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DIESEL ENGINE LUBRICATING OIL

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24 Claims. (Cl. 252—48)

This invention relates to mineral lubricating oils which have been modified by the addition of various constituents to impart to them special characteristics adapting them for severe service use over considerable periods of time in engines of the type represented by Diesel engines, high output aviation engines and the like, the adequacy of the modified oils being established by their satisfactorily withstanding rather drastic laboratory engine tests requiring, for example, four hundred or five hundred hours of use in the particular type of engine for which the oil is intended.

It is well known that severe service engines of the indicated types operate at high temperatures and tend to cause the formation of resinous and varnish-like deposits within the engine which would tend to cause ring and valve sticking. It is also well known that there is a tendency for many types of additive compounds to develop in use conditions in the oil which are corrosive to certain types of bearings, especially the highly corrosion-sensitive types represented by cadmium-silver and copper-lead bearings, or to exert catalytic effects tending toward the development of acidic compounds produced by oxidation in the oil during use, which compounds would attack such corrosion-sensitive bearings.

By the present invention all of these objectionable difficulties are overcome. The present invention resides in the discovery of the unexpected effects produced in a mineral lubricating oil by the employment as addition agents of relatively small proportions of each of oil-soluble salts of petroleum sulphonic acids, oil-soluble salts of alkyl-substituted phenol sulfides or alkylated phenolic thio ethers, and the reaction complex produced therewith by the introduction of correspondingly smaller proportions of alizarin. A possible substitute for alizarin, at least for some uses, is quinizarin. This also is true to some extent of anthragallol. The alizarin appears to form adsorption complexes with the metallic constituent of a portion of one or both of said salts (most likely both of them) whereby an intimate and stable dispersion of the otherwise relatively oil-insoluble alizarin is obtained, and possibly with an incidental release of some of the free acidic material of the thio-ether salt. That there is a definite chemical change in the alizarin when introduced into the said oil solutions of sulfonate and thio-ether salt, is evidenced by the following facts. Alizarin, although sparingly soluble in lubricating oils, yields a yellow to orange oil solution. When added to an oil solution of the sulfonate, a deep red color develops. This characteristic deep red changes to a blue to purple or "grapejuice" color when the oil solution of the alizarin-sulfonate complex is added to an oil solution of the thio-ether salt. Development of a full purple color possibly depends upon the particular base oil; but a kindred color nevertheless develops which is indicative of the change.

A phenolic thio-ether salt and the sulfonate mentioned, both of which will commonly be referred to herein as "soaps," are freely soluble in the mineral lubricating oil employed, or are at least in a permanent state of complete dispersion which is herein considered to constitute them "oil-soluble" in the small proportions of around 1% to 2% employed. Similarly the alizarin complex resulting from the combination also is "oil-soluble" in a similar sense and remains in a permanent state of dispersion in the proportions employed which ordinarily are between about 0.05% and about 0.2%. It has been found that with this combination of constituents at least two important and unexpected results are obtained. In the first place the alizarin complex remains permanently dispersed or solubilized in the presence of the two soaps, and also in the presence of the sulfonate alone. Also, tendencies of the modified oil to develop conditions corrosive especially to the mentioned highly corrosion-sensitive metal bearing where the two soaps are used alone, are unexpectedly overcome by reason of the presence of the alizarin complex obtained by the addition of alizarin. At the same time the characteristic functions of the sulfonate and the mentioned phenolate are not diminished.

The sulfonate is employed as a "detergent" material and is so termed because of the fact that it acts to prevent the deposition of the resinous and varnish-like materials mentioned, or to effect their removal if once deposited. The phenolic salts or soaps described are considered as "anti-corrosion" agents, because of the fact that they appear to combine with the highly corrosive carboxylic acids which are produced by oxidation of oil during use in the engine and attack the mentioned highly corrosion-sensitive metallic bearings. The weakly acidic phenolics released from their salts by reason of the combination of their metallic constituent with the corrosive acids are not corrosive to said bearings, and are formed instead of the corrosive acids. It is possible also that these weakly acidic phenolics possess some corrosion inhibiting effect, but if

this be true it is nevertheless inadequate to meet the requirements of the very heavy use to which these oils are put in many Diesel engines and the like. On the other hand, when the alizarin complex is obtained in the modified oil, sufficiently complete inhibition of catalysis of corrosive conditions or other production of corrosive conditions is obtained. It does not appear that this inhibiting condition is a mere neutralization of corrosive materials produced, as appears to be primarily the case with the phenolic salts described, but it appears that there is an actual inhibition of conditions by means of the alizarin complex. This observation and theory are not to be taken as binding upon the applicant, but are believed to represent the true conditions.

In practicing the present invention, it is intended primarily that the described addition agents shall be employed in the modern so-called highly "paraffinic" mineral lubricating oils which are produced by the more modern refining methods such as heavy solvent treatments and the like which yield products of high viscosity index. For example, a western lubricating oil produced from a waxy stock by propane dewaxing and heavy selective solvent treatment to yield a viscosity index of about ninety or above has been successfully used, and is the type of oil now preferred for the practice of the present invention. However, the invention is not limited to these high viscosity index oils but may be extended to the more naphthenic types such as oils having, for example, viscosity indexes as low as 20 V. I. and ranging up through 45, 60 and 80 V. I.

Terms employed herein possibly will be better understood by reference to the following definitions.

The term "Viscosity index" (V. I.) is well understood in the art and is defined in Chemical and Metallurgical Engineering, vol. 36, No. 10, pages 618–619 (1929). It is an indication of the type of oil, whether more or less paraffinic or naphthenic, a paraffin base oil being assigned 100 V. I., and certain Gulf Coast naphthene base oils being assigned zero V. I., so that mixed base oils have intermediate values. Thus, the high V. I. oils are the so-called highly "paraffinic" oils, such as Pennsylvania oils and those highly refined with selective solvents such as phenol, aniline, liquid sulfur dioxide, nitro-benzene, furfural, dichlor-ethyl ether and the like.

The term "soap," which is sometimes herein used to indicate the salts of this invention, indicates those metal salts of high molecular weight acidic materials possessing at least ten carbon atoms per molecule (thereby imparting good dispersibility or "solubility" in the mineral lubricating oil) which salts are sufficiently oil-dispersible or "soluble," as here required.

By the term "detergent" is meant the property of removing, or materially retarding the accumulation of resinous, varnish-like and carbonaceous materials which otherwise tend to deposit upon or around piston rings or valve stems and cause sticking thereof.

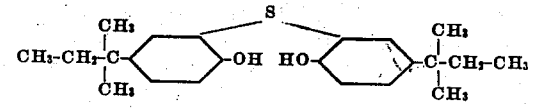
The term "sulfonates" means those oil-soluble metal soaps which are produced from the well-known sulfonic acids obtained by acid treatment of petroleum and known as "mahogany acids," and have high detergent value, such as sodium, potassium, calcium, barium, strontium and magnesium salts, and some heavy metal salts such as copper, zinc, aluminum, lead, nickel, cobalt, manganese, chromium, tin and iron, especially the alkaline earth metal soaps. The term also includes other organic sulfonates from other sources than petroleum as hereinafter mentioned.

When the term "phenolic" is used in referring to the alkyl-substituted thio-ethers mentioned, it is intended to differentiate from any phenolic aspect which may be attached to the constitution of alizarin, or to its possible substitutes quinizarin and anthragallol, in that metal phenates or salts of said phenolics are themselves oil-soluble or dispersible in oil without the necessity for other solubilizing agents; whereas the phenate-type metallic salts of alizarin, quinizarin and anthragallol are oil-insoluble. These are to be distinguished from oil-soluble adsorption complexes formed by addition of alizarin to oil solutions of the "oil-soluble" soaps described. In referring to said phenolic sulfides or thio ethers, the sulfur constituent disposed between the phenolic rings may consist of one or more sulfur atoms. The sulfur content of these sulfides or thio ethers will be such as to correspond generally with approximately 10% of the disulfides or more or less, e. g. possibly between 5% and 50% disulfides. Instead of disposing the plural sulfurs between two rings, the whole molecule may, at least in part, represent a condensation product containing three or more rings with one or more sulfurs between each pair of rings.

In preparing soaps or salts of these phenol sulfides for the purpose of dissolving them in the mentioned lubricating oils, various metals may be employed. These will include lithium, sodium, potassium, copper, aluminum, zinc, manganese, magnesium, calcium, barium, strontium, lead, nickel, cobalt, chromium, tin and iron. I particularly prefer the alkaline earth metal salts, namely calcium, barium, magnesium and strontium salts. The aluminum and zinc salts are also of considerable value because of their greater solubility and the possibly lower catalytic activity.

The oil-soluble metal salts such as the calcium salts of the phenolic compounds are employed in the lubricating oil in amounts up to about 3%, but in amounts less than that required to cause an undesirable thickening of the oil, the optimum apparently being from about 0.5% to 2.0%.

A specific usable phenolic material of which I have produced the calcium salt is a para-tertiary-amyl phenol sulfide which may be represented by the unit formula:



which may be extended by the addition of more alkylated phenol groups connected by additional sulfur atoms, to impart adequate oil-solubility.

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. This material, apparently, is in general composed of mixed poly-alkyl phenol sulfides, that is, poly-alkyl-substituted hydroxy phenyl thio-ethers containing, for example, a thio-ether of amyl or butyl phenol which may be designated for example as bis (2-hydroxy-4-butyl phenyl) sulfide. This commercial product apparently contains

various materials of the following general unit formulas:

$$R(C_6H_3OH)S(C_6H_3OH)R$$

which is extended by additional sulfur atoms and additional phenol groups, thus:

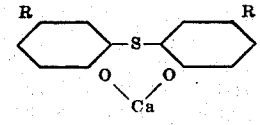
$$R(C_6H_3OH)S(C_6H_2OH)R.S(C_6H_3OH)R.S \ldots .$$

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 mono-sulfides; R is an alkyl group preferably containing four or five carbon atoms (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; and other R's may replace one or more of the remaining hydrogens in one or more of the benzene nuclei. The material may contain higher polymers such as indicated in the second formula above.

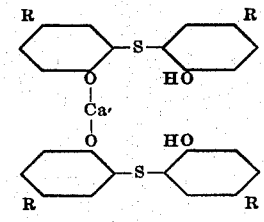
The metal salts of the above described phenolic materials may properly be considered soaps because of an apparent detergent action. When about 1% or between about 0.5% and about 2.0% or 3.0% of such a suitable oil-soluble soap such as the calcium soap is dissolved in mineral lubricating oil, it has the combined effect of imparting to the mineral lubricating oil where intended for severe service internal combustion engines, some required detergency characteristics and at the same time of acting apparently as a neutralizing agent or, at least in some manner, as an agent for preventing the corrosion of bearings such as those of cadmium-silver and copper-lead alloys.

In practicing this phase of the invention commercially, the soaps of suitable phenolic compounds such as the calcium soaps of dibutyl or other alkyl or mixtures 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 an approximately equal quantity or even greater quantity of a suitable lubricating oil such as a naphthenic base mineral oil having good solvent properties for the phenolic material and for the salts to be produced. This oil 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 only to 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 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 (i. e. 20% concentrate) having good solvent power for the soap. Much higher concentrations of the phenol sulfides are too viscous for convenient handling. 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 operations yield concentrates consisting of soap in oil.

These salts are readily soluble in lubricating oils in the required proportions and yield alkaline solutions. Representative salts thus produced appear to be represented by the following structural unit formulas:



and



wherein R represents one or more substituted alkyl groups on each ring to impart good oil-solubility as previously indicated.

The oil-soluble metal sulfonate to be employed in conjunction with the phenolic soap and the alizarin material may be a salt of the so-called "mahogany acids." The sulfonate preferably is in the form of a calcium salt, although the other alkaline earth metal salts or soaps, namely the barium, strontium and magnesium soaps may be employed. Also the alkali metal soaps are often useful, and sometimes the heavier metal soaps such as the soaps of zinc, aluminum, copper, lead, nickel, cobalt, manganese, chromium and iron.

The sulfonated acids employed to prepare the sulfonate additive of this invention may be those synthetically produced, as by du Pont of Wilmington, Delaware, and obtainable on the open market, or those obtained from the treatment of petroleum fractions and 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. These salts, or the potassium salts, sometimes may themselves be used, at least in some combinations.

In order to obtain the calcium sulfonate from this mahogany acid soap or from the sodium soaps of other sulfonates, 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 to 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 is 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, other inorganic salts including excess calcium chloride will have crystallized and been largely removed along with the sodium chloride.

In one instance 900 grams of the sodium salts of oil-soluble petroleum sulfonic acids containing 40% of mineral oil 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 about 300° F., the batch was filtered.

The resultant material was an oil concentrate containing about 0.05% water and about 20% of oil-soluble calcium petroleum-sulfonic-acid soap, which otherwise may be referred to here as a calicum mahogany acid soap, or calcium mahogany soap or calcium sulfonate. This concentrate is liquid at normal temperatures, is substantially free from 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 two-soap combination with the alizarin material, sufficient of said sulfonate 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 (preferably distillates) of high viscosity index, as well as in naphthenic base oils, in proportions larger than required in the final composition. The concentrate may be prepared with a high viscosity index oil, e. g. 90 V. I., or a low V. I. oil.

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 the said materials in the order of from perhaps 0.5% to 3%. In actual practice there is commonly employed about 1% of each of the phenolic soap and the sulfonate. In addition there is added to the oil from about 0.05% to 0.2%, or ordinarily about 0.1% of alizarin. The alizarin may be added to the oil, wherein it forms the mentioned complex, as such, or may be added in proper proportions to the sulfonate concentrate and the resulting alizarin-sulfonate complex concentrate then added to the oil already containing the proper proportion of phenolic materials concentrate in amount sufficient to supply the required percentage of alizarin and sulfonate, or the proper amount of the phenolic materials concentrate may be added to the oil subsequent to the addition of the proper proportion of the alizarin-sulfonate complex concentrate.

On the other hand the various concentrates and the alizarin in whatever form it is to be employed may all be combined to form a unitary concentrate of appropriate proportions which can then be added to the oil and solution effected by sufficient agitation accompanied by heating if necessary.

When the alizarin is added to the oil or concentrate containing the sulfonate material a red color results from the formation of a stable dispersion of the alizarin-sulfonate complex. When this mixture is admixed with the phenolic materials concentrate the composition promptly takes on a magenta to purple color, the shade of color varying with the nature of the oil present, and the characteristic red of the alizarin-sulfonate complex disappears. Final products compounded with the higher viscosity index oils tend to give a purer purple color than do those compounded with naphthenic or aromatic type oils.

In employing the methods of production described a small water content necessarily exists. Normally this will amount to about 0.015% of water in the final product or perhaps 0.15% of water in one or more of the various concentrates. The water range in the final product apparently may be between about 0.005% and 0.02%. There is some indication that somewhat greater proportions of water may be employed, for example, up to as high as 0.2% may be employed without detriment, and in fact with some possible benefit toward further activating the detergent sulfonate and at the same time improving the bearing corrosion inhibiting properties of the oil. In any event such percentages of water do not appear to be objectionable.

In addition to having the indicated small proportions of the mentioned ingredients present as apparently desirable constituents, it also appears to be desirable to have present a small amount of the free phenol thio-ether as distinguished from the salt thereof, for example, about

0.005% to 0.1% or around .05% based on the final product or around 5% based upon the thio-ether soap in which it usually appears. If the presence of this free phenol thio-ether is necessary or desirable, it does not appear that it must be initially present in the thio-ether soap but may be added separately as desired.

The proportions above are not critical, as indicated by the fact that a good oil has been prepared initially containing 1.2% of calcium sulfonate, about 0.7% of the calcium salt of diamyl di-phenol sulfide, and about 0.1% of alizarin.

As has been indicated, high V. I. oils are preferred, inasmuch as especially good products have been obtained with highly solvent refined paraffinic type oils in the range of 85 to 95 V. I. But naphthenic base oils, i. e. low V. I. oils, have been found satisfactory, for example, oils as low as 20 V. I.

In addition to using phenol thio-ethers, it will be possible also to substitute selenium or tellurium for the sulfur at least for some uses. Similarly quinizarin and anthragallol may be ordinarily employed with substantially equivalent results as a substitute for alizarin.

In using anthragallol, a reddish brown color develops when the anthragallol-sulfonate complex forms upon addition of the anthragallol to the sulfonate concentrate, whereas only a slight darkening results when anthragallol is added to the lubricating oil alone. When this anthragallol-modified soap concentrate is added to the phenol thio-ether soap concentrate or to an oil containing the phenol thio-ether soap, the color changes to a bluish color with a faint tinge of red or brown, as distinguished from a definite violet or purple. Thus, the color changes in the case of anthragallol and alizarin indicate the formation of complexes with the sulfonate through the double-bonded oxygen and the hydroxyl in the 1-position which colors are modified by the formation of additional complexes with the remaining unbound hydroxyl, as indicated by a color change, when the phenolic thio-ether salt is added.

When quinizarin is dissolved in a lubricating oil, particularly in a highly solvent-refined highly paraffinic type oil, the oil solution has a characteristic orange color or yellow with a red tinge. When quinizarin is introduced into an oil solution of a described metal sulfonate, or a sulfonate concentrate, the red tinge deepens as compared with the orange of the quinizarin solution. When the quinizarin-modified sulfonate concentrate or oil is added to an oil or concentrate containing the phenolic thio-ether soap, the red-orange color changes to a deep or brilliant red, or intense cherry red, with perhaps a purple tinge.

These colors are developed when using a highly solvent refined highly "paraffinic" type mineral lubricating oil. There are variations in these colors sometimes when other base oils are used.

The foregoing discussion has related to that invention which resides in combinations of the oil-soluble soaps of the sulfonic acids and the alkylated phenolic thio-ethers with alizarin, quinizarin, or anthragallol. However, another phase of invention resides in the use of other substances which are useful for the purpose intended and function similarly.

Thus, any detergent soap may be used where the sulfonate was used above, such as soaps of the phosphonic or phosphinic acids, or of acid phosphorous or phosphoric esters, where the soap is an "oil-soluble" soap and forms stably dispersed adsorption complexes with the class of substances represented by alizarin, quinizarin and anthragallol. This probably applies most particularly to the non-carboxylic acid soaps including those above mentioned, and naphthenic acid or rosin or modified rosin soaps; but it is not necessarily limited thereto, because carboxylic acid soaps may sometimes be employed, such as oil-soluble high molecular weight or saponifiable fatty acid or modified fatty acid soaps including stearates, chlorinated stearates, phenyl stearates, salts of synthetic acids produced by the oxidation of highly paraffinic petroleum fractions, and the like such as are known for use in this type of oil. This may be true even though the complexes may be insoluble in the oil, so long as they can be kept in suspension in use, as by agitation in the engine and/or in partial solution under the influence of the heat in Diesel engines and other internal combustion engines, or otherwise.

Similarly, the soaps of the alkylated phenolic thio-ethers may be replaced by other oil-soluble anti-corrosion substances, or "reserve-alkalinity" substances, such as the oil-soluble metal alkoxides or alcoholates of which examples are calcium octylate and calcium laurylate, or the oil-soluble salts of formaldehyde-phenol (e. g. amyl phenol) condensation products, other substituted phenols and thio-phenols (both monohydroxy and polyhydroxy phenols), heterocyclic phenols, and other non-carboxylic alkalinity-reserve salts having low ionization constants.

By the term "reserve alkalinity," or "anti-corrosion," it is meant to signify the property of the metal compound to combine with strong organic acids, developed during use of the oil in internal combustion engines, whereby to neutralize excess acidity so developed. The mentioned phenol thio-ether soaps and materials of low ionization constants, as mentioned, have this property.

For the purpose of preparing salts of these various materials, the same metals may be employed as previously mentioned in connection with sulfonates and the substituted phenol thio-ether salts or soaps.

Also a larger number of substances may be used in place of the alizarin, quinizarin, and anthragallol. In describing the complexes formed between the soaps discussed above and alizarin, quinizarin and anthragallol, they were referred to as adsorption complexes. These complexes also may be designated as "coordination complexes" or compounds, and in general any organic compound having the structural characteristics necessary to permit it to form said coordination complexes with a metal, may be substituted for the alizarin, quinizarin or anthragallol for the purpose of this invention.

The structural characteristics necessary in such an organic compound to enable it to form "coordination complexes" with a metal are two in number. First, it must contain a definite acidic atomic grouping such as the sulfonic, sulfinic, phosphorous, phosphoric, phosphonic, phosphinic, and carboxylic acid groups, and the hydroxyl, sulf-hydryl, oxime, and imine groups, in which the hydrogen is replaceable by a metal; and second, its remaining structure must be such that the secondary valences of the metal contained as a neutral part in the molecule can

be saturated, that is, the metal can form a coordinate linkage with some other atom in the molecule.

For example, the molecules of alizarin, quinizarin and anthragallol contain acidic hydroxyl groupings in the 1-position, and the secondary valences of metals replacing the hydrogen in these groupings may be saturated by the double bonded oxygen also present in each molecule. As further examples, organic dioximes in which the two oxime groups are on adjacent carbon atoms which are connected by a single bond, or organic oximes also containing a hydroxyl group in the molecule, may form coordination complexes or adsorption complexes with metals, because such compounds possess both the necessary acidic atomic grouping and a grouping capable of saturating the secondary valences of the metal. In general any organic compound the molecules of which contain a definite acidic atomic grouping such as those given above, and at the same time contains an atom such as oxygen, sulfur or nitrogen which can function as an electron donor in the formation of the coordinate linkage, and thereby act to satisfy secondary valences of the metal, will form coordination complexes as required by the present invention. Thus, in addition to the specific compounds above mentioned, other specific examples are naphtha- and anthra-quinone sulfonic acids. Thus, an anthra-quinone sulfonic acid would act as an alizarin substitute to form a coordination complex with a calcium sulfonate, such as the described calcium salt of sulfonic acids obtained from petroleum. Another example is 2-phenyl-6-sulphonic acid-1,7-phenanthraline.

It is, therefore, another feature of this invention to employ in oil solution a combination of an "oil-soluble" "detergent" type soap capable of forming adsorption complexes or coordination complexes stable in oil solution or dispersion, with organic compounds or substances selected from the class consisting of the substituted quinones, naphthaquinones, anthraquinones, including alizarin, quinizarin and anthragallol, dioximes, oximes, imines, phenols, and the like above described, and the modified sulfonic, sulfinic, phosphorous, phosphoric, phosphonic, phosphinic and carboxylic acids mentioned. It is also a feature of the invention to use these materials with the reserve alkalinity-agents as described. It is also a part of the invention to use these organic materials with both the detergent soaps and the reserve-alkalinity agents.

I claim:

1. A composition of matter comprising a mineral lubricating oil containing a minor proportion of an oil-soluble metal sulfonate, and a minor proportion of an oil-soluble metal salt of an alkylated diphenol sulfide, the two salts being present in proportions to control the deposition of resinous and varnish-like materials in internal combustion engines, and in amounts insufficient to materially increase the viscosity of the original lubricating oil, to which oil has been added a minor proportion of alizarin in quantity such that the resultant products are dispersed in the compounded lubricating oil, the product having a purple color.

2. A composition according to claim 1 wherein the sulfonate and the phenol sulfide salt are present in the order of about 1% each, and the alizarin is added in amount less than about 0.2%.

3. A composition according to claim 1 containing also a minor proportion based on the phenol sulfide salt of the phenol sulfide in uncombined form.

4. A composition according to claim 1 wherein the phenol sulfide salt and the sulfonate are each present in the order of about 1% of the total composition, moisture is present in the order of about 0.002%, and a minor proportion of the alkylated phenol sulfide in uncombined form.

5. A lubricating composition comprising mineral lubricating oil, a minor proportion between about 0.5% and about 2% of oil-soluble metal sulfonate, between about 0.5% and about 2% of oil-soluble metal salt of alkylated diphenol sulfide and a minor proportion of a metal-alizarin-sulfonate complex dispersed in the compounded oil.

6. A lubricant according to claim 5 wherein the mineral lubricating oil is one having a high viscosity index in the order of 85 to 95.

7. A lubricant comprising a mineral lubricating oil containing between about 0.5% and about 2% of each of an oil-soluble metal sulfonate and an oil-soluble metal salt of an alkylated phenol thio-ether, with which compounded oil has been combined a small amount in the order of 0.05% and 0.2% of material from the class consisting of alizarin, quinizarin and anthragallol.

8. A lubricant according to claim 7 which is freely liquid at normal temperatures and contains a minor proportion based on the thio-ether salt of the thio-ether itself in uncombined form.

9. A method for preparing a lubricating oil comprising preparing an oil-soluble metal sulfonate in solution in mineral lubricating oil, combining therewith a minor proportion of material from the class consisting of alizarin, anthragallol and quinizarin, preparing a mineral lubricating oil solution of an oil-soluble metal salt of an alkylated phenol thio-ether, and combining said two oil solutions.

10. A method according to claim 9 wherein said two oil solutions are prepared as concentrates of the two oil-solulbe metal salts, and said two solutions are blended and diluted with a high V. I. mineral lubricating oil to yield a lubricant suitable as a Diesel engine lubricant substantially free from viscosity increase over that of the original lubricating oil, and containing in the order of 1% each of the oil-soluble metal salts and less than 1% of the product resulting from the addition of the material from the class consisting of alizarin, quinizarin and anthragallol.

11. A lubricant comprising a major proportion of mineral lubricating oil, a minor proportion of an oil-soluble metal sulfonate, a minor proportion of an oil-soluble metal salt of an alkylated phenol thio-ether, and a minor proportion of a complex of said sulfonate, said thio-ether salt and a third material of the class consisting of alizarin, quinizarin and anthragallol.

12. A fluid lubricant for internal combustion engines according to claim 11 wherein the third material is alizarin.

13. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of an oil-soluble metal detergent soap, to which has been added a minor proportion of an organic cyclic compound having a definite acidic atomic grouping seletced from the class consisting of sulfonic, sulfinic, phosphorous, phosphoric phosphonic, phosphinic, and carboxylic acid groups capable of forming a coordination com-

plex with the metal of the detergent soap, and also having in its structure a group capable of satisfying secondary valences of a metal.

14. A lubricant according to claim 13 wherein the added agent is alizarin.

15. A lubricant according to claim 13 wherein the added agent is anthragallol.

16. A lubricant according to claim 13 wherein the added agent is quinizarin.

17. A lubricant according to claim 13 wherein the soap is a sulfonate.

18. A lubricant according to claim 13 containing also an anti-corrosion agent possessing reserve alkalinity.

19. A lubricant comprising a minor proportion of an oil-soluble metal salt of an alkylated phenol thio-ether to which has been added a minor proportion of a material selected from the class consisting of alizarin, anthragollol and quinizarin.

20. A lubricant comprising a major proportion of a mineral lubricating oil and a minor proportion of reserve-alkalinity material selected from the class consisting of oil-soluble metal salts of alkylated phenolic thio-ethers, other oil-soluble substituted phenolics, oil-soluble metal alcoholates, oil-soluble metal alkoxides, possessing reserve alkalinity characteristics, to which has been added a minor proportion of an agent selected from the class consisting of alizarin, quinizarin, anthragallol, other quinones, naphthaquinones, and anthraquinones, phenols, which agent contains an acidic grouping capable of satisfying one valence of a metal and another grouping capable of satisfying secondary valences of the metal.

21. A lubricant according to claim 20 containing a minor proportion of a detergent soap capable of forming adsorption complexes with said added agent.

22. A lubricant comprising a major proportion of a mineral lubricating oil and a minor amount of a complex of an oil-soluble metal sulfonate with a material selected from the class consisting of alizarin, quinizarin, and anthragallol.

23. A lubricant comprising a major proportion of a mineral lubricating oil, a minor amount of a complex of an oil-soluble metal sulfonate with a material selected from the class consisting of alizarin, quinizarin, and anthragallol, and a minor amount of an oil-soluble non-carboxylic acid detergent soap.

24. A lubricant according to claim 23 wherein the oil-soluble, non-carboxylic acid detergent soap is an oil-soluble metal salt of an alkylated phenol thio ether.

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