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LUBRICANTS AND METHODS OF PREPARING SAME

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This invention relates to lubricants and methods of preparing same, and more particularly to mineral lubricating oil compositions for use as crankcase lubricants for internal combustion engines, and especially for Diesel engines.

It is known that the addition of certain types of metal compounds to lubricating oils improves various properties thereof such as their oiliness characteristics, and their performance in engines as by maintaining a clean engine condition during operation. Various metal compounds which have been used for such purposes include the metal derivatives of organic compounds such as fatty acids, naphthenic acids, alcohols, phenols, ketones and even hydrocarbons. However, these various metal compounds generally have the disadvantage of tending to corrode alloy bearings such as those of cadmium-silver and copper-lead; and this is especially true in engines which operate at relatively high temperatures such as high speed and heavy duty Diesel engines. It has also been suggested to use metal salts of alkylated phenol sulfides for improving the engine performance of lubricating oils, and in certain instances these compounds have been found to be substantially non-corrosive to alloy bearings of the type mentioned above.

It has now been found that these metal salts of alkylated phenol sulfides, which may also be called metal salts of aroxy sulfides, are not only non-corrosive improvers of engine performance in lubricating oils, but also have the surprising property of substantially reducing, if not entirely preventing, the corrosiveness of other types of metal compounds such as those mentioned above, which improve the characteristics of a mineral lubricating oil but tend to increase the corrosiveness thereof toward sensitive alloy bearings. Furthermore, these anti-corrosive sulfide compounds appear to cooperate with the other type of metal compounds in some way so as actually to enhance the engine performance characteristics of the lubricating oil compositions even more than could reasonably be expected from the mere addition of the separate addition agents. These and other objects and advantages of the invention will appear more clearly in the following more detailed description.

The relatively corrosive type of metal compounds to be used in the lubricating oil compositions of this invention include the metal derivatives of all types of carboxylic acids such as aliphatic, e. g., stearic acid, oleic acid, etc., aromatic, naphthenic or synthetic acids such as those obtained by the oxidation of paraffin wax, petrolatum, sweater oil or other petroleum hydrocarbons, and also metal derivatives of either aliphatic alcohols such as stearyl alcohol, cetyl alcohol, etc. or of aromatic alcohols, e. g., benzyl alcohol or of naphthenic alcohols, or other metal compounds such as the metal phenolates, metal enolates (derived from the enolic structure of ketones), metal sulfonates, sulfates and phosphates. The metals contemplated include aluminum, calcium, nickel, barium, magnesium, cobalt, chromium, lead, tin and their mixtures.

The amount of such corrosive metal compounds used will usually range between the approximate limits of 0.01% to 2.0% and generally about 0.1%–1.0% will give the best results. How much should be used will depend to some extent upon a number of factors such as the type of mineral oil base stock, the type of metal compound being used and the severity of the operating conditions, as well as upon the type and amount of anti-corrosive metal compound to be used. A series of corrosion and engine tests, to determine the optimum proportions with the particular materials to be used, may be run in the laboratory before marketing such lubricating oil compositions for commercial use.

The anti-corrosive metal compound to be used according to this invention may be considered in a general way to be a metal salt of an alkylated hydroxy aryl sulfide. A representative example of such a compound is the cobalt salt of hydroxy tertiary amyl phenyl sulfide. Broadly, these compounds may be considered as having the following general formula:

$$\begin{array}{c} M—Y—Ar—Z_x—Q \\ | \\ R_m \end{array}$$

in which M is a metal; Y is either oxygen or a member of the sulfur family; Ar is an aromatic nucleus such as benzene or a condensed ring nucleus, e. g., naphthalene, anthracene, etc.; Z is sulfur, selenium or tellurium; x is an integer of from 1–5, preferably 1 or 2; Q is an organic group which may be identical with the part of the compound which is on the left side of the Z, or a group having a somewhat similar type of structure, or it may be a hydrocarbon group such as alkyl, e. g., amyl, octadecyl, etc.; or aralkyl, e. g., benzyl; or aryl, e. g., tolyl etc.; and R_m represents one or more hydrocarbon groups, such as alkyl, or alkenyl, e. g., amyl, octyl, octenyl, etc.; or cyclo aliphatic, e. g., cyclo hexyl; or aralkyl, e. g., benzyl; or alkaryl, e. g., amyl phenyl; or various substituted derivatives thereof containing ele-

ments such as halogen, sulfur, nitrogen, oxygen, phosphorus, etc., so long as these groupings do not interfere with the desired solubility and effectiveness of the metal compounds for the purposes of this invention. In this general formula the connecting dashes are not intended to indicate necessarily single bonds, but merely the location of the group in a general way; for instance if there are two Z atoms between Ar and Q, each Z atom might be connected to the Ar by one bond and to the Q by one bond in a dithioether formation, or the sulfurs might be attached to each other in a disulfide form, and also if there are a plurality of R groups each will require at least one bond connecting it to the aromatic nucleus Ar. It should also be pointed out that as in the case of the specific cobalt compound illustrated above, a single bivalent metal atom may be connected through Y atoms to two aromatic nuclei which may in turn be connected to the same or different Z atoms. The number and location of the metal linkages will depend upon the valency of the metal and upon the proportions of the raw materials used in preparing the metal compounds.

These anti-corrosive metal compounds are usually made by first reacting a suitable phenolic compound such as an alkylated phenol with a sulfur halide, and the resulting product then reacted with a metal oxide or hydroxide or other suitable derivative. The amount of Z atom in the final product need not necessarily correspond to an even integer; for example, analysis of the compound may indicate $S_{1.5}$, in which case it is likely that the product contains a mixture of compounds having a single sulfur linkage and other molecules having two sulfur linkages.

Various metals may be used in preparing these anticorrosive metal compounds; the following are representative examples: cobalt, calcium, barium, aluminum, zinc, magnesium, cadmium, tin, lead, chromium, manganese, and nickel, and although polyvalent metals, especially in groups 2, 3 and 8 of the periodic table, such as those mentioned above, are preferred, monovalent metals such as sodium and potassium may also be used. Also, such complexes as ammonium or amino groups may be used in place of metal elements in these phenolate sulfides.

The proportion of metal to non-metal in the anti-corrosive compound, may vary over a fairly wide range, due both to the fact that with various valencies the metal may combine with one to three or even more hydroxy aryl sulfide radicals, and to the fact that where there are two or more hydroxy groups present the metal may be used to replace only one of the hydroxyl hydrogen atoms. Furthermore mixtures of these various compounds may be prepared and used.

In the above described general formula, Y is preferably oxygen from practical considerations, although if desired it may also be sulfur, selenium or tellurium.

The aromatic nucleus Ar may be a phenyl group or it may be a polycyclic group such as in biphenyl, naphthalene, phenanthrene, anthracene, and the like.

Z is preferably sulfur, especially from the point of view of cost and availability, although selenium and tellurium can also be used if desired. Although as indicated previously, x is a number from 1–5, it should preferably be about 1–2, and sometimes best results are obtained by using products containing an amount of Z which is intermediate between whole numbers, for example 1.3 or 1.5. In such cases the products are mixtures as they may also be even when x is a whole number. The value of x, that is, the number of sulfur atoms, is determined by the quantity and type of sulfur halide used. Furthermore, sulfur dichloride appears usually to link the aryl nuclei with single sulfur bridges, whereas sulfur monochloride results in the formation of disulfide linkages.

These reactions of alkyl phenols with sulfur halide are preferably carried out in an inert solvent such as dichlorethane, chloroform, carbon tetrachloride, and the like.

The anti-corrosive metal compound should contain at least 6 carbon atoms in either aliphatic or cyclo aliphatic groupings to obtain adequate oil solubility, but much better results are obtained if they contain 10 to 24. For example, if the sulfide compound has a symmetrical thioether structure and contains two alkylated aromatic nuclei, the alkyl groups may appropriately be amyl, branched octyl groups (e. g. tetramethylbutyl) octadecyl, dodecyl, etc. With amyl groups as in the cobalt salt of tertiary amyl hydroxy phenyl sulfide, there are a total of 10 aliphatic carbon atoms present, and this is sufficient to give the desired oil solubility.

If the anti-corrosive metal compound is not symmetrical on both sides of the Z portion of the molecule, it is desirable that the radical Q should contain a sufficient number of aliphatic carbon atoms to supplement those present in the radical, $=ArR_m$, to impart to the total metal compound a sufficient oil-solubility for the purposes desired.

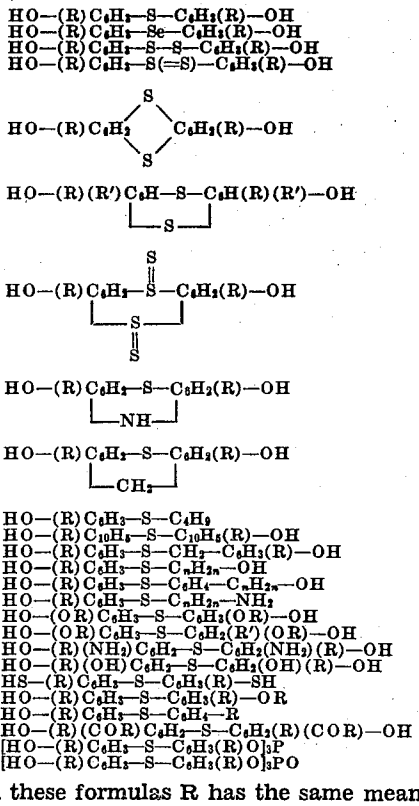
The metal salts of alkylated aroxy sulfides are preferably obtained from phenolic compounds which are readily prepared by alkylation of simple phenols or which may be obtained by extraction of high boiling petroleum oil. One common method of alkylating phenols is to condense them with olefins, the reaction being catalyzed by such agents as activated clay, hydrogen chloride, sulfuric acid, phosphoric acid, or an active metal halide. For example, phenol may be alkylated with diisobutylene or with tertiary amylene obtained from petroleum refinery gases, to make disiobutyl phenol (or perhaps more properly called tetramethylbutyl phenol), or paratertiary amyl phenol, or the phenol may be alkylated by condensing it with chlorinated wax or with olefins derived by dehydrogenating paraffin wax or dehydrochlorinating chlorinated wax. Similarly, isohexyl phenol, tertiary butyl phenol, diamyl phenol, and the like may be prepared. Alkylated phenols may be obtained also by extraction of certain petroleum stocks, particularly those obtained during cracking operations, with caustic soda followed by acidification of the alkaline extract with a weak mineral acid.

Such inorganic substituents as may be desired in the alkylated phenols are introduced by any well-known method. For example, alkyl chlorophenols may be prepared by direct controlled chlorination of the alkyl phenol, or by chlorinating the phenols before alkylation. Similarly, nitro groups may be introduced by direct nitration and these may be reduced to amino groups, if desired.

After the phenols have been alkylated and then converted into corresponding sulfides by reaction with either sulfur monochloride or sulfur dichloride, for example, they are then converted into corresponding metal derivatives as by first reacting with metallic sodium in alcohol, or with sodium hydroxide, and then converting the resulting sodium salt into the corresponding salt

of the desired metal by reacting the sodium salt with the chloride, nitrate, or other suitable inorganic salts of the desired metal. In some cases the alkylated phenol sulfide may be converted directly into a polyvalent metal derivative by reaction with the oxide or hydroxide of the desired polyvalent metal, or the metal itself.

For the sake of illustration, the following list of separate phenolic sulfides is shown in order to give some idea of the range of such compounds which can be converted into the desired anti-corrosive metal derivatives.



In these formulas R has the same meaning as explained in connection with the general formula previously referred to, R′ representing a radical selected from the same class as R, and being either the same as R or different; and n is an integer of at least 1.

It is not known just how the metallic compounds of these hydroxy aryl sulfides function as corrosion inhibitors. It may be that they act as antioxidants to retard the formation of corrosive products in the oil, that they exert a pacifying effect on metal surfaces to render them resistant to attack by corrosive materials, or that certain of them (such as the ammonium, amino or alkali metal derivatives) serve as buffers because of their alkaline nature. However, the invention is not to be limited by any explanation of the possible mechanism of the corrosion preventing effect.

The amount of the anti-corrosive metal compounds to be used should be about 0.1–2.0%, preferably about 0.2–1.0% in the finished lubricating oil. The exact amount for optimum results will depend partly upon the particular type of anti-corrosive metal compounds used, as well as upon the type and amount of corrosive metal compounds used and upon other factors such as the severity of the operating conditions to which the lubricating oil will be exposed, and the mineral oil base stock itself.

The lubricating oil base stock for this invention may be a mineral oil distillate or blend and may contain a residual oil, or it may be a fraction resulting from various physical and chemical refinery treatments, such as solvent extraction, precipitation, etc. Since one advantage of this invention is that it makes feasible the employment of normally less satisfactory mineral oils by use of the hereinbefore described addition agents, no strict rule can be laid down for the choice of the mineral oil base stock. However, the oil should possess the viscosity and volatility characteristics required for the service contemplated and it must also be a satisfactory solvent for the several addition agents. For the lubrication of medium or high speed Diesel engines, for which this invention has special advantages, the lubricating oil base stock should have a minimum A. P. I. gravity of about 15°, a minimum flash point of about 300° F., and a viscosity of about 40–95 seconds Saybolt at 210° F. For the lubrication of ordinary gasoline engines of the spark ignition type, the lubricating oils should preferably also have a viscosity index of about 50 or over. The lube oil base stock may be naphthenic, paraffinic, or mixed base, or it may be a synthetic lubricating oil, for instance as made by polymerization of low molecular weight, e. g. gaseous olefins, or by cracking, hydrogenation and other chemical processes. In addition to the two types of metal compounds to be added according to the present invention, other addition agents may be used such as fatty oils, dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organometallic compounds, bright stocks, viscosity index improvers, rubber, resins, olefin polymers, graphite, voltolized fatty oils, mineral oils or waxes, etc.

Also, when the lubricants contain other additives or assisting agents such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, either with or without corrosive metal compounds of the types hereinbefore described the metal salts of the alkylated phenol sulfides may serve also to inhibit any corrosive action which the additives may impart either because they tend to be corrosive per se or because they tend to become corrosive under certain conditions in which the lubricating oil is used.

The following examples will serve to illustrate typical methods of preparing these compounds:

EXAMPLE 1

Cobalt Salt of Hydroxy Tertiary Amyl Phenyl Sulfide

A solution of the sodium salt of hydroxy tertiary amyl phenyl sulfide was prepared by reacting 7.7 grams (⅓ mol) of sodium dissolved in 150 cc. of absolute ethyl alcohol with 60 grams (⅙ mol) of hydroxy tertiary amyl phenyl sulfide dissolved in 110 cc. of absolute alcohol.

A solution of 23 grams (⅙ mol=21.7 grams) of anhydrous cobalt chloride in 250 cc. of absolute ethyl alcohol was added with agitation causing the mixture to turn brown. The alcohol was stripped off and the brown residue was agitated with a light solvent naphtha (boiling range 150–240° F.) in which the cobalt salt of hydroxy tertiary amyl phenyl sulfide dissolved readily, leaving a residue of insoluble sodium chloride. The solution was filtered free of sodium chloride and then distilled to remove the naphtha, giving a residue of 70 grams of a dark chocolate colored product which was identified as the desired cobalt salt. The cobalt salt dissolved readily in a

naphthenic base lubricating oil having a Saybolt viscosity of about 55 seconds at 210° F., such as is suitable as a crankcase lubricant for Diesel engines.

With the more alkaline metals such as calcium and barium it is possible to react the metal directly with the hydroxy phenyl sulfide in a manner similar to that for the preparation of the sodium salt.

EXAMPLE 2

Barium Salt of Hydroxy Diisobutyl Phenyl Sulfide

Diisobutylene was condensed with phenol, using stannic chloride and dry hydrochloric acid gas as catalysts, to prepare diisobutyl phenol. Three mols (618 grams) of diisobutyl phenol which had been recrystallized from naphtha were dissolved in 1200 grams of chloroform, and a solution of 2.25 mols (232 g.) of sulfur dichloride (SCl_2) in 300 grams of chloroform was added gradually with stirring, care being taken to keep the reaction temperature between 20 and 25° C. Following this step the mixture was heated on a water bath and refluxed for two hours. The solvent was then stripped off. The recovered hydroxy diisobutyl phenyl sulfide was found to contain an average of 1.41 atoms of sulfur per molecule.

One mol (456 grams) of the above sulfide was dissolved in 3000 cc. of benzene and the solution placed in a reaction vessel equipped with a condenser having a trap for removing water. A total of 321 grams (315 g.=1 mol) of barium hydroxide octahydrate, $Ba(OH)_2.8H_2O$ were added (in four equal portions) to the solution which was then heated for 26 hours under reflux, any evolved water being trapped out. The reaction mixture was then filtered and the solvent stripped off, leaving a solid residue which could be pulverized to a fine yellow powder. This was found to be soluble in mineral lubricating oils. The yield of barium salt was 540 grams, or 91% of the theoretical yield.

The effect of adding these anti-corrosive metal salts of alkylated hydroxy phenyl sulfides to lubricating oils containing corrosive metal addition agents is shown in the following data obtained from corrosion tests and from tests made in Diesel engines.

EXAMPLE 3

The cobalt salt of hydroxy tertiary amyl phenyl sulfide was dissolved in a naphthenic base lubricating oil in the concentration of 0.5%. In another portion of the same oil, barium diisobutyl phenolate [1] was dissolved in the concentration of 0.25%. These two blended oils were then compared as to corrosiveness toward copper-lead bearings and cadmium-silver bearings, the test conducted in the Underwood corrosion apparatus for 5 hours at 325° F. Tests were also made with blends of the same oil which contained various concentrations of both the sulfide and the phenolate. The test results are given in the accompanying Table I.

[1] Barium salt of phenol which has been alkylated with diisobutylene.

Table I

5-hour Underwood corrosion tests at 325° F. Weight losses, expressed in milligrams, are for 2 Cu-Pb half bearings and for 2 Cd-Ag half bearings.

Test No.	Per cent addition agent		Bearing wt. loss, mg.	
	Ba salt [1]	Co salt [2]	Cu-Pb	Cd-Ag
1	0.25	0.0	526	1,326
2	0.25	0.25	109	1
3	0.25	0.5	64	3
4	0.2	0.5	62	1
5	0.1	0.5	19	2

[1] Barium diisobutyl phenolate.
[2] Cobalt salt of tertiary amyl hydroxy phenyl sulfide.

It will be readily seen that the barium diisobutyl phenolate renders the oil very corrosive toward both types of bearings but that when the cobalt phenol sulfide salt is also added the corrosion is greatly reduced.

EXAMPLE 4

Blends of the cobalt salt of tertiary amyl hydroxy phenyl sulfide alone and with barium diisobutyl phenolate in a naphthenic base oil (the same as in Example 3) were compared with the oil itself as to behavior in a single-cylinder Caterpillar Diesel engine. The oils were rated according to the condition of the engine after a certain number of hours of running. The results are given in the accompanying Table II. It should be observed that the higher the numerical rating demerits the worse the condition of the engine or its parts.

Table II

Tests in single cylinder Caterpillar engine

Test No.	Oil treated	Hours on test	Over-all piston demerit	Demerits of individual parts					
				Ring grooves	SGLS [1]	Carbon	Skirt and liner	Skirt varnish	Oil filter
1	Naphthenic oil A	110	1.45	3.1	1.86	3.4	2.17	1.5	2
		242	1.96	4.3	2.58	3.9	2.92	2.0	4
2	Oil A+0.5% cobalt salt	60	1.18	2.4	1.55	4.0	0.88	0.87	1.5
3	Oil A+0.5% cobalt salt [2]+0.25% barium salt [3]	100	1.11	2.3	1.49	3.6	0.83	0.75	2
		254	1.46	3.8	2.39	3.5	1.17	1.25	2

[1] Cleanliness of ring slits, grooves, lands and sides.
[2] Cobalt salt of tertiary amyl hydroxy phenyl sulfide.
[3] Barium salt of diisobutyl phenol.

It will be seen from the results given that the blend containing both the cobalt compound and the barium compound gave a much better engine condition in both approximately 100 hours and 250 hours of operation. The cobalt compound alone will give some improvement, but it will be noted that after only 60 hours the engine condition in this instance was inferior to that after 100 hours with the blend containing both the barium salt and cobalt salt.

EXAMPLE 5

To a naphthenic base SAE 30 motor oil there was added a mixed aluminum-calcium soap of acids obtained in the oxidation of sweater oil. Blends were also made of this soap compounded oil with, in one case, a calcium salt of tertiary amyl hydroxy phenyl sulfide and, in the other, with the barium salt of diisobutyl hydroxy phenyl disulfide. These three oils were all compared as regards corrosiveness toward cadmium silver and copper-lead bearings with the results presented in Table III. The particular corrosion test in this instance involved spinning bearing sections in the heated oil while air was passed through. After intervals of 1, 3, and 5 hours the bearings were removed and weighed. The tabulated results indicate that both the sulfur-containing calcium and the barium compounds reduced the corrosion markedly and that the calcium compound proved somewhat superior in this respect to the barium.

TABLE III

S. O. D. bearing corrosion tests at 325° F.

Oil No.	Oil	Wt. losses per 25 sq. cm. area, mg.					
		One hour		3 hours		5 hours	
		Cu-Pb	Cd-Ag	Cu-Pb	Cd-Ag	Cu-Pb	Cd-Ag
1	Base oil+0.25% Al-Ca soap	32	26	77	137	147	294
2	No. 1+1% calcium salt [1]	1	0	2	0	17	1
3	No. 1+1% barium salt [2]	0	0	43	3	126	82

[1] Salt of tertiary amyl hydroxy phenyl sulfide.
[2] Salt of diisobutyl hydroxy phenyl disulfide.

EXAMPLE 6

A blend was prepared of nickel oleate in a naphthenic base lubricating oil. Blends were also made of nickel oleate and of the cobalt salt of tertiary amyl hydroxy phenyl sulfide together in various proportions in the same oil. These were all compared as regards corrosiveness toward cadmium-silver and copper-lead bearings, as in Example 3. From the data presented in the accompanying Table IV it will be seen that the cobalt salt greatly minimized the corrosive tendencies of nickel oleate.

TABLE IV

5-hour Underwood corrosion tests at 325° F.

Test No.	Percent addition agent		Bearing wt. loss, mg.	
	Ni oleate	Cobalt salt [1]	Cu-Pb	Cd-Ag
1	0.5	0.0	337	1,753
2	0.5	0.5	282	37
3	0.2	0.5	67	8
4	0.2	0.6	56	4
5	0.2	0.7	51	5

[1] Salt of tertiary amyl hydroxy phenyl sulfide.

EXAMPLE 7

A blend of 0.2% nickel oleate and 0.5% of the cobalt salt of tertiary amyl hydroxy phenyl sulfide was prepared in a naphthenic base lubricating oil. This blend was compared with the oil alone in an 84-hour test conducted in a Hercules Diesel engine under severe operating conditions. Similarly a blend of the cobalt salt in a naphthenic oil was compared with the oil itself. From the results given in Table V it will be seen that the blend of nickel soap and the cobalt salt greatly improved the engine performance of the lubricating oil, the demerit being only 78% of that for the oil alone. For comparison, the blend containing only the cobalt salt had a demerit rating of 88% of that for the oil alone.

TABLE V

84-hour tests in Hercules Diesel engine

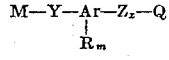
	Test No. 1	Test No. 2		Test No. 3	Test No. 4	
	Oil tested		Per cent of ref.	Oil tested		Per cent of ref.
	Naphthenic oil B	Oil B+0.5% cobalt salt [1]		Naphthenic oil A	Oil A+0.5% cobalt salt+0.2% Ni oleate	
Over-all demerit	1.95	1.71	88	2.14	1.68	78
Individual demerits:						
Combustion chamber	2.42	3.00	124	3.33	3.25	98
Sludge	1.89	1.86	98	1.94	1.83	94
Valves	1.70	1.64	97	1.72	1.72	100
Piston skirts	0.83	0.50	60	1.08	0.75	69
Crankshaft	1.00	0.50	50	2.00	0.50	25
Rings and grooves	2.48	1.85	75	2.61	1.63	63

[1] Cobalt salt of tertiary amyl hydroxy phenyl sulfide.

It is not intended that this invention be limited to any theory as to the mechanism of the operation of the invention nor to any of the specific examples which have been given merely for the sake of illustration, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. A lubricant comprising a mineral oil base stock, a small amount of an oil soluble metal salt having the general formula



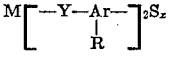
where M is a metal, Y is a member of the right-hand side of group 6 of the Mendeleeff Periodic Table of Elements, Ar is an aromatic nucleus, Z is a member of the sulfur family, x is an integer of from 1 to 5, Q is an organic group, R represents a hydrocarbon group, and m is an integer indicating the number of R groups, said lubricant also containing a small amount of an oil soluble metal salt of an acidic organic compound.

2. A lubricant comprising a mineral oil base stock, a small amount of an oil soluble metal salt of the reaction product of an alkylated hydroxy aromatic compound with a sulfur halide, and a small amount of an oil-soluble metal salt of an acidic organic compound.

3. A lubricating oil composition comprising a mineral oil base stock containing dissolved therein a small amount of an oil-soluble metal salt of an acidic organic compound, said metal salt being adapted to improve the engine performance of said mineral oil base stock but normally tending to promote the corrosiveness thereof toward alloy bearings of the copper-lead, cadmium-silver type, and also a small amount of an oil soluble polyvalent metal salt of an alkylated hydroxy aryl sulfide adapted to make the lubricating oil composition non-corrosive to such alloy bearings.

4. Composition according to claim 2, in which the corrosive compound is a metal derivative of an organic compound selected from the group consisting of fatty acids, naphthenic acids, alcohols, phenols, ketones, and hydrocarbons.

5. A lubricating oil composition comprising a major proportion of a mineral oil base stock, and a small amount of an oil soluble metal salt having substantially the general formula



where M is a divalent metal, Y is oxygen or sulfur, Ar is an aromatic nucleus, R is an alkyl or substituted alkyl group having at least 4 carbon atoms, and x is 1–5, and a small amount of an oil-soluble metal salt of an acidic organic compound.

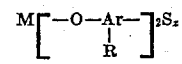
6. A lubricating oil composition comprising a major proportion of a mineral lubricating oil base stock having a minimum A. P. I. gravity of about 15°, a minimum flash point of about 300° F., and a viscosity of about 40–150 seconds Saybolt at 210° F., containing dissolved therein about 0.01–2.0% of a metal soap and about 0.1–2.0% of a metal salt of an alkylated hydroxy phenyl sulfide.

7. Composition according to claim 6, in which the sulfide is a salt of a divalent metal.

8. Composition according to claim 6, in which the sulfide is a salt of cobalt.

9. Composition according to claim 6 in which the sulfide is the salt of an alkaline earth element.

10. A lubricating oil composition comprising a major proportion of a mineral oil base stock, a small amount of an oil soluble metal phenolate, and a small amount of an oil soluble metal salt of a hydroxy aryl sulfide having substantially the general formula



where M is a metal, Ar is an aromatic nucleus, R is an alkyl or substituted alkyl group having at least 4 carbon atoms, and x is 1–5.

11. A lubricating oil composition comprising a major proportion of a mineral lubricating oil base stock having a minimum A. P. I. gravity of about 15°, a minimum flash point of about 300° F., and a viscosity of about 40–150 seconds Saybolt at 210° F., containing dissolved therein about 0.1–1.0% of a metal phenolate and about 0.1–1.0% of a metal salt of an alkylated hydroxy phenyl sulfide.

12. Composition according to claim 11, in which the sulfide is a salt of a divalent metal.

13. Composition according to claim 11, in which the sulfide is a salt of cobalt.

14. Composition according to claim 11, in which the sulfide is the salt of an alkaline earth element.

15. A lubricating oil composition especially adapted for lubrication of Diesel engines, which comprises a major proportion of a mineral lubricating oil base stock having a minimum A. P. I. gravity of about 15°, a minimum flash point of about 300° F., and a viscosity of about 40–95 seconds Saybolt at 210° F., containing dissolved therein about 1.0% of nickel oleate, and a sufficient amount, between the approximate limits of 0.1 and 1.0% of a cobalt salt of tertiary amyl hydroxy phenyl sulfide, which makes the lubricating oil composition non-corrosive to sensitive alloy bearings.

16. Composition according to claim 1 in which said second metal compound is a member of the class consisting of metal sulfonates, metal sulfates and metal phosphates.

17. Composition according to claim 2 in which the said second metal compound is a member of the class consisting of metal sulfonates, metal sulfates and metal phosphates.

18. Composition according to claim 3 in which the said first metal compound is a member of the class consisting of metal sulfonates, metal sulfates and metal phosphates.

19. Composition according to claim 3 in which the said first metal compound is an alkaline earth sulfonate.

20. A liquid lubricating oil for severe service internal combustion engines comprising mineral lubricating oil containing a small proportion of metal compound of a phenol thioether in quantity sufficient to control development of corrosive conditions without imparting substantial viscosity increase to the base oil, the oil containing also a small proportion of an oil-soluble detergent soap of a saponifiable carboxylic acid.

21. A freely fluid mineral lubricating oil containing a minor proportion of an oil-soluble metal salt of a phenol sulfide, the oil containing also a small proportion of an oil-soluble detergent metal soap of a relatively strong saponifiable carboxylic acid.

22. An oil according to claim 21, wherein the metal of the salt of the phenol sulfide is from the class consisting of alkali metals and heavy metals.

23. A mineral lubricating oil containing a small proportion between about 0.5% and 2.0% of an oil-soluble metal salt of an alkylated polyphenol sulfide, and a small proportion in the order of 1% of oil-soluble metal detergent soap of saponifiable organic acids.

24. A lubricant comprising a mineral oil base stock, a small amount of an oil-soluble metal salt of the reaction product of an alkylated hydroxy aromatic compound with a sulfur halide, and a small amount of an oil-soluble metal salt of an acidic organic compound.

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