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2,501,732

UNITED STATES PATENT OFFICE

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MODIFIED LUBRICATING OIL

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12 Claims. (Cl. 252—33)

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This invention relates to lubricating oils and is a continuation-in-part of my copending applications, Serial No. 458,459, filed September 15, 1942, now abandoned, and Serial No. 703,097, filed October 14, 1946.

Primarily, the object of the invention is to produce mineral lubricating oils for internal combustion engines which possess a very high degree of detergent power for the removal of resinous and similar deposits from the piston skirts, piston rings and ring grooves of internal combustion engines.

In many internal combustion engines, especially Diesel engines, where severe service conditions are encountered, there is a stronger tendency than ordinarily to deposit on the piston skirts and upon the rings and in the ring grooves an objectionable amount of resinous and varnish-like materials. The deposition of these materials may be controlled and largely prevented, and to some extent may be removed after formation, by the use of certain types of additives in the lubricating oil.

One form of additive which possesses some merit consists of metal soaps of oil-soluble petroleum sulfonic acids obtained by the sulfonation of mineral oil fractions, such as mineral lubricating oil fractions. The particular sulfonic acids employed are the so-called "mahogany acids," that is, the oil-soluble sulfonic acids produced in the process as distinguished from the water-soluble, so-called "green" acids, although it is possible sometimes to use a mixture of both the mahogany acids and green acids because of the fact that mahogany acid soaps possess some solubilizing properties for the green acid soaps when added to mineral lubricating oil. These sulfonic acids are produced according to well known processes by treating the oils with strong or fuming sulfuric acid or chlor-sulfonic acid. The green acids are separated in the sludge, and the mahogany acids may be recovered as soaps by introducing the desired base material, for example, lime or calcium hydroxide, to produce the corresponding metal soap in the treated oil. Or, where the mixed soaps are desired, the whole batch may be treated with the desired base material. Or, the sodium soap may be recovered by any well known or preferred method and a desired soap prepared therefrom in any known manner and combined with oil to yield a suitable concentrate of the metal sulfonate in a petroleum oil fraction.

In preparing the final lubricating oil, the desired sulfonate, or a concentrate thereof, is

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added to the oil and dissolved therein by the simple expedient of admixture and agitation, to produce the desired concentration. The percentage of soap in the final oil is ordinarily in the neighborhood of 1% to 3% but may vary from about 0.5% to 5% or more as desired or required.

The particular improvement of this invention resides in further treating the recovered sulfonate or sulfonate concentrate, with a base for the purpose of increasing the detergent properties of the soap. I have found that the soap or soap concentrate may have additional base combined therewith by a more or less simple mixing and heating operation followed by filtering. It is not clear whether the result is a loose complex formed by the sulfonate and the base, or whether the sulfonate serves as a solubilizing agent to hold the base material in solution in the oil. Since its oil solution exhibits the Tyndall effect and since the number of moles of base per mole of sulfonate can be made larger than would normally be expected for any new type of complex other than a loose addition compound, the sulfonate very likely holds the base in solution in the form of a colloidal suspension. In addition to improving the detergent properties of the oil, the inclusion of the base in the sulfonate imparts the further characteristic of increasing what has been called the "alkaline reserve" of the oil. Soaps of this type in oils serve to neutralize acidity which is formed in the oil during use or in some manner to counteract the development of corrosive conditions formed in the oil during use which are detrimental to bearings sensitive to such conditions. Apparently, when these soaps are acted upon by liberated acids in the oil, the strong acids so liberated are neutralized.

In preparing the improved oil of this invention a solution or slurry of the desired base is added slowly at somewhat elevated temperatures and with stirring to the desired oil-soluble metal sulfonate. The sulfonate is preferably in solution in oil in the form of a concentrate. The temperature to which the mixture is heated during the addition of base is preferably between about 200° F. and about 450° F., although it is possible to produce the desired result at lower temperatures such as about 150° F. or at even higher temperatures such as about 500° F. It is essential that the resulting product be dehydrated so that when temperatures below about 250° F. are employed it may be necessary to apply vacuum to the reacting mass in order to

cause removal of water and insure dehydration. Following the mixing and dehydration which may take place, for example, within about one hour, the product is filtered to remove unreacted base or other material which has not been solubilized during the treatment.

In preparing a sodium hydroxide-calcium sulfonate complex, a 50° Bé. solution of sodium hydroxide is introduced dropwise into a small batch of calcium sulfonate concentrate. During the addition, the mass is heated to 200° F. and continuously stirred. Vacuum may be applied during the addition of the hydroxide or after the addition is complete to effect dehydration. The product is then filtered.

In preparing lead oxide-calcium sulfonate concentrate, an aqueous slurry of lead oxide is added slowly to a calcium sulfonate concentrate. The mixture is maintained at a temperature of about 200° F. and agitated during this addition. The batch is dehydrated with vacuum at a temperature of 200° F. as above indicated and the dehydrated product is filtered.

In some cases it is desirable to prepare the sulfonate-base complex at higher temperatures in order to eliminate the necessity for carrying out the dehydration under reduced pressure thus a sodium hydroxide-calcium sulfonate complex may be prepared by heating a calcium sulfonate concentrate to about 300° F. and adding a 50° Bé. solution of sodium hydroxide dropwise to the concentrate. The temperature is then increased to about 450° F. to insure rapid and complete dehydration.

The preparation of the corresponding carbonates may be carried out in the manner described for the hydroxides and oxides or the carbonate-sulfonate complex may be prepared by treating the hydroxide-sulfonate complexes or the oxide-sulfonate complexes with carbon dioxide. Particularly in the case of the alkali metal complexes, they may be converted into the bicarbonate-sulfonate complexes by continued treatment with carbon dioxide. Thus a sodium hydroxide-calcium sulfonate product may be converted into the sodium carbonate-calcium sulfonate complex, or the corresponding bicarbonate complex, by blowing the hydroxide complex with carbon dioxide at elevated temperatures, such as about 200° F. or above or at temperatures indicated for the formation of the complexes. The carbonate and bicarbonate complexes may have particular value where the more highly basic character of the hydroxide-sulfonate complex might be objectionable. The carbonate and bicarbonate complexes, although having the same total alkaline reserve, are not as strongly basic in character as the hydroxide complex.

The above described operation results in a concentrate containing the desired modified sulfonate. Any of the metal hydroxides capable of producing soaps suitable for this purpose may be employed instead of sodium hydroxide, for example, calcium hydroxide. Also, it may be feasible to introduce lime.

Another and very desirable form of the invention resides in combining the corresponding carbonates with the sulfonate, for example, sodium carbonate or sodium bicarbonate. This has been accomplished in one manner by first treating with sodium hydroxide and then passing carbon dioxide gas through the resultant concentrate until the desired carbonate has resulted from the sodium hydroxide portion of the modified sulfonate.

In adding the base constituent to the soap, it has been found that the base can be introduced into the soap, or solubilized in the oil, as the case may be, until the amount of base taken up approximates 5% to 45% of the original sulfonate. Apparently, 45% is normally more than is necessary, and perhaps more than is desired, but it appears that up to about 20% of base figured on the sulfonate content is desirable. Normally, the content may be figured on the final oil to be produced. Thus, in the final oil the proportion of base may vary from 0.05% to about 1.0%. Commonly, it is desirable apparently to employ about 0.2% to 0.5% of base in the final oil.

In employing the modified sulfonate in the oil, this ordinarily is done in the order of from about 1% to about 7.0%, although larger proportions may be used up to about 10% with correspondingly beneficial results, and larger proportions also may be used but without any apparent increased benefit. The proportion of modified sulfonate will depend to an appreciable extent on the metal or metals employed in the modified sulfonate. Thus if the metal is one having a relatively low atomic weight such as calcium, sodium and the like, the amount of complex sulfonate to be used in preparing the finished lubricant will be less than that which would desirably be employed if one of the heavy metals such as lead were present in the complex sulfonate. On the lower side, benefits are obtainable down to as low as 0.5% and of course correspondingly lower benefits are obtained with still lower proportions, e. g. 0.2% or 0.5% of the modified sulfonate. It is to be noted that even with the larger proportions of complex sulfonate indicated there is no apparent increase in viscosity of the resulting lubricating oil.

In addition to employing sodium and calcium materials as constituents of the base, it is also feasible to employ the other alkaline earth metals such as magnesium, strontium and barium. These as well as other alkali metals such as lithium and potassium impart a desirable alkaline characteristic. It may also be in order to employ other metals such as boron, tin, aluminum, zinc, lead and the like. Besides using base materials of the type indicated, neutral salts which become properly solubilized may offer suitable detergent characteristics, and to this extent might be substituted for the bases. Similarly, other salts which are properly solubilized may offer adequate detergent properties at least for some purposes. Such salts may be phosphates, acid phosphates, borates, and the like.

Moreover, although the invention has been described as employing a calcium sulfonate as the material which is modified by the incorporation of a basic metal compound, other polyvalent metal sulfonates may be employed in place of the calcium sulfonate. Other metals which may be employed include the other alkaline earth metals, magnesium, strontium and barium and the polyvalent metals, lead, tin, zinc, aluminum, and possibly even copper, cadmium, mercury, vanadium, chromium, molybdenum, manganese, iron, cobalt and nickel. The various metal sulfonates may be prepared by the direct reaction of a basic compound of the desired metal with the sulfonic acids, or preferably the polyvalent metal sulfonate may be prepared by first forming an alkali metal sulfonate, such as sodium sulfonate, and metathesizing an aqueous solution of the alkali

metal sulfonate with a water-soluble, or at least partially water-soluble salt of the desired polyvalent metal.

Although the metathesis may be effected in any well known manner, a particularly desirable method of effecting the metathesis reaction consists in adding a water-soluble solvent, preferably isopropyl alcohol to an aqueous solution of sodium sulfonate and adding to the resulting solution an amount of a water-soluble polyvalent metal salt sufficient to convert the alkali metal sulfonate to the polyvalent metal sulfonate. The salt is dissolved in water or slurried in water before its addition and there is added to the reaction mixture a light petroleum thinner in an amount sufficient to aid in extracting the polyvalent metal sulfonate from the aqueous phase as it is formed. The resulting mixture is agitated to obtain good dispersion of the petroleum solvent in the aqueous phase, the agitation being continued until the metathesis reaction is complete. This reaction may be effected at ordinary atmospheric temperatures but preferably it will be carried out at temperatures between about 100° F. and 200° F. or 210° F. When the reaction is complete or after a period of thirty minutes to about two hours, or even longer depending upon the size of the batch being prepared, agitation is discontinued and the reaction mixture allowed to separate into two phases. The upper phase consists of petroleum thinner containing the polyvalent metal sulfonate in solution and the bottom phase consists of water containing inorganic salts, any unreacted alkali metal sulfonate, and water-soluble solvent. The upper phase is then washed with water to remove suspended salts and may then be evaporated or distilled to remove the petroleum thinner and dehydrate the sulfonate.

Where it is desired to form the modified sulfonate, i. e., the sulfonate complex, the sulfonate after being freed from petroleum thinner and water may be dissolved in mineral oil and treated with the desired metal base or preferably the petroleum thinner solution, after washing with water, is agitated with an aqueous slurry of the desired metal base at elevated temperatures. The temperature is preferably high enough to vaporize the thinner and water during this treatment and thus is preferably maintained at around 200° F. to 230° F. or higher, depending upon the boiling range of the thinner employed. In case the water is evaporated before the complexing reaction is complete more water may be added to the mixture. After most of the added metal base is solubilized and the thinner and water evaporated mineral lubricating oil may be added to dissolve the sulfonate complex and the mixture filtered as by means of clay or the like.

The water-soluble solvent employed in the metathesis step referred to above is preferably one which also has at least some oil miscibility characteristics, i. e., one which is solubule to some extent in mineral oil fractions and has the power to dissolve mineral oil to some extent. Moreover, the water-soluble solvent will desirably have some solvency for the polyvalent metal sulfonates produced in the metathesis reaction. At least the solvent should not be one which when dissolved in the petroleum thinner solution of polyvalent metal sulfonate will reject the sulfonate from the petroleum thinner solution. Such solvents apparently serve as common solvents for the aqueous and oil phases present in the reaction mixture thus serving to present a homogeneous

system in which the metathesis reaction may occur. Moreover, such solvents have the effect of reducing the tendency for the reaction mixture to emulsify thereby facilitating rapid phase separation at the end of the reaction. Solvents of this type in addition to the preferred isopropyl alcohol include other alcohols, such as normal propyl alcohol and ethyl alcohol; ketones, such as acetone and in some instances methyl ethyl ketone; the glycols, such as ethylene glycol, and propylene glycol and derivatives of these glycols, such as the alkyl esters, as for example ethyl esters of ethylene glycol; aliphatic diols particularly those in which the OH groups are in conjugate position, such as 2-methyl pentanediol-2,4 and 2-ethyl hexanediol-1,3 and the like solvents. In selecting a water-soluble solvent it is desirable that the boiling point is below about 200° F. so that any solvent remaining in the petroleum thinner soap phase may be removed by a tapping operation.

The petroleum thinner or naphtha employed in the metathesis step is preferably a low boiling hydrocarbon or hydrocarbon fraction such as one boiling below about 400° F. or 450° F., and preferably it is one boiling within the range between about 100° F. to 350° F.

In preparing a lead sulfonate-lead oxide complex one volume of an aqueous solution of sodium sulfonate containing approximately 35% by weight of sodium sulfonate is mixed with an equal volume of isopropyl alcohol and the resulting solution heated to about 135° F. To this solution is added approximately one-half volume of a petroleum thinner boiling in the range of about 150° F. to 350° F., and a sufficient quantity of a 33% solution of lead nitrate in water to convert the sodium sulfonate to the lead sulfonate, i. e., an amount containing slightly more than a chemical equivalent of the lead nitrate. The resulting mixture is heated to 150° F. to 200° F., and vigorously agitated for about one hour and allowed to separate into phases. The lower phase consisting of a water solution of isopropyl alcohol, sodium nitrate and excess lead nitrate with possibly small amounts of unreacted sodium sulfonate is withdrawn and the upper phase consisting primarily of a petroleum thinner solution and lead sulfonate is washed with water until the washings are free from inorganic salts.

The lead sulfonate in petroleum thinner solution is complexed with lead oxide (PbO) by adding an aqueous slurry of a chemical equivalent amount of the lead oxide and agitating the mixture at a temperature of about 200° F. to 220° F. until most of the lead oxide is solubilized. A small amount of mineral lubricating oil is then added to the reaction mixture and the temperature raised to about 300° F. to 350° F. in order to dehydrate the product and vaporize any remaining petroleum thinner. The product is a concentrate of lead sulfonate-lead oxide complex in mineral oil. This concentrate may then be blended with additional quantities of lubricating oil to produce an oil containing preferably between about 0.3% and about 2.0% of lead having exceptional detergency, anti-corrosion and anti-wear characteristics.

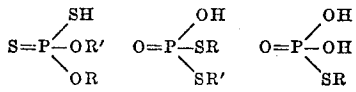
Although mineral lubricating oils containing the modified sulfonate of this invention are particularly valuable lubricating oils, it is sometimes desirable to include one or more other detergents and/or one or more anti-corrosion agents in the final lubricating oil composition along with the modified sulfonate.

Anti-corrosion agents

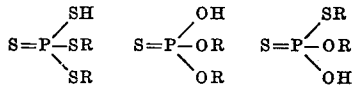
Anti-corrosion agents which may be added to cooperate in maintaining proper anti-corrosion conditions, particularly in engines containing highly corrosion sensitive bearings, include all of the various types of anti-corrosion agents well known in the art. Oil-soluble metal salts of the acidic reaction products obtained by reacting phosphorus pentasulfide, or in some instances, phosphorus pentoxide, with an alcohol are particularly desirable anti-corrosion agents. The preferred reaction products are those obtained with phosphorus pentasulfide and these products may be referred to as organic substituted thiophosphates.

The alcohols which may be employed in the preparation of desirable thiophosphates include the aliphatic alcohols, such as butyl, amyl, isoamyl, hexyl, and heptyl, octyl alcohol, lauryl alcohol, cetyl alcohol and the like. These alcohols may be modified by the inclusion of phenyl and kindred aromatic groups forming alkaryl or aralkyl substituted alcohols. Also cyclo aliphatic alcohols such as cyclopentanol, cyclohexanol, cycloheptanol or the alkyl substituted cyclo aliphatic alcohols in which the alkyl substituent contains less than about 10 carbon atoms and preferably about 5 or less carbon atoms may be employed. Thus the substituted groups will include preferably the methyl, ethyl, propyl, and amyl radicals and the methyl, ethyl, propyl, and amyl cyclohexanols are the preferred alcohols of this class. Other alcohols which may be employed are those containing an aromatic nucleus such as benzyl alcohol. Also in some instances phenols may be employed in place of the alcohol giving aryl substituted thiophosphates as for example phenyl substituted thiophosphates or methylphenyl substituted thiophosphates.

In reacting an alcohol with phosphorus pentasulfide, with reaction may be effected for example by heating the mixture at 200° F. to 250° F. for about four hours, the reaction product consists of a mixture of acid thiophosphate esters, such as may be represented by the following formulas in which R is the hydrocarbon radical derived from the alcohol and R′ is hydrogen or R:



Other possible acid esters which may be present are the following:



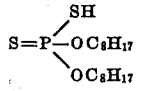
The reaction products may be converted into the corresponding metal salts by direct reaction with a basic compound of the desired metal or by first neutralizing with sodium hydroxide to form the sodium salt and subsequently metathesizing the sodium salt with a salt of the desired metal. Thus the sodium salt may be reacted with zinc chloride to form the zinc salt of the reaction product.

A typically desirable thiophosphate was prepared in the following manner:

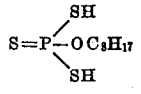
One gram mol of powdered phosphorus pentasulfide is added to four gram mols of octyl alcohol in a glass or ceramic container, and the mixture agitated at temperatures between 250° F. and 300° F. for about two hours, i. e., until the phosphorus pentasulfide dissolves. When

250° F. is reached, the reaction is rapid with evolution of hydrogen sulfide. This liquid product is then treated at similar temperatures, e. g., 250° F., with an excess of either powdered metal or powdered metallic oxide, for example, powdered zinc or zinc oxide, until no more dissolves, as by standing over night at 250° F. Usually it is deemed preferable to use the metallic oxide. The resultant metal octyl thiophosphate, for example, the zinc salt, is readily taken up in mineral oil solution, employing either paraffinic or naphthenic type oil. The mere introduction of the salt into the oil with mild agitation and limited heating is sufficient to produce an oil solution to yield a concentrate, which in turn readily disperses in the final oil product to which it is added.

One particular material made in this manner analyzed 18.1% sulfur and 9.3% phosphorus, indicating the di-octyl thiophosphate as the principal constituent of the product with the probable formula:



Apparently the mono-octyl thiophosphate also is present with the probable formula:



Quite likely other thiophosphate esters of the types above indicated in connection with the cyclohexanol product are also present in greater or lesser proportions.

Another class of anti-corrosion agents includes those compounds which may be defined as oil-soluble metal salts or soaps of high molecular weight, non-carboxylic weak acids having ionization constants below about 5×10^{-6}. This class of compounds includes the oil-soluble metal salts of alkyl substituted phenol sulfides or alkylated phenolic thio ethers. It also includes the oil-soluble metal soaps or salts of thio phenols, alcohols, enols, oximes or sulfo-amides. These weak acid salts and soaps are described in the United States Patent No. 2,280,419 to Wilson.

Another class of anti-corrosion agents which may be employed includes the oil-soluble metal salts of phosphorus and sulfur containing reaction products of a sulfide of phosphorus and a hydrocarbon. These materials are obtained by reacting phosphorus pentasulfide with a hydrocarbon having a molecular weight greater than about 120 and subsequently neutralizing the reaction product with a basic metal compound. A description of these materials and methods for their preparation are given in United States Patent No. 2,316,082 to Loane et al.

Still another type of anti-corrosion agent consists of the oil-soluble metal salts of phosphinic or phosphonic acids obtained by treating hydrocarbons with elementary phosphorus and subsequently forming the metal salts of the reaction products. Such compounds are described in United States Patent No. 2,311,305 to Ritchey.

Oil-soluble metal salts of the condensation products of alkyl substituted phenols and formaldehyde are anti-corrosion agents which may be employed in the lubricating oil composition of this invention. These compounds and methods for their preparation are described in United States Patent No. 2,250,188 to Wilson.

Supplemental detergents

Supplemental detergents which may be included in the final lubricating oil together with the modified sulfonate of this invention or together with the modified sulfonate and one of the above described anti-corrosion agents include oil-soluble petroleum sulfonates, such as those described above for use in connection with the preparation of modified sulfonates as well as any of the well known detergents which are employed in lubricating oil compositions. These include the oil-soluble metal salts of rosin acids, such as abietic acid, hydrogenated rosin acids, and the like. The metal salts of rosin acids are described in United States Patent No. 2,233,203 to Flaxman and the soaps of hydrogenated rosin acids are described in United States Patent No. 2,280,338 to Merrill.

Other detergents which may be employed as supplemental detergents include the oil-soluble metal salts of synthetic organic acids produced by oxidizing hydrocarbons or hydrocarbon fractions, such as highly paraffinic lubricating oil fractions, paraffin wax, and the like. Preferably the acids will contain in excess of 10 hydrocarbon atoms per molecule. These compounds are described in United States Patent No. 2,270,620 to Bray.

Still other types of supplemental detergents include the oil-soluble metal salts of fatty acids, halogenated fatty acids and aryl substituted fatty acids, such as dichloro stearic acid, phenyl stearic acid. and the like.

Desirable metals to be employed in the preparation of the oil-soluble metal anti-corrosion agents and detergents include the alkaline earth metals, such as strontium, barium and calcium and the polyvalent metals, zinc, aluminum, tin, copper, magnesium, iron, nickel, mercury and chromium. Also in some instances alkali metal salts or soaps may be employed, such as sodium, potassium and like compounds, particularly in those instances in which the alkali metal compounds are sufficiently oil-soluble.

The anti-corrosion agents may be employed in amounts ranging from about 0.1% to about 3.0% of the final lubricating oil composition although generally amounts ranging from about 0.5% to about 1.5% of the anti-corrosion additives will be employed.

The proportion of supplemental detergent to be employed will fall within the limits mentioned for the anti-corrosion agents and thus will be between 0.1% and about 3.0% and preferably between about 0.5% and 1.5%.

Final lubricating oil compositions

The following examples illustrate typical lubricating oil compositions which have highly desirable detergent, anti-corrosion and alkaline reserve characteristics.

To a solvent treated Western lubricating oil having a viscosity of about 90 is added 1.3% of a sodium hydroxide-calcium sulfonate complex prepared as indicated herein. The modified sulfonate is readily incorporated in the oil by simple mixing operations. The resulting oil has very good detergent and alkaline reserve characteristics. This product is a freely fluid oil possessing no appreciable viscosity increase beyond that of the mineral lubricating oil employed. Moreover, this oil has a detergent action which is improved up to a rating which might be called "most excellent" as compared to a rating of "rather poor" where a similar quantity of unmodified sulfonate is used. This oil will remain free from insoluble oxidized products arising from oil deterioration much longer than the corresponding base oil or the base oil containing the usual unmodified sulfonates under service conditions.

Lubricating oil having unusually high detergent characteristics and anti-corrosion characteristics may be prepared by blending a mineral lubricating oil such as the solvent treated Western lubricating oil referred to above with 1.0% of a sodium hydroxide-calcium sulfonate complex and 0.5% of a zinc salt of the reaction product of octyl alcohol and phosphorus pentasulfide. This zinc salt may be referred to as a zinc dioctyl thiophosphate.

Another highly desirable lubricating oil composition may be prepared by adding to a lubricating oil, such as the one described above, 1.0% of a modified sulfonate such as lead oxide-calcium sulfonate complex and 0.7% of unmodified calcium sulfonate.

Still another highly desirable lubricating oil having exceptional detergent, anti-corrosion and alkaline reserve characteristics is prepared by incorporation in mineral lubricating oil 0.9% of a sodium hydroxide-calcium sulfonate complex 0.5% of an unmodified oil-soluble calcium sulfonate and 0.5% of zinc di-octyl thiophosphate.

The above examples of desirable lubricating oil compositions may be varied by varying the amounts and the types of modified sulfonates, the types of supplemental detergents and the types of anti-corrosion agents without departing from the invention described herein.

The additives described may be employed in substantially any oil of the lubricating oil type. Normally the highly refined so-called highly paraffinic lubricating oils will be employed, however, naphthenic and other paraffinic lubricating oils are also usable.

It is sometimes desirable to prepare concentrates containing up to 20% or 30% of the modified sulfonates alone or together with added supplemental detergents and/or anti-corrosion agents. Such concentrates are generally still fluid and do not set up like a grease. The concentrates are readily diluted by addition of lubricating oil to prepare the final lubricating oil compositions.

Other improvements within the scope of the appended claims will occur to those skilled in the art.

I claim:

1. A mineral lubricating oil containing a minor but effective proportion, in the order of about 0.5% to 10%, sufficient to impart detergency characteristics to said oil, of a complex formed by heating an oil-soluble lead petroleum sulfonate with an amount of an inorganic base selected from the group consisting of lead oxides, hydroxides, carbonates and bicarbonates in the presence of mineral oil to a temperature of about 150° F. to 500° F., sufficient to solubilize said complex in the oil, to take up about 5% to 45% based on the sulfonate of the inorganic base in said complex and dehydrate the mixture, said inorganic base having the function of enhancing the detergent capacity of the sulfonate.

2. An oil according to claim 1 in which the proportion of complex is from 0.2% to 3%.

3. An oil according to claim 1 in which the temperature is about 350° F.

4. An oil according to claim 1 in which said composition contains between about 0.1% and

about 3% of an oil-soluble metal sulfonate as a supplemental detergent.

5. An oil according to claim 1 in which said composition contains between about 0.1% and about 3.0% of an anticorrosion agent selected from the group consisting of oil-soluble metal thiophosphates, oil-soluble metal salts of a substituted phenol, oil-soluble metal salts of the condensation product of formaldehyde with an alkyl phenol and oil-soluble metal salts of a weak non-carboxylic organic acidic material having an ionization constant not exceeding about 5×10^{-6}.

6. A mineral lubricating oil containing a minor but effective proportion, in the order of about 0.5% to 10%, sufficient to impart detergency characteristics to said oil, of a complex formed by heating an oil-soluble lead petroleum sulfonate with an amount of lead oxide in an amount of from 5% to 45% in the presence of mineral oil to a temperature of about 150° F. to 500° F., sufficient to solubilize said complex in the oil, to take up about 5% to 45% based on the sulfonate of lead oxide in said complex and dehydrate the mixture, said lead oxide having the function of enhancing the detergent capacity of the sulfonate.

7. An oil according to claim 6 in which the proportion of complex is from 0.2% to 3%.

8. An oil according to claim 6 in which the temperature is about 350° F.

9. An oil according to claim 6 in which said composition contains between about 0.1% and about 3.0% of an oil-soluble metal sulfonate as a supplemental detergent.

10. An oil according to claim 6 in which said composition contains between about 0.1% and about 3.0% of an anticorrosion agent selected from the group consisting of oil-soluble metal thiophosphates, oil-soluble metal salts of a substituted phenol, oil-soluble metal salts of the condensation product of formaldehyde with an alkyl phenol and oil-soluble metal salts of a weak non-carboxylic organic acidic material having an ionization constant not exceeding about 5×10^{-6}.

11. An oil according to claim 6 in which said composition contains between about 0.1% and about 3.0% of an oil-soluble metal thiophosphate as an anticorrosion agent.

12. An oil according to claim 6 in which said composition contains between about 0.1% and about 3.0% of an oil-soluble metal salt of the condensation product of formaldehyde with an alkyl phenol.

RICHARD W. MERTES.

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The following references are of record in the file of this patent:

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Patent No. 2,501,732

Certificate of Correction

RICHARD W. MERTES March 28, 1950

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 11, lines 19 and 20, strike out "in an amount of from 5% to 45%"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of September, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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