

UNITED STATES PATENT OFFICE

2,280,419

COMPOUNDED OIL

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No Drawing. Application July 16, 1940,
Serial No. 345,844

24 Claims. (Cl. 252-33)

This invention relates to mineral lubricating oils which have been modified by the addition of constituents to impart to them special characteristics especially adapting them to severe service uses, such as are encountered in Diesel engines, high output aviation engines and the like.

In Diesel and similar engines the high temperatures developed in the cylinders tend to act upon lubricating oils to cause the deposition of resinous and varnish-like products on the pistons and elsewhere to produce lacquer-like coatings and carbonaceous materials which tend to cause ring and valve sticking and interfere with engine operation. Furthermore, fuel residues from incomplete combustion of fuel contribute to the deposition of lacquer-like and carbonaceous materials in the engine. Many oils used for these purposes also develop corrosive tendencies toward highly corrosion-sensitive bearings.

Primarily, the object of this invention is to produce for such severe service conditions as are encountered in Diesel engines, lubricating oils which possess detergent properties and thereby avoid the deposition of lacquer and varnish-like materials upon pistons and overcome carbon deposition behind the rings, and which will also be non-corrosive to highly corrosion-sensitive bearings of the copper-lead and cadmium-silver type. By detergent property is meant that property of preventing the deposition of such materials or that property of lifting or removing such materials, if it be that they are actually deposited, whereby, whatever the action, the sticking of valves and rings which has been common ordinarily in the lubrication of severe service engines, such as Diesel engines, is overcome or prevented.

The present invention resides in mineral lubricating oils containing small amounts in the order of about 0.3% to 2.0% or 3.0% of an oil-soluble metal salt of a sulfonic acid to insure good detergency, together with a quantity of the same order of oil-soluble metal salt of high molecular weight non-carboxylic weak acid having an ionization constant below about 5×10^{-6} . Such acids are the phenols, thiophenols, alcohols, enols, oximes and sulfonamides to assist detergency and avoid development of the mentioned corrosive conditions. The description of the sulfonic acids and the weak acids are detailed hereinafter. The metal sulfonate and the metal salts of the above mentioned weak acids when present together in a mineral lubricating oil in the amounts indicated above produce an oil which is non-corrosive to alloy bearings, such as those composed of cadmium and silver or copper and

lead. Furthermore, this oil has a reduced tendency toward deposition of varnish-like, resinous or carbonaceous materials in the combustion cylinders or on the pistons or piston rings or the like.

As stated above, my new composition contains a small quantity of an oil-soluble metal salt of sulfonic acids, such as the so-called "mahogany" acids. The sulfonate is preferably in the form of the calcium salt. However, the other alkaline earth metals, such as barium, strontium and magnesium may be employed. The salts of the weak non-carboxylic acids are from acids having ionization constants of 5×10^{-6} or less and preferably 1×10^{-6} or less, such as 1×10^{-8} or within the range of 1×10^{-7} to 1×10^{-11} . The salts may be in the form of lithium, sodium, potassium, copper, zinc, magnesium, calcium, barium, strontium, aluminum, lead, nickel, cobalt, manganese, chromium or iron salts, but I prefer to employ the alkaline earth metal salts, e. g., Ca, Mg, Sr and Ba. Of this group of weak acid salts, I prefer to use the oil-soluble metal salts of the phenols.

My invention is particularly novel in that the combination of salts of weak acids with the salts of the sulfonic acids has beneficial effect on the detergent properties of the oil and on any tendency toward development of corrosive conditions in the oil during use, which effect is not obtained when the substances are used by themselves. This effect can result from the use of smaller combined amounts of the materials than can be even approximated by the collective results from the separate use of larger amounts of the individual materials. Neither alone is sufficiently detergent. This will become evident from the examples given hereinafter. This is possibly explained by a theory that the soap of the weak non-carboxylic acid improves the colloidal property of the sulfonate in the oil and thereby enhances the detergency of the sulfonate. Also, the sulfonate may cause improvement in the functioning of the weak acid soap. Although the combination may be used in any good lubricating oil (including naphthenic base oils—low V. I. oils), it was found to be unexpectedly satisfactory in oils of a high viscosity index (V. I.), for example, oils with a V. I. of 85 to 95, possibly because of the unexpectedly high "solubility" or dispersion in this type of oil.

The term "viscosity index" is described in Chemical and Metallurgical Engineering, vol. 36, No. 10, pages 618-619 (1929). The term "soap," which is sometimes herein used to indicate the salts of this invention, indicates salts of high

molecular weight materials possessing at least ten carbon atoms per molecule so as to impart good dispersibility or "solubility" in the mineral lubricating oil when in the form of salts of those metals whose salts are oil-dispersible or "soluble" as here required.

The sulfonated acids employed to prepare the sulfonate additive of this invention may be those synthetically produced, as by du Pont, and obtainable on the market, or those obtained from the treatment of petroleum fractions, and also obtainable on the market as from Sonneborn Company of New York city. Acids of the latter type, which are valuable here, are the oil-soluble so-called "mahogany" acids.

The "mahogany" acids are well known to the industry. They are those sulfonic acids which are formed when lubricating oil fractions or similar petroleum oil fractions are treated with concentrated or fuming sulfuric acid. These so-called "mahogany" acids dissolve in the oil phase, whereas the so-called "green" acids are the water-soluble sulfonic acids which pass into the sludge. The mahogany acids may be recovered by treatment of the oils with sodium hydroxide to produce sodium sulfonate which is removed from the oil solution by means of the addition of an alcohol such as ethyl alcohol or propyl alcohol with heating whereupon the sodium sulfonates pass into the alcohol solution which is separated from the oil, the alcohol being then distilled off to leave the sodium sulfonates.

Sodium salts of suitable oil-soluble sulfonic acids of this type from petroleum are obtainable from the Sonneborn Company under the trade name "Petronate" which contains about 60% sulfonates and about 35% to 40% mineral lubricating oil.

In order to obtain the calcium sulfonate from this mahogany acid soap, the sodium or potassium sulfonate is dispersed in hot water and a solution of calcium chloride is added with agitation while maintaining the mixture near the boiling point of water. The result is the formation of calcium sulfonate in a sodium chloride and calcium chloride water solution. The mixture is cooled to coagulate the water-insoluble calcium soap, the water solution is drawn off, and the calcium sulfonate mass is washed with water in the cold. In order to eliminate all of the water and the remaining sodium chloride, from two or three volumes of mineral lubricating oil, based on the calcium sulfonate, are added to the calcium sulfonate mass and the mixture boiled until all of the water is eliminated, the temperature being finally raised to about 325° F. or within the range of perhaps 275° F. to 375° F. During this treatment, the calcium sulfonate passes into solution in the oil, the water is driven off and the residual sodium chloride which crystallizes in the oil from the water droplets is then removed by filtering the hot oil solution. Incidentally, any other inorganic salts including excess calcium chloride will have crystallized and been removed along with the sodium chloride.

In one instance 900 grams of the sodium salts of oil-soluble petroleum sulfonic acids were dispersed in 3000 grams of water and brought to a boil. To this was added 225 grams of calcium chloride dissolved in 1000 grams of water. The batch was agitated vigorously. The excess water was then expressed from the mass thrown down, and the mass washed with cold water with removal of the excess wash water. To the washed soap mass 2000 grams of lubricating oil

such as described herein was added and the batch dehydrated as above. After adding 75 grams of a finely ground diatomaceous earth and heating to 300° F., the batch was filtered.

The resultant material is an oil concentrate containing from 25% to 35% of the oil-soluble petroleum sulfonic acid soap of calcium which otherwise may be referred to here as a calcium mahogany acid soap, or calcium mahogany soap. This concentrate is liquid at normal temperatures, is free from water and mineral salts and, while it has an increased viscosity over the original oil, it has no typical grease-like characteristics, that is, it is free from all gel structure typical of greases. The soap is contained in the oil in what appears to be a state of perfect dispersion approximating possibly a true solution, which appears to be neutral and without the presence of any appreciable acid number.

For the present combination, sufficient of this concentrate will be employed to impart to the oil a sulfonate content of around 0.3% to 3%, approximately 1% representing an average use. These salts are readily dispersible in paraffinic base oils of high viscosity index as well as in naphthenic base oils, in proportions larger than required in the final composition. Even the concentrate may be prepared with a high viscosity index oil.

Whereas the sulfonate additive is used primarily for its detergent properties, the weak non-carboxylic acid soap is added to activate or increase the detergent properties of the sulfonate as well as to impart resistance to the development of corrosive conditions affecting the particularly corrosion-sensitive bearings. This second additive ordinarily may be used in percentages somewhat under those for the sulfonate. For example, if 0.8% to 1% of calcium sulfonate is used, then about 0.5%, or apparently sometimes as low as 0.2% or 0.25% of the weak-acid soap, will ordinarily be used. This is especially true of the phenol soaps.

By the term "phenols" it is meant to include not only the hydroxy aromatic ring compounds in which an hydroxyl group is directly attached to a carbocyclic aromatic ring, but also heterocyclic compounds in which the hydroxyl group is attached to a ring containing a sulfur, oxygen, nitrogen or other atom, said compound being capable of forming an oil-soluble metal salt. It is to be further understood that the term "phenols" includes not only monohydroxy but polyhydroxy compounds and those in which more than one ring is present, such as naphthols and the like. In addition to the hydroxyl group or groups, the ring is preferably substituted by one or more other substituents, for example, an alkyl group or a sulfur atom linking two phenolic radicals together such as in di-para-tertiary-amyl diphenol sulfide, the only limits being that the compound must have a sufficient low ionization constant as defined, must be non-carboxylic and must contain at least one hydroxyl group of sufficient acidity to exhibit an ionization constant within the limits described above, and must form an oil-soluble metal salt. For the sake of simplicity in the following specification and claims, these compounds will be referred to merely as the metal salts or metal soaps of phenols.

Although it is not definitely known why the metal salts of phenols act to prevent corrosion of alloy bearings, and I do not wish to be bound by the theory, it is presumed that this inhibiting power is at least in part connected with the abil-

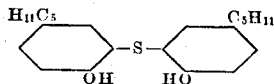
ity of the salts to react with the corrosive acids formed in the lubricating oil during use to produce non-corrosive metal salts of the corrosive acids, thereby liberating the non-corrosive, weakly acidic phenolic compounds. As an indication of the manner in which the above mentioned compounds are presumed to react to neutralize corrosive acidity, thereby rendering the oil non-corrosive, the following exemplary equation may be given:



In this equation R represents a hydrocarbon radical, M represents a metal, X represents the acid radical of a corrosive acid, and H represents a replaceable or acidic hydrogen atom.

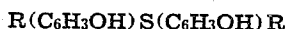
The oil-soluble metal salts, such as the calcium salts of the phenolic compounds are employed in the lubricating oil in small amounts from about 0.2% up to about 3%, but in amounts less than that required to cause any undesirable thickening of the oil, the optimum apparently being from about 0.5% to 1.5%.

A specific usable phenolic material of which I have produced the calcium salt is di-para-tertiary-amyl diphenol sulfide, in which the amyl group is now believed to be para to the hydroxy position of the phenol, and which apparently has the formula:



Alkyl hydroxyl phenyl thio ethers of this type are described in the Mikeska et al. Patent, No. 2,139,766 and other similar compounds and their method of preparation are given in Mikeska et al. Patent, No. 2,139,321.

A phenolic material believed to be kindred to that of the Mikeska et al. Patent, No. 2,139,766, is at present obtainable on the market under the trade name "Paranox" which is available from the Standard Oil Development Company of Elizabeth, N. J. This material, apparently, is in general composed of mixed poly-alkyl polyphenol sulfides, that is, poly-alkyl substituted hydroxy phenyl thio ethers containing, for example, a thio ether of butyl phenol which may be designated as Bis (2-hydroxy-4-butyl phenyl) sulfide. This commercial product apparently contains various materials of the following general formulas:



and

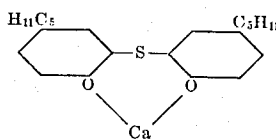


In these formulas and similar formulas herein, S, in general, indicates one sulfur atom, but in some molecules two or more sulfur atoms may be represented, the major proportion, however, preferably being monosulfides; R is an alkyl group preferably containing four or five carbon atoms (butyl or amyl) but may contain more, which groups may be different for the different components of the mixture or may be different for the two or more benzene nuclei in one of the components. R, S and OH may occupy any of the possible positions in the benzene rings. The material may contain higher polymers, such as indicated in the second formula above, and even more extensively polymerized materials.

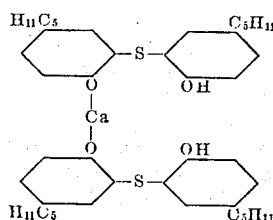
In practicing this phase of the invention commercially, the soaps of suitable phenolic compounds, such as the calcium soaps of diamyl, or di-butyl, or other alkyl, or mixture of alkyl,

phenol sulfides above indicated, may be formed without particular difficulty by any suitable procedure, as will be obvious to the skilled chemist. For example, the calcium salts of these compounds may be conveniently obtained by first adding the starting material to any approximately equal quantity or even greater quantity of a suitable lubricating oil, such as a naphthenic base mineral oil, or preferably for the purpose of the invention a paraffinic base oil of high V. I., having good solvent properties for the phenolic material and for the salts to be produced. This mixture is then commingled with hydrated calcium oxide and a small proportion of water, followed by heating to about 300° F. with agitation for a time sufficient to insure neutralization and dehydration. The resultant mixture is filtered to remove solids, such as excess calcium oxide. The ash (calcium content) has been increased when desired by first heating to only about 200° F. to 210° F. for a time to insure complete admixture and partial neutralization, the mixture being then cooled to 150° F. to 170° F. and a small quantity in the order of about 3% of 95% alcohol added, and the temperature of the mix then raised to the previously mentioned temperature of 300° F. Another method employed has been to neutralize the alkyl phenol sulfides with sodium hydroxide and then by metathesis, with calcium chloride or the like, convert the sodium salt to the calcium salt. In preparing for a treatment of the "Paranox" described above as probably comprising a mixture of alkyl phenol sulfides, about 20% of the sulfides should appear in about 80% of lubricating oil having good solvent power for the soap. Otherwise, a greater proportion of lubricating oil is added as its soap-dissolving power decreases. The above described neutralization to produce the calcium salts thereof is more or less easily accomplished due to the fact that the pure phenolic material has been found to have an acid number of about 98. The other alkaline earth metal salts may also be readily produced in a similar manner. In preparing soaps of other metals previously mentioned, the metathesis procedure just mentioned may be preferable as will be readily determined by the skilled chemist.

These salts or soaps are readily soluble in lubricating oils in the required proportions and yield alkaline solutions. Representative salts thus produced appear to have the following structural formulas:



60 and



70

Or the alkyl may be a butyl group, or a group of more than five carbons, thereby to impart good oil-"solubility" or dispersibility. Also the alkyl positions may be para to the sulfur or in any other position on the rings.

These materials thus may be viewed as sulfides, or as thioethers, or as metal oxides or as phenolates.

In preparing lubricating oil according to the present invention, the soaps or the soap-oil mixtures are stirred into an appropriate mineral lubricating oil and solution or dispersion is effected by agitation, a slight elevation of temperature being produced if desired to facilitate the operation.

Then the calcium soaps of these two types of compounds are dissolved in the lubricating oil to yield in the final product a total soap content of from about 0.5% to 3%, the detergent action of the resultant lubricating oil is sufficient to overcome or prevent the deposition of objectionable amounts of said resinous and varnish-like materials, in Diesel engines and the like. At the same time these quantities of soaps are insufficient to increase substantially the original viscosity of the mineral base lubricating oil. The ratio of the quantity of the phenol soap to the quantity of the sulfonic acid soap may be varied, but preferably approximately equal quantities of the two compounds are generally used, that is quantities to yield substantially equal amounts of ash figured as CaSO_4 . The two soaps employed in conjunction with one another give excellent detergency characteristics to the oil, while the phenol soap itself acts also as an alkaline reserve to prevent the formation of, or neutralize the effects of, the objectionable corrosive acids which attack detrimentally the highly corrosion-sensitive alloy bearing of the copper-lead type.

In addition to the general detergent functions of the soap which are imparted to the oil by the calcium phenol soap, the presence of the sulfur in the soap molecule tends to impart to a non-sulfur-containing lubricating oil, extreme pressure characteristics, and the small percentage of actual sulfur present in the soap further acts to impart in itself some anti-corrosive properties.

In addition to the calcium soaps of the phenol thio-ethers indicated, soaps of other metals of the alkylated phenol thio-ethers may be employed, such as those of barium, magnesium and also zinc and aluminum, the important requirements being good solubility in the chosen mineral lubricating oil, detergent properties and freedom from appreciable viscosity increase when used in detergent quantities such as the indicated range from about 0.25% to 2.0% or possibly 3%. Also, these metals appear to possess less undesirable catalytic activity than some of the heavier metals such as lead. Soaps of other phenol ethers, such as alkyl-substituted phenol selenium or tellurium ethers or the like containing other suitable sulfur substitutes in the ether position, are also within the scope of this invention for some uses where possessing sufficient solubility or dispersibility in oil and adequate detergent properties.

I have also found that an alkyl phenol such as amyl phenol can be condensed with formaldehyde under appropriate conditions to form a viscous polymer in which free hydroxyl groups of the phenolic type are present, and that appropriate oil-soluble soaps such as calcium soaps can be produced therefrom. For example, I have manufactured the condensation product of p-tertiary amyl phenol with formaldehyde employing both an acid catalyst and a basic catalyst. Where employing an acid catalyst I have used about 82 grams (0.5 mol.) of amyl phenol with from about 27 grams to about 49 grams (0.33 to 0.5 mol.)

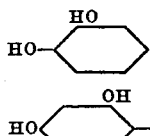
of 37% formalin (formaldehyde) with 2 ml. of 37% of hydrochloric acid. These materials were combined and refluxed for one hour where the higher, molecular proportions of formaldehyde were used and up to three hours where the lower proportions of formaldehyde were used. The refluxing temperatures were conveniently carried between about 200° F. and 212° F., any appropriate range obvious to the skilled chemist being suitable. When the condensation product was formed by refluxing as above, a thick liquid, resinous material was obtained when the smaller proportions of the formaldehyde were used and a more pasty material when the higher proportions of formaldehyde were used. In these cases the resultant liquid or paste as one part was then added to nine parts variously of SAE 20 and SAE 30 grades of California or naphthenic base mineral lubricating oils and high viscosity index (80 to 90 V. I.) paraffinic lubricating oils. (In some cases, there was added to this mass the water layer from the refluxing operation, this water being that of the formaldehyde solution.) To this mass there was then added 37 grams (0.5 mol.) of hydrated lime and the batch was agitated for two hours at temperatures ranging between 180° F. and 200° F., and then cooled. In some instances 60 ml. of ethyl alcohol was then added and the batch further agitated for about two hours at 180° F. Where alcohol is used there is less hydrolysis and the calcium content is increased. In each instance the temperature and time of treatment and the nature of the treatment was such as to effect conversion of the phenolic resin into the calcium soap thereof. In order to remove completely any unconverted lime and other solvents there was mixed into the batch a quantity of suitable filter aid such as ground diatomaceous earth (e. g. "Super-Cel") approximating the amount of the hydrated lime employed (about 37 grams), and the batch heated to 300° F. and filtered at about that temperature.

Suitable resins were produced in the same manner by employing 2 ml. of ammonium hydroxide containing 28% NH_3 as the catalyst instead of hydrochloric acid, the refluxing in these particular cases being slightly longer, the results apparently being equally satisfactory.

These products constituted 10% concentrates, that is 10% of the calcium soap of the phenolic condensation product with 90% of the naphthenic mineral lubricating oil mentioned. These concentrates were dilutable in all degrees with either naphthenic base oils or paraffinic-type lubricating oils without precipitation of the soap after long standing. A higher soap concentrate can be obtained by using smaller amounts of oil, although the larger amounts render the mass more workable.

The same soaps have also been prepared directly by adding the hydrated lime to the original mass, thereby employing the lime as a catalyst. Thus 82 grams of amyl phenol, 328 grams of the mentioned 600 viscosity mineral oil and 37 grams of hydrated lime were charged into a closed flask, having a sealed agitator and a reflux condenser, and heated to 150° F. at which temperature the amyl phenol was melted. To this heated batch about 30 grams of 37% formaldehyde was introduced through the reflux condenser. Here the batch was refluxed at between 200° F. and 212° F. for about six hours. The product was then transferred to open vessel and agitated with 60 ml. of ethyl alcohol at 180° F. for 2 hours and filtered at 300° F. with the filter

5. Products of the type in all previous examples in which

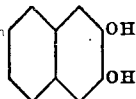
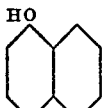
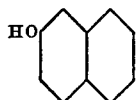


and the like appear in place of

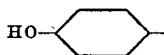


1. Products of the type in (a) and

(b) above in which

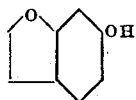
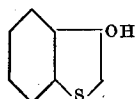


and the like appear in place of



1. Compounds of the types in (a).

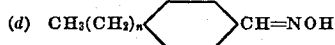
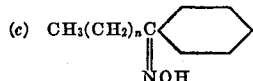
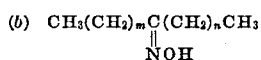
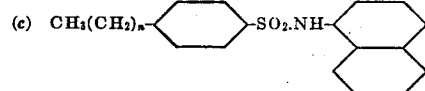
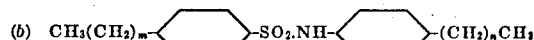
(b), (c) above, in which



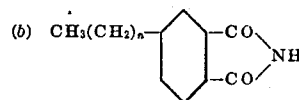
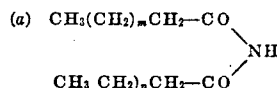
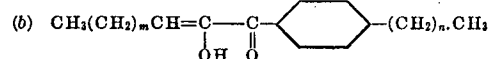
and the like appear in place of



An OH group in the phenol compounds of Group I is replaced with SH.

$$(a) \text{ 'CH}_3(\text{CH}_2)_n\text{CH}=\text{NOH}$$

$$(a) \text{ CH}_3(\text{CH}_2)_m\text{---}\text{Cyclohexane ring}\text{---SO}_2\text{NH}(\text{CH}_2)_n\text{CH}_3$$


V. Imids


$$(a) \quad \text{CH}_3(\text{CH}_2)_m \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \underset{\text{OH}}{\underset{|}{\text{C}}} = \text{CH} - (\text{CH}_2)_n - \text{CH}_3$$


Oil-soluble soaps or salts of these various materials may be prepared in manners as outlined above and added in indicated proportions to yield the type of product described and claimed. Important requirements are good solubility of the soaps in oil in the proportions required, without substantial increase in the viscosity of the base oil, and low ionization constants as above defined with consequent freedom from development of corrosive conditions in the oil during engine use which is presumed to be due to the indicated neutralizing character of the soaps which may be termed "reserve alkalinity."

The salts or soaps of these materials from the indicated metals, may be considered as metal oxides as well as the phenolates, or ethers, or thio ethers as the case may be. They will be used with the indicated sulfonates in the percentage ranges previously indicated, but not sufficient to promote appreciable viscosity increase where to be used in internal combustion engines. As specific examples of the preparation of the combination of the invention and the effect of some of the hereindescribed materials, the following are presented:

One thousand grams of the above-mentioned oil-soluble sodium sulfonate in oil, known as "Petronate," produced by the Sonneborn Company, was agitated in 4000 cc. water during the addition of 220 g. CaCl_2 in 1000 grams water. After complete metathesis, the product was washed and added to 4000 grams of a propane dewaxed highly solvent-treated highly-paraffinic SAE 30 high viscosity index mineral lubricating oil (about 90 V. I.) together with about 25 grams of lime to insure complete neutralization. The mixture was dehydrated at 300° F. and filtered at 300° F. to give a filtrate component (I) which was a dispersion of 600 grams of oil-soluble calcium sulfonate in 4400 grams of oil.

To prepare the second additive for my composition, 2000 grams "Paranox" (amylphenol thioether) obtained from the Standard Oil Development Company, was mixed with 500 grams lime, 440 ml. 90% isopropanol and 8000 grams of the same high viscosity index (90 V. I.) SAE 30 motor oil mentioned in the above example. The

mixture was agitated for two hours at 180° F., dehydrated for thirty minutes at 330° F. with 500 grams of diatomaceous earth to give component (II) consisting of 2000 grams of calcium soap of alkyl phenol thioether together with some unreacted alkyl phenol thioether in 8000 grams of oil.

These two preparations were added to a similar high V. I. solvent treated SAE 30 lubricating oil in quantities to give a composition containing 0.8% by weight of calcium sulfonate and 0.5% by weight of calcium soap of alkyl phenol thioether. This composition, on testing in Diesel engines running with a high load, proved to have excellent detergency properties. After the usual period of 100 hours, the piston was free of lacquer deposit, and all of the rings were free and in good condition. The corrosion of copper lead bearings was also at a minimum.

However, using the same high V. I. motor oil to which had been added 1.2% by weight in one case and 2.5% by weight in another case of the calcium sulfonate by means of component I, the products showed relatively poor detergency action in Diesel engines. The use alone of about 2.0% by weight of the described calcium soap of alkyl phenol thioether by means of component (II), whose active ingredient was probably calcium diamyl-diphenol sulfide, in a higher V. I. oil gave a correspondingly poor lubricant for severe service engines. At the end of forty hours deposits had appeared on the ring lands and the rings were beginning to show symptoms of sticking, and on the piston skirt a quantity of a varnish-like material was noticeable.

The above two-component composition is illustrative of the various compositions which can be made under the above disclosures employing sulfonates and any other weak-acid soap having the "reserve alkalinity" property.

It will be understood that examples are given for the purpose of illustration and not as necessarily limiting beyond the requirements of the prior art.

I claim:

1. Mineral lubricating oil containing a small proportion of oil-soluble petroleum sulfonate and a small proportion of the salt of a weak non-carboxylic organic acidic material having an ionization constant not exceeding about 5×10^{-6} .

2. A mineral lubricating oil containing a small proportion of oil-soluble soap of the oil-soluble sulfonic acids obtained by sulfonating petroleum fractions, together with a small proportion of oil-soluble salt of weak non-carboxylic organic acid having an ionization constant not exceeding about 1×10^{-6} .

3. A lubricant comprising mineral lubricating oil and a small quantity of each of (1) an oil-soluble metal soap of a weak non-carboxylic organic acid having an ionization constant less than 5×10^{-6} , and (2) an oil-soluble metal soap of oil-soluble sulfonic acids from petroleum.

4. A mineral lubricating oil containing a small quantity of an oil-soluble metal soap of a substituted phenol together with a small quantity of an oil-soluble metal petroleum sulfonate, the combination of these two substances in the lubricant having superior detergent and anti-corrosive properties which the substances do not possess alone.

5. A lubricant according to claim 3 wherein each of the soaps is present in amount between about 0.25% and about 3%.

6. A lubricant according to claim 4 wherein each of the soaps is present in amounts between 0.3% and 3%.

7. A lubricant according to claim 3 wherein the soaps are alkaline earth metal salts.

8. A lubricating oil according to claim 4 wherein the soaps are alkaline earth metal salts.

9. A lubricating composition as in claim 3 wherein the weak non-carboxylic organic acid soap is the soap of an alkylated phenol thioether oil is one having a viscosity index above about 80.

10. A lubricating composition according to claim 4 where the mineral oil has a high viscosity index.

11. A lubricating oil containing a small quantity of oil-soluble metal alcoholate together with small quantity of oil-soluble metal salt of sulfonic acid from petroleum.

12. A lubricant comprising mineral lubricating oil, a small proportion of an oil-dispersible aryl metal oxide and a small proportion of an oil-dispersible metal petroleum sulfonate.

13. A lubricant according to claim 12 wherein the lubricating oil is high viscosity index highly paraffinic mineral oil.

14. A lubricant according to claim 12 wherein the metal of the additives is an alkaline earth metal.

15. A lubricant comprising mineral lubricating oil having a viscosity index of at least about 80 containing a small proportion of oil-dispersible metal petroleum sulfonate and a small proportion of oil-dispersible metal phenolate.

16. A lubricant according to claim 12 wherein the aryl oxide contains substituents increasing the carbon atoms to at least ten per molecule.

17. A lubricant according to claim 1 wherein the weak acid contains at least ten carbon atoms per molecule.

18. A normally liquid lubricant comprising a mineral lubricating oil having a viscosity index at least as high as about 80, a small proportion in the order of 1% of an oil-soluble calcium soap of sulfonic acids derived from sulfonating petroleum fractions, and a small quantity in the order of 0.5% of an oil-soluble calcium salt of an alkylated hydroxy phenyl thio ether.

19. A lubricant according to claim 3 wherein the soaps are salts of metals other than alkaline earth metals.

20. A lubricating oil according to claim 1 wherein the salts are those of alkaline earth metals.

21. A lubricating oil according to claim 1 wherein the salts are salts other than alkaline earth metals.

22. A lubricating oil according to claim 1 wherein the base oil is an oil having a viscosity index of at least about eighty.

23. A lubricant according to claim 3 wherein the base oil is one having a viscosity index of at least about eighty.

24. A lubricant according to claim 3 wherein the salts are salts of heavy metals.

CHESTER E. WILSON.

CERTIFICATE OF CORRECTION.

Patent No. 2,280,419.

April 21, 1942.

CHESTER E. WILSON.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 7, second column, lines 14 and 15, claim 9, strike out "oil is one having a viscosity index above about 80"; 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 4th day of August, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.