral lubricating oil. No special technic is required in preparing these oil solutions because the additive materials are oil soluble, however, mixing is facilitated if the additive is incorporated in the oil at elevated temperatures, as for example, at temperatures of 200-325° F. The resulting lubricating oils prepared with metal sulfonates will have metal contents varying between about 0.001% and about 0.20% by weight and those prepared with complex sulfonates will have metal contents between about 0.002 and about 0.3% by weight. Generally the metal contents will be between about 0.01% and 0.1%.

Lubricating oils which may be used in preparing the finished oils of this invention includes substantially all 70 types of mineral lubricating oils of both paraffinic and naphthenic types. Thus, the additive material is found to be effective in solvent treated paraffinic type mineral lubricating oils having viscosity indices between about 80 and about 100, although oils of lower V. I., e. g., 5-

this invention are found to raise the viscosity indices of such oils into a range which is entirely satisfactory for automotive engines. In the case of all of these oils the detergency is greatly increased, the viscosity index is improved by the addition of the oil-soluble metal sulfonates or complex sulfonates derived from the polyesters described herein. In any oils of objectionably high pour point it is found that the pour point is lowered to a desirable degree by such additions.

In determining the detergency of mineral lubricating 10 oils containing the additives of this invention tests have been carried out on the finished oils in Lauson single cylinder standard test engines. In this test, which is referred to herein as the Lauson engine test, the engine is operated for a total of 72 hours under a load of about 2.1 H. P. with a coolant temperature of about 160° F. and an oil temperature of about 150° F. These conditions are designed to simulate passenger car service. At the end of the test period the cleanliness of the engine is observed and given a numerical "detergency rating" be- 20 tween 0% and 100%, where 100% indicates a perfectly clean engine. Thus, a detergency rating of 100% would indicate that there were substantially no lacquer or varnish-like deposits within the engine.

Although mineral lubricating oils containing additives 25 of this invention have the desired characteristics referred to herein, it is sometimes desirable to add a second additive material which imparts anti-corrosion characteristics to the mineral lubricating oil. Anti-corrosion agents which cooperate with the sulfonates and complex sulfonates of this invention to produce outstanding lubricating oils include the following materials which are known to be anti-corrosion agents, but which have been found to be particularly effective in maintaining proper anti-corrosion conditions in engines when used in conjunction with the sulfonates and modified sulfonates described herein.

One form of anti-corrosion agent which may be employed is an oil-soluble metal salt of the acidic reaction product obtained by reacting phosphorus pentasulfide 40 or phosphorus pentoxide with an alcohol. The preferred reaction products are those obtained with phosphorus pentasulfide. These materials are represented by oilsoluble metal salts of alkyl thiophosphates such as zinc dioctyl dithiophosphate or the corresponding calcium or 45 other polyvalent metal salt. Salts of reaction products of phosphorus pentasulfide and aliphatic and cycloaliphatic alcohols having more than about 6 carbon atoms per molecule are preferred.

Other anti-corrosion agents which may be employed 50 in conjunction with the sulfonates of this invention include metal salts of phenols and phenol sulfides. These agents are included in the group of agents which may be referred to as oil-soluble metal salts of high molecular weight non-carboxylic weak acids having ionization con- 55 stants below about 5×10-6. These salts which are described in U. S. Patent No. 2,280,419 are suitable in that they cooperate with the additive of this invention to produce oils having all of the desired characteristics.

Another class of anti-corrosion agents which may be 60 employed includes the oil-soluble metal salts formed by reacting phosphorus pentasulfide with hydrocarbons. Such materials and methods for their preparation are described in U.S. Patent No. 2,316,082.

employed to impart the desirable anti-corrosion characteristics consists of the oil-soluble metal salts of phosphinic or phosphonic acids obtained by treating hydrocarbons with elementary phosphorus and subsequently pounds of this type are described in U. S. Patent No.

Oil-soluble salts of the condensation products obtained by reacting a hydrocarbon substituted phenol with a low molecular weight aldehyde such as formaldehyde are out- 75 6

standing in their ability to cooperate with the sulfonates and complex sulfonates of this invention to produce oils having extremely good anti-corrosion and detergency characteristics. These compounds are described and methods of their preparation are given in U. S. Patent No. 2,250,188.

Metals which may be used in the preparation of the anti-corrosion agents include the alkaline earth metals, calcium, barium, strontium and magnesium and the polyvalents metals, zinc, aluminum, tin, copper, iron, nickel, mercury and chromium. In some instances alkali metal salts or soaps may be employed when they are sufficiently soluble in oil.

In employing the anti-corrosion agents, in the order of 1% of the constituent ordinarily will be adequate, such as 0.5% or 1.5%, or possibly less, e. g., 0.2%, for some uses. Although not more than 3% or 5% based on the final product is necessary for most uses, a number of modern heavy duty engines require more, up to 8% or 10%, and amounts up to 20% or more may be desirable for some uses. The anti-corrosion agents are conveniently employed in the form of concentrates containing 30 to 60% additive dissolved in lubricating oil. They may also be employed in the form of concentrates also containing the sulfonates of this invention. In this case, the total additive concentration may be about 30 to 60%, with the modified sulfonate preferably in slight excess over the anti-corrosion agent.

#### Example 1

A solution of 100 parts of a commercial polymerized lauryl methacrylate having a molecular weight of approximately 20,000 in 200 parts of a paraffinic hydrocarbon solvent, having a boiling point within the range of about 140° F, to about 170° F, was heated to 100° F, and to the heated solution 33 parts by weight of 15% fuming sulfuric acid was added slowly, over a period of approximately 45 minutes, with vigorous agitation. The reaction mixture was maintained between 100° F. and 110° F. for an additional 30 minutes. Sufficient sodium hydroxide dissolved in equal parts of isopropanol and water to give a 10% solution of NaOH was then added and agitation continued until neutralization was effected. The neutralized product was permitted to settle and the aqueous and alcoholic phases were removed, leaving a solvent phase containing the sodium salt of sulfonated polylauryl methacrylic acid. The solvent solution was washed with a 50% solution of isopropanol in water to remove inorganic materials.

One portion of the solvent solution was evaporated to recover the sodium sulfonate. This material will be referred to hereinafter as Product A.

A second portion of the solvent solution of sodium sulfonate was converted into the calcium salt by metathesis with calcium chloride. An amount of calcium chloride equivalent to the sodium sulfonate salt, in the form of a 10% aqueous solution, was added and the mixture vigorously agitated for approximately 30 minutes. The aqueous phase was permitted to separate and was discarded. The calcium sulfonate salt was recovered by evaporating the hydrocarbon solvent. This calcium sulfonate will be referred to hereinafter as Product B.

A third portion of the solvent solution of sodium sulfonate was converted into the barium salt, using barium Another type of anti-corrosion agent which may be 65 chloride and following the procedure outlined for the preparation of calcium salt. The recovered barium sulfonate will be referred to as Product C.

A fourth portion of the solvent solution of sodium sulfonate was converted to the strontium salt by metathesis forming the metal salts of the reaction products. Com- 70 with strontium chloride in the manner described for the calcium sulfonate. The recovered strontium sulfonate salt will be referred to as Product D.

A fifth portion of the solvent solution of sodium sulfonate was converted into the lead salt by metathesis with lead nitrate following the procedure outlined for the

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calcium salt. The recovered lead sulfonate will be referred to as Product E.

A portion of the lead sulfonate, Product E, was converted into a lead sulfonate-lead oxide complex by dissolving 7 parts of Product E in 5 parts of a mineral lubricating oil of SAE 5 grade. The resulting oil solution was heated to a temperature of 300° F. and to the heated solution was added 1.25 parts by weight of lead oxide in the form of a slurry in 5 parts by weight of water. This addition was made slowly, over a period of approximately 20 minutes, with vigorous agitation. The resulting product was heated to 325° F., and filtered through a filter aid. The filtered oil solution, consisting of a concentrate of lead oxide-lead sulfonate complex in oil will be referred to as Product F.

Lubricating oils were prepared by dissolving each of the above products (Products A to F, inclusive) in mineral lubricating oil of SAE 30 grade having a viscosity index of 86 and a pour point of 0° F. This base oil had a detergency rating in the Lauson engine test of 35. The amount of metal sulfonate employed was in each case the amount necessary to impart a metal content of about 0.01% with the exception that in the case of Product F the metal content of the finished oil was 0.02%. Each of the oils operates satisfactorily in the Lauson engine and in this test the detergencies are all above 80. Moreover, these oils have viscosity indices greater than 105 and pour points of -20° F. or lower.

#### Example II

A polylauryl methacrylate of approximately 20,000 molecular weight was sulfonated, the sulfonated product converted into its lead salt, and the lead sulfonate complexed with lead oxide as described in Example I. The product corresponded to Product F of that example.

Lubricating oils containing various concentrations of this complex sulfonate were prepared and evaluated and for purposes of comparison lubricating oils containing various proportions of unsulfonated polylauryl methacrylate were also prepared and evaluated using the same

Data regarding these oils together with the corresponding data for the base oil are shown in the following table. The base oil was a solvent-extracted Western paraffinic lubricating oil of SAE 30 grade.

Ŏ1I	Metal Con- tent, Percent	V. I.	Pour Point, ° F.	Deter- gency, Per- cent
Hase Oil		86 110 121	0 -20 -15	35 43 39
+ 0.85 Pb sulf. polymer PbO	0. 029 0. 055	111 125	-20 -15	73 86

## Example III

Product C of Example I, converted to the barium hydroxide-barium sulfonate complex by treatment of the sulfonate in naphtha solution with an aqueous slurry of barium hydroxide at a temperature of 230° F., when dissolved in a naphthenic lubricating oil of 30 V. I. to impart a metal content of 0.05% gives an oil of about 110 V. I. having good detergency.

## Example IV

A concentrate consisting of 50% of a polymerized lauryl methacrylate, having a molecular weight of about 15,000, 70 in a neutral oil was dissolved in 2 parts of paraffinic hydrocarbon solvent per part of concentrate and the resulting solution treated with 53% by weight of 15% fuming sulfuric acid, based on the polymerized lauryl methacrylate, at a temperature of about 110° F. The fuming acid was 75 ide. This product when added to an SAE 30 solvent ex-

added over a period of approximately 30 minutes while vigorously agitating the mixture. Following completion of the sulfonation, the product was neutralized with sodium hydroxide dissolved in isopropanol and water. After separation of the aqueous and alcoholic phases, the hydrocarbon solvent phase was separated into two portions, one of the portions was evaporated to recover the sodium sulfonate and the second portion was metathesized with lead nitrate and the methathesized product evaporated to recover the lead sulfonate. A portion of the lead sulfonate so recovered was dissolved in 2 parts of mineral lubricating oil and heated with 2 equivalents of lead oxide per equivalent of metal sulfonate in the presence of a small amount of water to form the lead oxide-lead sulfonate complex.

Oils containing each of the above sulfonates were found to have good detergencies, improved viscosity indices and lowered pour points as compared with the base oil.

#### Example V

Polymerized cetyl alphamethacrylate, having a molecular weight of 25,000, was sulfonated in the manner described in Example I and the sulfonated product neutralized with sodium hydroxide. The resulting sodium sulfonate was converted into the corresponding lead sulfonate by metathesis with lead nitrate. This product, when dissolved in an SAE 30 solvent extracted paraffinic mineral lubricating oil in an amount to give an oil having a lead content of 0.05% by weight was found to give good detergency, improved viscosity indices and lowered pour point as compared with the base oil.

#### Example VI

Lubricating oils were prepared with a sodium salt of a sulfonated polylauryl methacrylate, having a molecular weight of approximately 20,000, by blending the oil concentrate of the sulfonate with an 86 V. I. paraffinic oil of SAE 30 grade. The sodium sulfonate was prepared in the manner described in Example I and corresponds to Product A of that example. For comparison an oil was prepared using the unsulfonated polymer in approximately the same proportion. Test results on these oils were as follows:

5	Oil	Metal Con- tent, Percent	V. I.	Pour Point, ° F.	Deter- gency, Per- cent
0	Base Oil + 1.75% unsulf. polymer + 1.0% Na Sulf. polymer + 1.87% Na Sulf. polymer + 1.68% Na Sulf. polymer	. 0026 . 0048 . 0034	86 110 105 120 108	$     \begin{array}{r}       0 \\       -20 \\       -20 \\       -20 \\       -20 \\       -20 \\    \end{array} $	35 79 82

#### Example VII

Lubricating oils were made by blending a calcium salt of a sulfonated polymer prepared in the manner described in Example I and corresponding to Product B of that example, in a solvent treated SAE 5 grade naphthenic oil of 28 viscosity index. Data obtained on these oils and on an oil containing the unsulfonated polymer were as follows:

Oil	Deterg- ency	Viscosity Index	
Base Oil+0.850% Ca sulf. polymer	20	28 81	
+1.125% Ca sulf. polymer +1.500% Ca sulf. polymer +1.875% Ca sulf. polymer	70	103 111 122	

### Example VIII

Polymerized butoxyethyl acrylate having a molecular weight of about 15,000 was sulfonated as described in Example I and the product neutralized with barium hydroxtracted paraffinic mineral oil in an amount to give a barium content of 0.08% gives an oil with good detergency and improved V. I. characteristics.

The above examples are illustrative but are not to be taken as limiting the invention to the particular metals and the particular sulfonated polymers described since the other metals and other polyesters described hereinabove when substituted for the specific metals and specific polyesters shown in the examples give sulfonates and comof high detergency, high viscosity index and low pour point to mineral lubricating oils.

This application is a continuation-in-part of application Serial Number 355,408 filed May 15, 1953, now abandoned.

I claim:

1. A lubricating oil comprising mineral lubricating oil in major amount containing between about 0.2% and about 7% by weight of a metal salt of a sulfonated polymerized ester, said ester having the formula

in which R is a radical selected from the class consisting of hydrogen and alkyl and aryl radicals containing between about 1 and about 9 carbon atoms and R' is a monovalent radical selected from the class consisting of hydrocarbon and ether radicals containing more than 4 carbon atoms and obtained by sulfonating said ester with a sulfonating agent in an amount of one-third on the weight of 30 the polymer, the polymeric ester having an average molecular weight of about 5000 to 30,000.

2. A composition adapted for addition to mineral lubricating oil comprising a complex sulfonate consisting of between about 0.2 and 2 equivalents of a basically reacting 35 metal inorganic compound of the class consisting of metal oxides, hydroxides, carbonates and bicarbonates and 1 equivalent of metal sulfonate, said metal sulfonate being a metal salt of a sulfonated polymerized ester, said ester having the formula

$$\begin{array}{ccc} & R & O \\ & & \parallel & \parallel \\ CH_2 = C - C - O - R' \end{array}$$

in which R is a radical selected from the class consisting of hydrogen and alkyl and aryl radicals containing between about 1 and about 9 carbon atoms and R' is a monovalent radical selected from the class consisting of hydrocarbon and ether radicals containing more than 4 carbon atoms and obtained by sulfonating said ester with a sulfonating agent in an amount of one-third on the weight of the polymer, the polymeric ester having an average molecular weight of about 5000 to 30,000.

3. A lubricating oil comprising mineral lubricating oil in major amount containing between about 0.2% and about 7% by weight of a complex sulfonate, said complex sulfonate being a permanent dispersion of between 0.2 and 2 equivalents of a basically reacting metal, inorganic compound of the class consisting of metal oxides, hydroxides, carbonates and bicarbonates with 1 equivalent of metal sulfonate, sufficient to serve as dispersing agent for said basically reacting metal compound, said metal sulfonate being a metal salt of a sulfonated polymerized ester, said ester having the formula

in which R is a radical selected from the class consisting of hydrogen and aikyl and aryl radicals containing between about 1 and about 9 carbon atoms and R' is a monovalent radical selected from the class consisting of hydrocarbon and ether radicals containing more than 4 carbon atoms and obtained by sulfonating said ester with a sulfonating agent in an amount of one-third on the weight

of the polymer, the polymeric ester having an average molecular weight of about 5000 to 30,000.

4. A composition adapted for addition to mineral lubricating oil in major amount, said composition comprising a metal salt of a sulfonated polymerized ester, said ester having the formula

$$\begin{array}{c|c}
R & O \\
\parallel & \parallel \\
CH_2=C-C-O-R'
\end{array}$$

plex sulfonates which impart the desirable characteristics 10 in which R is a radical selected from the class consisting of hydrogen and alkyl and aryl radicals containing between about 1 and about 9 carbon atoms and R' is a monovalent radical selected from the class consisting of hydrocarbon and ether radicals containing more than 4 carbon atoms, the polymeric ester having an average molecular weight of about 5000 to 30,000, and the sulfonated polymeric ester being obtained by sulfonation with a sulfonating agent in an amount of one-third on the weight of the polymer.

5. A lubricating oil according to claim 1 in which said

metal is an alkaline earth metal.

6. A lubricating oil according to claim 1 in which said metal is an alkali metal.

7. A lubricating oil according to claim 1 in which said metal is lead.

8. A lubricating oil according to claim 3 in which said basically reacting metal inorganic compound is an alkaline earth metal hydroxide and said metal of the metal sulfonate is an alkaline earth metal.

9. A lubricating oil according to claim 3 in which said basically reacting metal inorganic compound is a lead oxide and said metal of the metal sulfonate is lead.

10. A composition adapted for addition to mineral ludbricating oil consisting essentially of alkaline earth metal polylauryl methacrylate sulfonate obtained by sulfonating said methacrylate with a sulfonating agent in an amount of one-third on the weight of the polymer.

11. A composition adapted for addition to mineral lubricating oil consisting essentially of alkali metal polylauryl methacrylate sufonate obtained by sulfonating said methacrylate with a sulfonating agent in an amount of

one-third on the weight of the polymer.

12. A composition adapted for addition to mineral lubricating oil consisting essentially of lead polylauryl methacrylate sulfonate obtained by sulfonating said methacrylate with a sulfonating agent in an amount of onethird on the weight of the polymer.

13. A lubricating oil comprising mineral lubricating oil in major amount containing between about 0.2% and about 7% by weight of an alkaline earth metal polylauryl methacrylate sulfonate obtained by sulfonating said methacrylate with a sulfonating agent in an amount of one-third

on the weight of the polymer.

14. A lubricating oil comprising mineral lubricating oil in major amount containing between about 0.2% and about 7% by weight of lead polylauryl methacrylate sulfonate obtained by sulfonating said methacrylate with a sulfonating agent in an amount of one-third on the weight of the polymer.

15. A lubricating oil comprising mineral lubricating oil in major amount containing between about 0.2% and about 7% by weight of complex sulfonate, said complex sulfonate comprising between about 0.2 and 2 equivalents of an alkaline earth metal hydroxide and 1 equivalent of an alkaline earth metal polylauryl methacrylate sulfonate obtained by sulfonating said methacrylate with a sulfonating agent in an amount of one-third on the weight of the polymer.

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