UNITED STATES PATENT OFFICE

2,378,820

LUBRICATING OIL

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20 Claims. (Cl. 252—33)

This invention relates to modified lubricating oils and especially to those which have been modified by the addition of constituents particularly adapting the oils to severe service uses as in Diesel engines, high out-put aviation engines and the like.

It is well understood that various lubricating oils as ordinarily refined are inadequate to meet many uses, particularly severe service uses, because of the development of resinous and varnish-like materials which cause ring sticking and similar difficulties. It is also well understood that, where highly corrosion sensitive bearings are used such as cadmium-silver and copper-lead bearings, the ordinary lubricating oils develop conditions during use which are corrosive to said bearings. In many instances where additives have been used to overcome ring sticking difficulties, these additives have promoted the development of corrosive conditions.

An important object of this invention is to produce a compounded oil wherein the additives overcome the formation of said resinous materials or prevent their deposition and at the same time avoid the development of the mentioned corrosive conditions.

According to this invention, two constituents ordinarily are employed, one of which is a "detergent" material having the properties of preventing the accumulation of said resinous or varnish-like deposits, and the other of which acts to overcome or prevent the development of corrosive conditions in the oil during use and may be termed an "anti-corrosion" agent. This latter additive may act as an anti-oxidant or it may act as a "reserve alkalinity" agent serving to neutralize synthetic acids produced in the oil during use. Both materials should be free from any impurities or other constituents which possess catalytic activity toward the production of corrosive conditions and the like.

According to a preferred form of the present invention, the detergent material is an oil-soluble metal soap of the sulfonates produced from petroleum, which sulfonates are to be free from salts exerting the mentioned catalytic activity. For example, calcium sulfonates obtained from sulfonic acids produced by strong sulfuric acid treatment of petroleum lubricating oils are used, these being so produced as to be free from iron sulfonates or other metal salts having said catalytic characteristics. In general the alkaline earth metal salts are found to be free from such catalytic properties. The other type of additive, which is referred to as an "anti-corrosion agent," preferably will be of the class which possess "reserve alkalinity" properties and may also contain a constituent having some inhibiting value. An example is an oil-soluble salt, such as the calcium salt, of a dialkyl-substituted phenol thioether. Such an alkylated phenol thioether, or alkylated diphenol sulfide, is obtainable on the market under the trade name "Paranox" and is produced by the Standard Oil Development Company. Another anti-corrosion agent that may be satisfactorily used with the pure oil-soluble sulfonate is a zinc salt of the reaction product of methyl cyclohexanol with phosphorus pentasulfide. Another suitable anti-corrosion agent is the calcium salt of phosphonic acids produced by heating a mineral lubricating oil or similar petroleum fraction with phosphorus and blowing the reaction product with air to produce a phosphonic acid. Also, oil-soluble metal salts of reaction products of P_2S_5 with other aliphatic alcohols may be used.

Another feature of the invention resides in the use of oil-soluble sulfonates as detergents which are free from the mentioned objectionable salts and are in the form of both the "green" acid sulfonates and "mahogany" acid sulfonates produced in situ in the sulfonated oil and without separation of the sulfonates from the oil and without separation of the water-soluble green acid sulfonates from the oil-soluble mahogany acid sulfonates. The invention also resides in the method of producing these mixed sulfonates, and in the production of oil containing them. The invention resides not only in the use of these sulfonates as detergents with other described types of materials in an oil but in their use as the sole constituent in an oil or with any other type of constituent not here specified.

In practising the invention, it is applicable to both paraffinic type oils and naphthenic type oils. Inasmuch as it has become desirable to employ oils of high viscosity index (V. I.) in the preparation of Diesel engine oils and other severe service oils, the adaptability of the present additives to high V. I. oils is another advantage of the present invention.

As the terms are used herein, "oil-soluble" refers to a high state of colloidal dispersion of the soaps or salts in question such that they maintain themselves permanently dispersed in the oil so as to approach a state of true solution. The term "reserve alkalinity," as has been indicated, refers to the property of the additive to neutralize synthetic acidity developed in the lubricating oil during use. The term "anti-corrosion" refers to the properties of the materials to neutralize such synthetic acidity or to inhibit oxidation which otherwise would result in corrosive conditions. The term "detergent" refers to the property of the additive either to remove deposits of resinous and kindred materials, or to prevent their formation or deposit. The term "viscosity index" (V. I.) indicates the type of oil. A paraffin base oil is assigned the V. I. of 100 and certain Gulf Coast naphthene base oils are issigned the V. I. of zero. Thus, high V. I. oils are the so-called "highly paraffinic" oils, such as Pennsylvania oils and those highly refined with selective solvents. The term is defined in Chemical and Metallurgical Engineering, vol. 36 (1929) pages 618 and 619. A kindred term is "viscosity-gravity-constant" (V. G. C.) where lower values indicate greater "paraffinicity"; see Journal of Industrial and Engineering Chemistry, vol. 20 (1928) page 641. The term "soap" indicates those metal salts of high molecular weight acidic materials possessing at least ten carbon atoms per molecule to impart good dispersibility or "solubility" in mineral lubricating oil. The term "sulfonates" refers to those salts or soaps produced from the well-known sulfonic acids obtained by sulfonation of petroleum fractions, especially certain lubricating fractions herein described, as by means of concentrated or fuming sulfuric acid, or chlorosulfonic acid, or sulfur dioxide, or the like, familiar to the skilled chemist.

In preparing the oil-soluble additive salts of this invention, various metals may be used so long as the salts themselves, or other salts which may form in use, do not catalyze or otherwise produce corrosive conditions. In general, the alkaline earth metal salts may be used throughout. Also zinc and apparently aluminum salts may be used. Apparently all these metals and most other metals may be used for the phosphorus-bearing salts described if the salts are oil-soluble.

The various additive materials employed according to this invention may be produced in manners herein described. In employing these various materials, small amounts are dispersed in a mineral lubricating oil in proportions to yield the desired effects without however materially increasing the viscosity of the oil and without imparting grease-like characteristics. Quite commonly about 1% of each of the two types of indicated additives is employed. Ordinarily between about 1% and 1.5% of the sulfonate is used, e. g. 1.2%, and from about 0.5% to about 1% of the anti-corrosion additive is used, e. g. 0.7% of the calcium salt of the indicated alkyl-substituted diphenol sulfide. In preparing the various oil-soluble additive materials, they may be obtained as concentrates in a lubricating oil similar to or identical with or different from the lubricating oil to which they are finally added. Production of the final product is readily obtained simply by dilution and by thorough mixing. Otherwise the various soaps or salts are readily dispersed in lubricating oil by sufficient agitation, accomplished if desired with a limited amount of heating, such as to 150° C. or thereabouts.

Where concentrates are prepared they will normally contain from about 10% to 40% or 50% of the additive, according to the method of preparation.

In the final product the over-all ranges for each of the two additives would normally be from around 0.4% or 0.5% to perhaps 1.5% or 2%. Commonly the total of all additives will not exceed about 2%. As to individual additives probably not more than 3% would ever be employed, both for the reason that viscosity increase is apt to be too great and for the further reason that larger amounts do not appear to offer any particular advantage and merely serve to increase the cost. For lower limits it is probable that any appreciable percentage would afford some advantage. The indicated intermediate range in the order of 1% appears to be commercially preferable.

Sulfonates

In preparing the sulfonates which constitute one of the two principal additives of this invention, it is important first to select a lubricating oil fraction which will provide a substantial yield of the desired sulfonate. For this purpose certain lubricating oils of both naphthenic and paraffinic type have been found acceptable, and this apparently is true regardless of their viscosity. In general, lubricating oils which have been prepared by a moderate degree of refinement are best. This distinguishes them from those lubricating oils which have been heavily refined as by the more modern severe solvent treatment, and from the lightly acid treated lubricating oils well known especially several years ago. To illustrate, a lightly acid refined naphthenic type oil, e. g. Western base oil treated with 20 to 30 pounds of 98% sulfuric acid per barrel, is not desirable for the present purpose; practically all of the acid used in subsequently sulfonating the oil is consumed in producing sludge, and the percentage of acceptable sulfonate is negligible. Similarly, where a highly solvent treated more modern type of lubricating oil, e. g. one of very high viscosity index produced by severe solvent extraction with benzol-sulfur dioxide mixtures, or furfural, or dichlorethyl ether or the like, is used, sulfonatable materials of the required type apparently have been largely removed and the result of attempting to sulfonate is the formation only of a small quantity of objectionable sludge.

On the other hand a naphthenic base oil which has been subjected to a light sulfuric acid treatment (e. g. 20 pounds of 98% acid per barrel) and also to a moderate treatment with liquid sulfur dioxide so as to yield a lubricating oil of about 25 V. I., is a good stock. Similarly a mixed base oil moderately treated as by selective solvent extraction to yield a V. I. of about 80 is a good stock. Again, a Pennsylvania oil moderately treated to a V. I. of 104 and having a viscosity gravity constant of 0.812, is a good stock. But a medicinal white oil having a V. I. of 72 and a viscosity gravity constant of 0.826 yields substantially no acceptacle sulfonates. Thus neither viscosity index nor viscosity gravity constant, nor in fact the type of oil, appears to determine a good stock. On the other hand it appears to be the degree of refinement, which has here been designated as an intermediate refinement. Of course it is true that, with the possible exception of white oils, a small amount of sulfonate may be obtained from almost any lubricating oil, but unless the oils come within the above designation of intermediate refinement they are not commercially acceptable. Oils of S. A. E. 40 grade have been commonly used but lighter stock such as S. A. E. 20 and heavier stock such as S. A. E. 60 also have been employed.

Specific oils which have been made are given below, the first six, indicated as "good" or better, being acceptable, whereas the last five, indicated as "bad" or worse, are of little or no practical value.

Oil type	Treatment	V. I.	V. G. C.	Sulfonate formation
Naphthenic:				
S. A. E. 40	25# H_2SO_4/bbl. followed by SO_3	25	0.862	Highest.
S. A. E. 20	Same as for S. A. E. 40	25	0.862	Do.
Paraffinic: S. A. E. 40	Very moderate selective solvent	82	0.815	High.
Pennsylvania: S. A. E. 40	Usual (no selective solvent)	104	0.812	Do.
Paraffinic:				
S. A. E. 40	Moderate selective solvent	90	0.804	Good.
S. A. E. 50	Same as for S. A. E. 40	90	0.81	Do.
Paraffinic: S. A. E. 40	Heavy selective solvent	100	0.80	Bad.
Paraffin wax: Deoiled	Normal	130	0.77	Do.
Naphthenic: S. A. E. 40	25# H_2SO_4/bbl	−20		Very bad.
Mixed base: S. A. E. 10	No treat	−20	0.88	Do.
Medicinal white oil	Heavy	72	0.826	Zero.

In sulfonating a suitable lubricating oil fraction, the desired quantity is heated to about 135° F. in a vessel which, under the conditions of treatment, will not yield in the product objectionable metal salts, e. g. iron salts. For example glass or silica vessels may be employed or steel alloys or the like not subject to attack in treating with the strong acids used. Higher and lower temperatures may be employed, such as down perhaps to as low as 50° F., or perhaps as high as 175° F., but most satisfactory results have been obtained where operating at 135° F. Similarly 30% by weight of a 40% fuming sulfuric acid has been found to be especially suitable for the present purposes, and as little as 20% or 30% fuming acid has been used with satisfactory results. According to a preferred procedure, having heated the oil to 135° F., the acid is gradually added at a rate slow enough to keep the temperature at about 135° F. If necessary to control the temperature, cooling will be employed and this may be a requirement where working large batches. In treating small amounts the time of addition may be as little as fifteen minutes, whereas in handling large batches two or three hours or even longer may be required for addition of the fuming acid. During the addition the mass is agitated continuously to insure complete contact and dispersion. Upon completion of the addition of the acid, sulfonation of the oil appears to be complete. In addition to the indicated fuming acids, other sufficiently effective acid strengths may be used. Thus, acids from 98% H_2SO_4 up to pure SO_3 may be used, i. e. from concentrated H_2SO_4 to 100% fuming acid. Possibly as low as 92% or even 90% H_2SO_4 may be employed in some instances.

After completion of the acid addition, it is desirable according to the preferred form of this invention to add a quantity of water to facilitate the subsequent neutralization operation. The addition of 10% of water is beneficial, and more may be conveniently added up to the optimum of about 30%, or even up to 100% based on the oil.

About 30% of water is adequate for the required purpose and the addition of more results chiefly in the objectionable necessity of subsequently boiling it off.

Following the addition of water, the next step is to neutralize the sulfonated oil batch. This is accomplished by slowly stirring in a lime slurry consisting of about equal parts of water and lime, the lime approximating about 30% of the sulfonated oil. The lime slurry is added at a rate such as to keep the temperature within the limits of about 125° F. to about 175° F. In practice about 150° F. to 160° F. is maintained for the reason that much higher temperatures tend to decompose some of the sulfonic acids. The presence of the added water makes it easier to keep down the temperature, and it also tends to facilitate the neutralization operation. By reason of the presence of the water the temperature of course can always be kept at least below the boiling point of the water.

Having completed the addition of the 30% of the lime, which is in excess, all excess sulfuric acid will have been neutralized with the formation of solid calcium sulfate, and the sulfonic acids will have been converted into calcium sulfonates.

It will be noted that according to this method of procedure, the acid sludge containing the so-called "green" acids has not been removed from the oil solution of the oil-soluble so-called "mahogany" acids. As a result, when the whole batch is neutralized with lime, both the oil-soluble mahogany acids and the oil-insoluble green acids are converted into calcium sulfonates. The mahogany acid soaps are inherently soluble in the oil and at the same time they act as solubilizers for the green acid soaps. Inasmuch as the green acid soaps are substantially as valuable for detergents as are the mahogany acid soaps, this method of procedure avoids the cumbersome and expensive separation of the two types of acids. At the same time it increases the sulfonate content of any given batch.

Having completed the neutralization operation whereby an oil solution is obtained of both the green acid soaps and the mahogany acid soaps, the next step is to evaporate the water. This is accomplished by heating the batch at about 325° F. (or within a range of about 275° F. to 375° F.) until the water is expelled.

The next step is to remove the solids and leave a product in the form of a soap-oil concentrate. Conveniently the dehydrated batch is diluted with about one-half again as much oil, or naphtha if preferred, and well mixed. No more additional oil or naphtha should be employed than sufficient to make the batch adequately fluid for subsequent separation of solids. Solid separation is best accomplished by settling the batch for about twenty-four hours at about 200° F., and then filtering or preferably centrifuging the batch. Where initial settling is effected, the subsequent filtering or centrifuging leaves a clear product consisting of unsulfonated oil containing about 20% of calcium sulfonate. This is an oil concentrate which may be added in appropriate quantities to any desired lubricating oil in blending a final product.

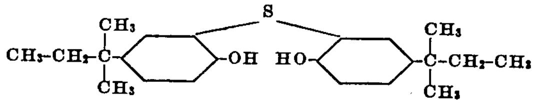
If, for any reason it be deemed desirable to eliminate the green acid soaps from the product, the acid sludge will have been separated from the batch following sulfonation and before neutralization.

If it should be that, in the sulfonation and soap making procedures, objectionable metal salts have been produced, such as iron salts, the oil-soap batch may be treated in any appropriate manner for the separation of the iron. For example materials which will react with the iron soap to form oil-insoluble compounds or inactive iron complexes may be added, such as cupferron, ammonium thiocyanate, acetylacetone, 8-hydroxyquinoline, diphenylamine, phenanthroline, and the like familiar to the organic chemist. Or, a finely divided active metal above iron in the electromotive series may be added, such as calcium, magnesium, aluminum or zinc, in which case metallic iron is formed, and the resultant soaps are not active oxidation catalysts. When using any of the above agents to bring down oil-insoluble forms of iron, this may take place before removing the excess lime and calcium sulfate, so that all insolubles may be removed in one settling, filtering or centrifuging operation.

The sulfonates are also made by recovering the sulfonic acids from the sulfonated oils as sodium sulfonates by sodium hydroxide treatment in the well known manner, and then converting by metathesis, as with $CaCl_2$ or $Ca(NO_3)_2$, to calcium or other desired salts. But, where necessary to eliminate objectionable impurities, the sulfonic acids are "cracked out" from the sodium sulfonates with sulfuric acid of about 50% or greater concentration (thereby avoiding any tendency for either "green" acids or "mahogany" acids to dissolve in weaker sulfuric acid solutions). The objectionable materials pass into the lower aqueous layer, and the top layer is the liberated sulfonic acids from which desired calcium or other soaps are produced, as with lime or calcium hydroxide or other suitable base. However, inasmuch as the sulfonates are eventually required in oil, round-about and expensive procedures are avoided merely by the production of the calcium sulfonates or other appropriate oil-soluble metal sulfonates in situ in the oil used for the sulfonation operation. Thereafter, simple dilution with more oil of appropriate grade is all that is required for the lubricating oil product desired.

Phenol-thio-ether soaps

With respect to the second additive required according to this invention for the purpose of introducing an anti-corrosion agent, ordinarily I prefer to employ calcium soap of the phenolic thio-ether above indicated as "Paranox." The Paranox type of material carries an alkyl substituent in each ring, such as butyl or tertiary amyl. One particular material is para-tertiary-amyl phenol sulfide, where one or more sulfurs appear in the ether position. Again instead of being a simple thio-ether containing two rings, it is probable that the commercial material contains several additional rings linked together with sulfur. Thus the structural formula for the para-tertiary-amyl phenol sulfide (thio-ether) with only two rings may be represented as follows:



The above probably is extended by the addition of further alkylated phenol groups connected with additional sulfur atoms, thus:

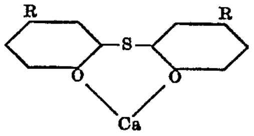
$$R(C_6H_3OH)S(C_6H_2OH)R.S(C_6H_2OH)R.S\ .\ .\ .\ .$$

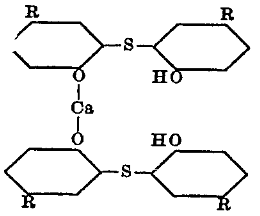
where R represents the alkyl substituent. Materials of this type have been described in the Mikeska Patents Nos. 2,139,766 and 2,139,321.

Suitable metal salts, such as calcium salts of the above phenolic sulfides may be prepared in any manner desired by the skilled chemist. One satisfactory method has been to add the starting material to an appropriate equal quantity, or even greater quantity of a suitable lubricating oil having good solvent properties for the phenolic material and for the salts to be produced. Good naphthenic base mineral oil of intermediate degree of refinement is a good example. This mixture of oil and phenol sulfide is commingled with an excess of hydrated calcium oxide and a small proportion of water, and the mass heated to about 300° F. under agitation for a sufficient time to insure neutralization and satisfactory subsequent dehydration. The resultant batch is then filtered or centrifuged to remove solids such as the excess calcium oxide. The ash content has been increased by partially neutralizing at a temperature around 200° F. to 210° F., then cooling to around 150° F. to 170° F., then adding around 3% of 95% alcohol, and then raising the temperature of the mass to said 300° F. to complete the neutralization.

According to another method the alkyl phenol sulfide has been neutralized with sodium hydroxide and then converted by metathesis with calcium chloride or the like to yield the calcium salt required. Commonly the starting material is a concentrate containing about 20% of phenol sulfides and 80% of a lubricating oil. If this is not too viscous for convenient handling further amounts of lubricating oil need not be added, unless the soap-dissolving powder of the oil is not entirely adequate.

The above described neutralization is easily accomplished due to the fact that the phenolic material itself has an acid number in the neighborhood of 98. The resultant salts may be generally represented as follows:





In compounding a lubricating oil of the present invention for practical uses, sufficient of the concentrate of the phenolic materials described, such as the mentioned calcium "Paranox" soap, and of the sulfonate concentrate, are added to impart a soap content of each of these materials in the order of from perhaps 0.5% to 3%. In actual practice there is commonly employed about 1% or a little less (e. g. 0.7%) of the phenolic soap, and about 1% or a little more (e. g. 1.2%) of the sulfonate.

Thio phosphates

As substitutes for the phenol thio-ether salts to be used as a second additive along with sulfonate, certain types of thio phosphates may be used. In general around ½% to 1% of these phosphates will be added to the final lubricating product. Any suitable oil-soluble metal salt is employed such as a zinc salt or a calcium salt. These phosphates are obtained by reacting phosphorus pentasulfide with aliphatic alcohols. Primarily these products will be referred to by their method of preparation because of the fact that their composition is not certain and for the further reason that the product probably consists of a mixture of compounds. One important alcohol employed is methyl-cyclo-hexanol and another is octyl alcohol or ethyl-hexyl-alcohol.

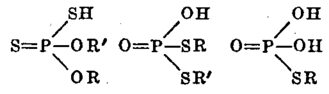
In some instances, where these phosphates are employed, it may be desirable to use them as a third constituent where the phenol sulfide salts are employed along with the sulfonates.

The oil-soluble metal salts of these reaction products may be prepared by reacting the phosphorus pentasulfide with the alcohol to prepare an intermediate acidic reaction product, and then treating such product with a metal oxide or the like to produce a metal salt thereof; or any appropriate single step operation may be used.

With respect to the reaction between the phosphorus pentasulfide and the alkylated cyclo-aliphatic alcohols mentioned, cyclo-hexanol alkylated with aliphatic chains containing less than ten carbon atoms and preferably about five or less, such as methyl, ethyl, propyl and amyl cyclo-hexanols are preferred. In fact, cyclo-hexanol or cyclo-heptanol or cyclo-pentanol may be used, and also methyl cyclo-heptanol and methyl cyclo-pentanol, and the like, so long as the respective salts desired are "oil-soluble." Or a mixture of these cyclo-aliphatic alcohols could be employed. While oil-soluble salts of other metals are acceptable, the zinc salt has so far been found preferable, and the methods of preparation given will refer particularly to the zinc salt. Nevertheless, those oil-soluble metal salts producible from other metals hereinbefore mentioned as being appropriate for the preparation of the sulfonates and the phenolic thio-ether soaps, may be used. For example, the lead salts of the reaction product of phosphorus pentasulfide with octyl alcohol have been found acceptable, as well as the zinc salts.

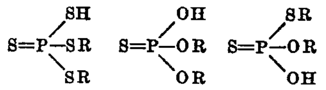
Thiophosphate of alkyl cyclo-hexanol.—Five mols of methyl cyclo-hexanol are reacted with one mol of P_2S_5. For example, five hundred grams of methyl cyclo-hexanol were mixed in an equal volume of benzene with one hundred ninety-five grams of phosphorus pentasulfide in a flask. This mixture was heated in a water bath at around 212° F. and refluxed for four hours. The batch was then cooled to about 140° F. and washed with an equal volume of water at about 140° F. The benzene was then removed from the washed material by distillation at atmospheric pressure.

The resultant reaction product is believed to be a mixture of acid thiophosphate esters such as represented by the following formulae where R is the cyclo-aliphatic radical derived from the alcohol, and R′ is hydrogen or R:



$$\mathrm{S{=}P}\begin{matrix}\diagup\mathrm{SH}\\-\mathrm{OR'}\\\diagdown\mathrm{OR}\end{matrix}\qquad\mathrm{O{=}P}\begin{matrix}\diagup\mathrm{OH}\\-\mathrm{SR}\\\diagdown\mathrm{SR'}\end{matrix}\qquad\mathrm{O{=}P}\begin{matrix}\diagup\mathrm{OH}\\-\mathrm{OH}\\\diagdown\mathrm{SR}\end{matrix}$$

Other possible materials are represented by the following:



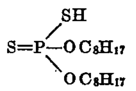
$$\mathrm{S{=}P}\begin{matrix}\diagup\mathrm{SH}\\-\mathrm{SR}\\\diagdown\mathrm{SR}\end{matrix}\qquad\mathrm{S{=}P}\begin{matrix}\diagup\mathrm{OH}\\-\mathrm{OR}\\\diagdown\mathrm{OR}\end{matrix}\qquad\mathrm{S{=}P}\begin{matrix}\diagup\mathrm{SR}\\-\mathrm{OR}\\\diagdown\mathrm{OH}\end{matrix}$$

Employing the mixed reaction product from the above described operation, this acid ester was mixed with water to make about a 20% mixture which was neutralized with aqueous caustic soda solution at about 180° F. To this solution was added an aqueous solution of zinc chloride with agitation, whereupon the zinc salt formed and settled out. The water was poured off and the zinc salt dehydrated by dissolving the wet zinc salt in about twice its volume of benzene, the water and benzene then being removed by vacuum distillation under maximum temperature conditions of 212° F. with seven inches vacuum.

In another instance the methyl cyclo-hexanol and zinc oxide were heated in a container to about 180° F. Phosphorus pentasulfide in finely divided form was then introduced over a period of about forty minutes at a temperature not exceeding 212° F., the temperature then being raised to 320° F. over a period of an hour maintained for an additional half hour. The product is recovered by dissolving in an approximately equal weight of mineral oil and filtering hot, employing preferably a filter aid, e. g. 2% of "Filtrol"; or the product may be dissolved in benzol, filtered and the benzol removed by vacuum distillation.

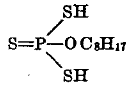
Thiophosphate of octyl alcohol.—One gram mol of powdered phosphorus pentasulfide is added to four gram mols of octyl alcohol in a glass or ceramic container, and the mixture agitated at temperatures between 250° F. and 300° F. for about two hours, i. e. until the phosphorus pentasulfide dissolves. When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



$$\mathrm{S{=}P}\begin{matrix}\diagup\mathrm{SH}\\-\mathrm{OC_8H_{17}}\\\diagdown\mathrm{OC_8H_{17}}\end{matrix}$$

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



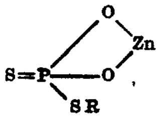
$$\mathrm{S{=}P}\begin{matrix}\diagup\mathrm{SH}\\-\mathrm{OC_8H_{17}}\\\diagdown\mathrm{SH}\end{matrix}$$

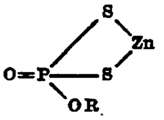
Quite likely other thiophosphate esters of the types above indicated in connection with the cyclohexanol product are also present in greater or lesser proportions.

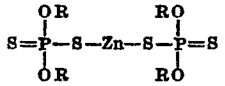
In addition to the zinc octyl thiophosphate described, the lead, copper, manganese, iron and tin salts also have been prepared by employing oxides thereof and allowing the mixtures to stand over night at about 250° F. as above. Upon decanting and filtering, viscous liquids were obtained. Other appropriate salts are the alkaline earth metal salts, such as the calcium salt, and salts of other metals as indicated in connection with the sulfonates and phenolic thio-ether salts.

As a substitute for octyl alcohol other alcohols which yield oil-soluble salts and contain fewer than ten carbon atoms are preferred, although alcohols containing ten or more carbon atoms may be used at least for some purposes. For example, butyl, amyl, iso-amyl, hexyl and heptyl alcohols may be employed. As to the heavier alcohols, lauryl, cetyl and the like may be employed, and these may sometimes be modified by inclusion of phenyl or kindred aromatic groups and the like, particularly as oil-solubility and stability may be improved.

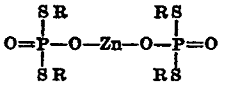
The various salts produced from the corresponding esters are probably mixtures of such types as the following, where R is the organic radical of the alcohol used and Zn represents any appropriate metal as well as zinc:



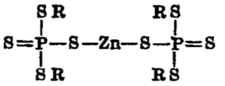




$$\mathrm{S{=}\underset{OR}{\overset{OR}{P}}{-}S{-}Zn{-}S{-}\underset{RO}{\overset{RO}{P}}{=}S}$$



$$\mathrm{O{=}\underset{SR}{\overset{SR}{P}}{-}O{-}Zn{-}O{-}\underset{RS}{\overset{RS}{P}}{=}O}$$



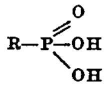
$$\mathrm{S{=}\underset{SR}{\overset{SR}{P}}{-}S{-}Zn{-}S{-}\underset{RS}{\overset{RS}{P}}{=}S}$$

These various metal salts of the thiophosphate esters described, that is, the reaction products of phosphorus pentasulfide with the indicated alcohols, are readily oil-soluble for the purpose of producing concentrates or final blends, and are employed in conjunction with the mentioned sulfonates and phenolic thio-ether salts ordinarily in the proportion of about 0.5% of the thiophosphate ester salt based on the total composition, or between about 0.1% and 1.5%.

Phosphorus acid salts

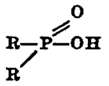
Another substituent for the phenol-thio-ether salts as a second additive to be employed with the sulfonates, is the salt produced from acids obtained by phosphorizing mineral oil in the lubricating range at temperatures around 200° F. to 800° F. whereby to cause phosphorus to enter the molecule, and then air blowing the phosphorized hydrocarbon at a temperature ranging around 150° F. to 250° F. to yield phosphorus acids, with which an appropriate metal salt may be reacted to obtain the desired metal phosphate.

Phosphonation.—The materials particularly used under this form of the invention are obtained from phosphorizing mineral lubricating oil fractions of so-called highly-paraffinic character or of high viscosity index. According to the best modern authorities on the constitution of mineral lubricating oil of this type, the molecules are not entirely aliphatic or chain compounds but are mixed or complex molecules containing aromatic or naphthenic rings protected by aliphatic or paraffinic side chains which may in themselves be straight chains or branched chains. Or such oils may be mixtures of molecules wherein aromatic or benzene rings are protected by aliphatic chains, and wherein naphthene rings are protected by aliphatic chains. Naphthenic type lubricating oils may be used, and also other hydrocarbons such as paraffin wax and the like as above mentioned. On phosphorizing these materials the phosphorus grouping apparently enters more readily to replace a hydrogen atom connected to one of the carbons of the aliphatic chain. This phosphorus grouping apparently may be connected either to an end carbon of the chain portion of the molecule or to an intermediate carbon of said chain portion, and the phosphorus grouping of the resultant phosphonic acids apparently has the arrangement:



$$\mathrm{R{-}\overset{\overset{O}{\|}}{P}{-}OH}\quad\mathrm{(OH)}$$

or



$$\mathrm{R{-}\overset{\overset{O}{\|}}{P}{-}OH}\quad\mathrm{(R)}$$

However, while there seems to be ample evidence that this is the structure, I nevertheless do not wish to be bound in all events by this theory. It is possible also that a portion of the total phosphorus may be attached to naphthenic rings, or to aromatic rings, when such are present.

Other hydrocarbons such as wax, gasoline, kerosene, gas oil, solvent extract from lubricating oil, coal tar distillate fractions, and hydrocarbon derivatives such as chlorinated or oxidized or otherwise modified hydrocarbons also may be similarly phosphorized with the production of similar useful compounds. Halogenation or oxidation may facilitate phosphonation or subsequent reactions. If oxidized starting materials are employed and they contain carboxylic acids, phosphonation should be complete enough to reduce all the acids before air-blowing, or the carboxylic acids may be removed before phosphonation as by selective solvent extraction, because the acids represent the objectionable type of material which it is sought to avoid in the present product.

In phosphorizing mineral lubricating oils, preparatory to oxidizing the phosphorized materials to yield the phosphonic acids, I have employed different procedures. According to one procedure the oil itself is heated to incipient "cracking" or decomposition and yellow phosphorus lumps are added with heating at appropriate temperatures such as up to about 600° F. until the phosphorizing reaction is complete. (Yellow phosphorus is the commercial term for white phosphorus which ordinarily contains small quantities of red phosphorus sufficient to give it a yellow color.) In this instance, a nitrogen, carbon dioxide or other inert atmosphere may be employed for safety purposes. According to another operation the mineral oil is first chlorinated to facilitate subsequent phosphorination. This may be done by bubbling a chlorine gas therethrough until the weight is increased by chlorine addition to an extent of perhaps 10% but preferably less, e. g. 2%. This material after a suitable washing is then phosphorized by heating for appropriate periods to incipient "cracking" or decomposition with addition of yellow phosphorus lumps until suitable phosphorination is produced. In this case lower temperatures such as a maximum of about 475° F. will suffice.

Oxidation.—Following phosphorization for an appropriate time, for example one to three hours, the charge is cooled to about 200° F. for example, and air then passed therethrough at a slow enough rate to prevent temperature rise much above 250° F. When the oxidation reaction ceases to promote temperature increase, further air-blowing may or may not be resorted to, but if continued for the purpose of insuring sufficient or further oxidation the air-blowing may be extended for a suitable time, for example about one hour, at a higher temperature, for example at about 300° F. In all cases, air-blowing should be carried out in a manner to attain sufficient oxidation of the phosphorus in the phosphonated oil, but should not be severe enough to oxidize more than minute quantities of the unphosphorized oil molecules. Formation of carboxylic acids by oxidation of the oil hydrocarbons is to be avoided as far as possible.

Saponification.—When suitable oxidation of the original phosphorized material has been accomplished to insure production of the desired phosphonic acids, the charge is then mingled with a suitable metal hydroxide, such as calcium hydroxide, in the presence of diluting quantities of water, and the batch heated at a temperature around or somewhat above the boiling point of water for a time to effect saponification or conversion of the phosphonic acids into the calcium soap or salt, which material after filtering and washing is ready for incorporation into an appropriate mineral lubriacting oil such as the high viscosity index or low viscosity index oils herein described, which oil in any given instance may or may not be of the same type as that which is phosphorized.

Examples of phosphonates.—One specific method for the preparation of calcium phosphonates as herein described was as follows:

A paraffinic oil which was a highly solvent-refined lubricating oil of SAE 20 grade having 89 V. I., was heated to 300° F. and four separate five per cent additions (20% total) by weight of yellow phosphorus were made while heating from 300° F. to 400° F. Heating was then continued until the temperature reached the boiling point of the oil (600° F. to 650° F.) and the temperature of the oil was held at that point for one-half to one hour. The oil was heated at all times in a nitrogen atmosphere. The oil was then cooled to 200° F. and a stream of air was passed through the oil at a rate slow enough to prevent temperature rise above 250° F. After air-blowing caused no further evolution of heat, the oil was cooled, washed free of water-soluble acids, and the calcium soap was prepared by heating the resulting phosphonic acid with calcium hydroxide at 300° F. for one-half hour. The batch was filtered at 300° F. for removal of solids. This resulted in about 4% soap in about 96% unmodified oil. The same method was used to produce a similar product from a Western naphthenic lubricating oil having a viscosity of 600 seconds Saybolt Universal at 100° F.

Another method which was employed is as follows:

Nine quarts of said SAE 20 grade oil having a V. I. of 89, were chlorinated at 150° F. to 170° F. by bubbling a rapid stream of chlorine through the oil. The process was continued until 2.0% of chlorine had been absorbed as judged by the increase in weight of the charge. The chlorinated oil was then heated and stirred with 2% of yellow phosphorus. The temperature was raised to 475° F. and held at that point for three hours. (In another instance the temperature was raised to about 625° F. which insured removal from the product of the trace of chlorine retained when a temperature of only 475° F. was used.) The total charge was cooled to 200° F. and a rapid stream of air passed through the oil until heat evolution ceased (approximately 15 minutes), the temperature being held in the meantime to a degree below 210° F. by use of cooling water. The charge was then filtered through a filter precoated with a fine diatomaceous earth. A small sample was then water washed, and the acid number found to be 8.05. The total charge was then again air-blown for one hour at 200° F. to 210° F. to insure complete oxidation of the phosphorus, after which the acid number of a small, water-washed sample was found to be 8.25. The whole charge was then washed with an equal volume of water, and the wash water drawn off.

The charge then heated and stirred for one hour with 200 grams of calcium hydroxide and 300 ml. of water at 200° F. The water was evaporated off by final heating to 230 F. The charge was cooled, 200 ml. of ethyl alcohol was added to insure complete saponification, and the heating and stirring was continued for one hour until the temperature reached 300° F. The total charge was then filtered as above.

The filtered oil tested as follows:

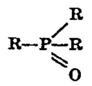
Soap number	8.4 mg. KOH/g. oil
Per cent phosphorus	0.25%
Sulfate ash	1.36%
Soap number, calculated from ash	11.4 mg. KOH/g. oil
Soap number, calculated from phosphorus	9.0 mg. KOH/g. oil

This signifies about 10% soap in about 90% of unmodified oil.

This same process may be used to treat naphthenic base oils as above described to produce corresponding products. Also all these procedures are appropriate for the treatment of the other hydrocarbons mentioned to yield similar useful products.

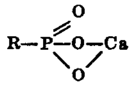
The amount of yellow phosphorus has been varied from about 0.5% to about 20%, but most desirable conditions apparently have been obtained when using phosphorus concentrations between about 2% and 10% based upon the original charge. Phosphonation has been effected at temperatures as high as 900° F. with contact time as low as about two minutes. Practical conditions appear to be to phosphonate in a range between about 500° F. to 700° F. at a gauge pressure of about 50 lb./sq. in. for at least two minutes and preferably about five minutes or somewhat more.

As to the nature of the phosphorus compounds formed there is evidence that phosphonic acids are produced having a molecular weight in the general range of 400 to 500. Aparently traces of compounds of the type

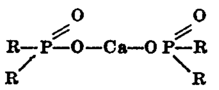


are formed. These may be very desirable oxidation inhibitors but on the other hand they may be objectionable in the combustion chamber where lead gasolines are used due to the tendencies to form P_2O_5 and thereby form objectionable lead phosphates. It is to be noted that most of the P_2O_5 formed in the phosphorizing operation will have been blown out and recovered in the oxidizing stage. The remainder is removed by filtration as the insoluble salt after saponification.

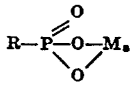
The calcium soaps produced apparently are of the form



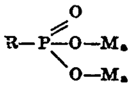
and



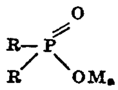
Thus the general soap structures as related to any appropriate metal or other base will possess one or more of the following forms:



or

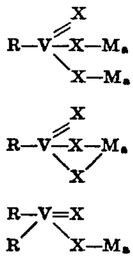


or



where R is any hydrocarbon radical or derivative thereof, and M is a metal or organic base material having alkaline properties, *a* being an integer or fraction according to the valence of the metal or organic base.

Similarly, sulfur or selenium may be substituted for oxygen. Also arsenic may be substituted for phosphorus for many uses, suitable proccesses being employed to produce the acids and their soaps. Thus, the soaps or salts used are of the following types:



where R is any hydrocarbon radical or derivative thereof, V is arsenic or phosphorus, X is oxygen, sulfur or selenium, M is a metal or organic base material having alkaline properties, and *a* represents a fraction or an integer according to the valence of M. The invention also extends to these features.

The arsenic, sulfur and selenium compounds mentioned may be more or less readily prepared. Arsenic compounds, e. g. arsenonic acid, may be made in much the same way as the phosphonic acids by heating the hydrocarbon with arsenic in corresponding temperature ranges up to perhaps 700° F., and the arsenated hydrocarbon then blown as described for the phosphonated hydrocarbon. The soap will then be prepared as previously described. Instead of blowing to form the acidic materials by oxidation, thio-acids or seleno-acids may be made by mixing a calculated amount of sulfur or selenium with the phosphonated or arsenated hydrocarbon and heating below temperatures at which the arsenic or selenium would replace hydrogen in the hydrocarbon molecule. Such a temperature would be for example about 300° F. or below but high enough for the reaction to proceed.

Final product

As in the case of the thiophosphates previously described, the described phosphorus acid salts may be used as a third constituent along with the phenol-thio-ether salts in addition to the sulfonates as the detergent constituent.

In blending oils according to the present invention, it has been previously indicated that it is necessary merely to add the salts or described oil concentrates to an appropriate base lubricating oil in proportion to yield the desired content of each of the indicated salts or soaps. In other words, around 1% or a little more of the sulfonate is used, and around 1% or a little less of the other constituent or constituents is used. Thus, for practical uses about 1.2% of the sulfonate is desirably employed in conjunction with around three-fourths of one percent (0.75%) of the phenol-thio-ether salt or one of the phosphorus compounds, although perhaps around 0.4% or 0.5% of any of the phosphorus compounds or of the phenol-thio-ether salt is adequate. The over-all ranges probably run around 0.2% or 0.3% to 2% or 3% of each of the additives employed. The described additives are all amply dispersible in lubricating oils of high viscosity index, i. e. highly paraffinic characteristics, and adequately adapt such oils to uses in internal combustion engines of the severe service type. Also these additives are equally usable in lower V. I. oils, e. g. naphthenic oils and oils of mixed base type. With respect to the percentage ranges of the various compounds, other than as just stated, other ranges indicated elsewhere herein also may be employed where advantageous.

Metals.—Regarding the metal constituents of the oil-soluble salts usable as the various types of additives described for the various final products herein disclosed, it appears that a wider range of metals may be employed in the phosphorus-containing additives than in the sulfonates or in the described phenolics.

Thus, it appears that iron, lead and copper sulfonates are especially objectionable both because their sulfonates act as catalysts for oxidation or the production of corrosive conditions and because the other described types of salts of these metals tend to produce similar effects. On the other hand, where other metals sometimes appear to offer some objection in sulfonates, e. g. thioether salts described. These phenomena are employed in the various organic phosphorus-containing compounds described, and in conjunction with acceptable sulfonates such as calcium sulfonate, these other metals in the phosphorus-containing compounds are not necessarily objectionable. Again, it appears that those metals which are objectionable in sulfonates, are likewise objectionable if they appear in the phenol thioether salts described. These phenomena are possibly explainable by the theory that the metal constituent is sufficiently tightly held to the acidic group of the phosphorus compound so that the stronger acid constituent of the sulfonate has no effect toward releasing the metal of the phosphorus compound. On the other hand, in view of the fact that the sulfonic constituent represents much stronger acids than are represented by the phenol thioether compounds, if one of the objectionable metals is present in the phenol thioether salt, it is possibly partly released therefrom and an exchange of metals between the sulfonates and the phenolics results, thereby producing objectionable metal sulfonate. In general, it may be said that most metals except iron, lead and copper, which will produce oil-soluble forms of the phosphorus compounds described, may be used in said phosphorus compounds. It also appears that, in producing the phenolic salts described, those metals should be used whose sulfonates are not objectionable. Also, the oil base stock is a factor in the oxidation, and the salt of a metal which is catalytic in one oil is not necessarily sufficiently catalytic in another oil to be objectionable. Generally speaking, the more paraffinic oils require greater care in selection of metals for the additive salts. This applies, for example, to oils in the 80 V. I. to 100 V. I. range.

It may be stated that for all purposes the calcium salts of all of the various additives mentioned are acceptable and probably preferable. There is good evidence that the barium and strontium salts are likewise acceptable. For the most part, salts of the other alkaline earth metal, magnesium seem to be acceptable. Again zinc salts seem to be good for all of the additives, and appear to be very desirable for the phosphorus-containing compounds described.

Thus, the invention lies in oils containing oil-soluble sulfonates and one or more of the other types of constituents described, wherein the oils are free from salts and other constituents, which would act in the composition to impart or to induce corrosive conditions. In a more specific aspect the invention lies in lubricating oils containing minor proportions of calcium salts of sulfonic acids, and calcium salts of one or more of the other constituents; that is, a calcium salt of one of the phosphorus-containing compounds and/or a calcium salt of the phenolic thioethers described, the oils being free from any added constituent which would promote corrosive conditions during use. In a somewhat broader aspect, the invention lies in the use of oil-soluble sulfonates with phenolic thioether salts of metals whose sulfonates are free from the characteristic of producing corrosive conditions, with or without similar metal salts of the phosphorus compound described. The invention also resides in the use in lubricating oils of oil-soluble sulfonates of metals whose sulfonates do not promote corrosive conditions in use, with any of the phosphorus-containing compounds described containing any metal which renders the salt soluble, other than iron, lead or copper, or more particularly containing only metals whose sulfonates are not objectionable.

More specifically, alkaline earth metal sulfonates and phenolics are used with alkaline earth metals or zinc salts of the phosphorus compounds described, or with the described phosphorous salts of any of the metals whose sulfonates are not objectionable. This includes, in addition to the calcium, strontium and barium salts, the zinc salts and probably the magnesium salts of the phenolics as well as of the sulfonates and of the phosphorus-containing compounds. Again, where conditions are not so severe as in the case of Diesel engines and high out-put aviation engines, it may be possible to use phenolic thioether salts of metals whose sulfonates are objectionable. This appears to be true especially where one of the mentioned types of phosphorus compounds is employed as a third additive. For instance, it has been found that where very small amounts of objectionable sulfonates (such as iron sulfonates) appear in calcium sulfonates used in the presence of the mentioned types of phosphorus-containing salts, the objectionable characteristics of the iron sulfonate or other objectionable sulfonate have been sufficiently overcome for use in lubricating Diesel engines.

Thus, this invention resides also in the employment, along with acceptable sulfonates and acceptable phenolics as described, of salts of the described types of phosphorus compounds as a third constituent. And, the invention also resides in lubricating oils containing described acceptable oil-soluble sulfonates with described oil-soluble metal phenolics and/or described oil-soluble metal-containing phosphorus compounds, where the oils are free from salts of metals which would produce corrosive conditions in the oils when in use in any given engine.

These combinations of described additives have produced lubricating oils of high V. I. type which have stood up under severe service conditions far better than any other combinations of additives. Resin and varnish formation and consequent ring sticking have been well controlled, and corrosion has been so well overcome that acid numbers in severe 500 hour tests have not exceeded about 0.5.

Various modifications of this invention and within the scope of the appended claims will occur to the skilled lubricating chemist.

I claim:

1. A lubricating oil comprising mineral lubricating oil and a minor proportion in the order of from about 0.5% to about 3% of oil-soluble mixed green acid soaps and mahogany acid soaps obtained from the sulfonation of a mineral lubricating oil followed by neutralization and formation of the oil-soluble sulfonates and separation of all solids the composition containing appreciable amounts of green acid soaps which are solubilized by the mahogany acid soaps present.

2. An oil according to claim 1 containing a minor proportion of an anti-corrosion agent of the class consisting of oil-soluble metal salts of alkylated phenol-thio-ethers, oil-soluble metal thio-phosphates of aliphatic alcohols, and oil-soluble metal salts of phosphonic acids produced by phosphorizing mineral oil fractions and air blowing said phosphonated fractions.

3. A lubricating oil for severe service combustion engines comprising mineral lubricating oil, and minor proportions within the range of about 0.2% to about 3% of each of oil-soluble mineral oil sulfonates free from corrosion inducing salts, and an anti-corrosion agent of the class consisting of oil-soluble metal salts of alkylated phenol-thio-ethers, oil-soluble metal thiophosphates from aliphatic alcohols, and oil-soluble metal salts of phosphonic acids produced from mineral

oil fractions the sulfonates being mixed green acid soaps and mahogany acid soaps, the composition containing appreciable amounts of green acid soaps which are solubilized by the mahogany acid soaps present.

4. An oil according to claim 3 wherein the sulfonates are calcium sulfonates.

5. An oil according to claim 3 wherein the sulfonates are mixed green acid and mahogany acid sulfonates obtained by sulfonating a mineral oil fraction and neutralizing the mixed sulfonic acids in situ and obtaining in situ the desired oil-soluble mixed sulfonates, and separating the solids.

6. A lubricating oil comprising mineral lubricating oil and a minor proportion of oil soluble mixed green acid soaps and mahogany acid soaps, the composition containing appreciable amounts of green acid soaps which are solubilized by the mahogany acid soaps present.

7. An oil according to claim 1 wherein the sulfonates are calcium sulfonates.

8. An oil according to claim 6 wherein the sulfonates are calcium sulfonates.

9. A lubricating oil comprising mineral lubricating oil and a minor proportion of oil soluble mixed green acid soaps and mahogany acid soaps, free from corrosion inducing salts, the composition containing appreciable amounts of green acid soaps which are solubilized by the mahogany acid soaps present.

10. An oil according to claim 6 also containing a minor proportion of an anti-corrosion agent.

11. An oil according to claim 6 substantially free from corrosion inducing salts and also containing a minor proportion of an anti-corrosion agent which is an oil-soluble metal salt of an alkylated phenol thio-ether.

12. An oil according to claim 6 free from corrosion producing constituents and also containing a minor proportion of an anti-corrosion agent which is an oil-soluble thiophosphate.

13. An oil according to claim 6 which is substantially free of corrosition producing salts and which also contains a minor proportion of an anti-corrosion agent which is an oil-soluble compound produced by phosphorizing a mineral oil fraction and air blowing the phosphorized material to yield phosphonic acids.

14. An oil according to claim 6 which is substantially free of corrosion producing salts and which also contains a minor proportion of an anti-corrosion agent which is an oil-soluble metal salt produced by the reaction of phosphorus pentasulfide with an aliphatic alcohol.

15. An oil according to claim 6 which is substantially free of corrosion producing salts and which also contains a minor proportion of an anti-corrosion agent which is an oil-soluble salt of the reaction product of phosphorus pentasulfide with octyl alcohol.

16. An oil according to claim 6 which is substantially free of corrosition producing salts and which also contains a minor proportion of an anti-corrosition agent which is an oil-soluble metal salt of the reaction product of methyl cyclohexanol with phosphorus pentasulfide.

17. An oil according to claim 6 which is substantially free of corrosion producing salts and which also contains a minor proportion of an anti-corrosion agent which is a metal salt of the reaction product of an aliphatic alcohol with phosphorus pentasulfide.

18. An oil according to claim 6 which is substantially free of corrosion producing salts and which contains a minor proportion of an anticorrosion agent of the class consisting of oil-soluble metal salts of alkylated phenol-thioethers, oil-soluble metal thiophosphates of aliphatic alcohols, and oil-soluble metal salts of phosphonic acids produced by phosphorizing mineral oil fractions and air blowing said phosphonated fractions.

19. An oil according to class 6 which is substantially free from corrosition producing salts and which also contains minor proportions of an anti-corrosion agent of the class consisting of oil-soluble metal salts of alkylated phenol-thioethers, oil-soluble metal thiophosphates from aliphatic alcohols, and oil-soluble metal salts of phosphonic acids produced from mineral oil fractions.

20. An oil according to claim 6 which is substantially free of corrosion producing salts and which also contains a minor proportion of an anticorrosion agent comprising both an oil-soluble metal salt of an alkylated polyphenol sulfide and an oil-soluble metal salt of an organic phosphorus-containing acid.

EARL AMOTT.

CERTIFICATE OF CORRECTION.

Patent No. 2,378,820.

June 19, 1945.

EARL AMOTT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 11, for "issigned" read --assigned--; line 68, for "150° C." read --150° F.--; and second column, line 59, for "acceptacle" read --acceptable--; page 4, first column, line 66, after "sulfur" strike out the comma and insert instead a period; and second column, line 42, for "powder" read --power--; page 7, first column, line 45, for "lubriacting" read --lubricating--; page 8, first column, line 1, for "Aparently" read --Apparently--; and second column, line 71, strike out "thioether salts described. These phenomena" and insert instead --tin or aluminum, where these other metals--; page 10, second column, lines 12, 14 and 34, for "corrosition" read --corrosion--; same page and column, line 33, for "class" read --claim--; 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 23rd day of October, A. D. 1945.

Leslie Frazer

(Seal)

First Assistant Commissioner of Patents.

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