

UNITED STATES PATENT OFFICE

2,362,293

LUBRICANT

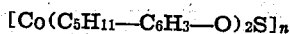
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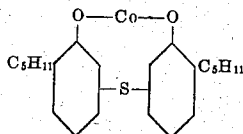
16 Claims. (Cl. 252-48)

This invention relates to a novel type of metal compounds and methods of preparing same, and relates more particularly to the use of these novel compounds as addition agents in hydrocarbon compositions, especially in lubricating oils, for improving the same.

It has been found that hydrocarbon compositions, especially hydrocarbon lubricating oils, are greatly improved by adding thereto in small amounts of a class of metal compounds of which the cobalt salt of tertiary amyl phenol thioether is representative. This compound, which might also be called a cobalt tertiary amyl phenol sulfide, or a sulfide of cobalt tertiary amyl phenolate, is believed to have the formula:



where n is one or more. If the various groups attached to the aromatic nucleus are so positioned that the amyl group is in an ortho position to the oxygen, and the sulfur linkage is in a meta position to the oxygen, this compound probably has the following graphic formula in its simplest form:



Obviously, with both the cobalt and the phenol divalent, quite large complexes can theoretically be built up. It should be understood that the position of the various substituents around the aromatic nucleus may be varied without departing from the scope of the invention.

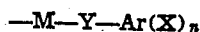
A similar disulfide compound may be used in which the group $-\text{S}-$ in the above graphic formula is replaced by the group



or if preferred by the group $-\text{S}-\text{S}-$, or even higher polysulfides may be used.

These various compounds can be produced by preparing the corresponding alkyl phenol sulfides or disulfides, which per se are known, and converting these into the corresponding sodium or potassium salts thereof, as by treatment with sodium or potassium hydroxide, and then converting the resultant derivative of the alkali metal into the corresponding derivative of cobalt by any suitable means, such as by double decomposition with a suitable corresponding cobalt compound, such as the chloride, nitrate, etc.

The invention may be described more broadly as comprising a substituted phenolate compound of a metal of group VIII, series 4, of the Mendeleeff Periodic Table, containing at least one grouping having the general formula:

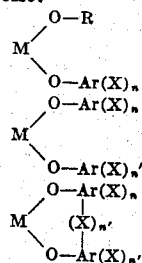


wherein M represents the metal constituent connected through Y to at least one aromatic nucleus, Y is an element in the righthand side of group VI of the periodic table (Mendeleeff), Ar represents an aromatic nucleus which contains like or unlike substituent X , n in number, replacing nuclear hydrogen, n being at least 1.

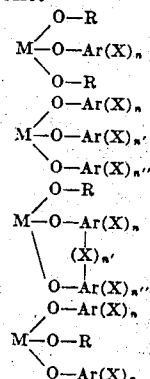
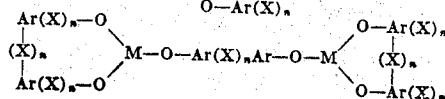
The substituents, X , may be organic, inorganic, or both, for example, alkyl radicals and groups containing one or more of the non-metallic elements belonging to groups V, VI, and VII of the periodic system (Mendeleeff): nitrogen, phosphorus, oxygen, sulfur, and halogens, as in amino, nitro, phosphite, phosphate, hydroxy, alkoxy, sulfide, thioether, mercapto, chloro groupings, and the like.

In the phenolate salts constituting blending agents featured by this invention, valences of the metal other than those connected to the substituted phenolic radicals, such as $-\text{O}-\text{Ar}(\text{X})_n$, are connected through oxygen to other organic groups or to inorganic constituents, such as hydrogen, phosphorus, etc. For convenience, non-phenolic radicals or groups, as well as phenolic groups, attached to the metal are indicated broadly by $-\text{O}-\text{R}$ in the following types of compositional formulae, which broadly represent metal derivatives of substituted phenolic compounds containing the characteristic compositional grouping described:

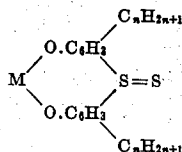
Where M is divalent:



Where M is trivalent:

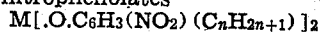


V. Disulfides of alkyl phenolates



e. g., salts of tert-amyl phenol disulfide

VI. Alkyl nitrophenolates

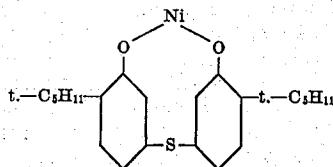


e. g., salts of alkyl nitro phenol sulfide

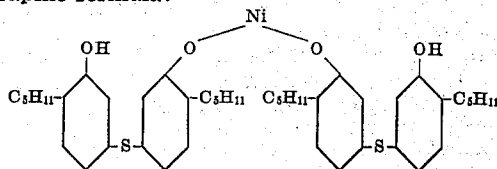
In the case where the metal is trivalent such as ferric iron, 1, 2, or all 3 of the valences of the metal may be connected to a phenolic oxygen (or sulphur in case a thio-phenolic compound was used). For instance, in case of a tri-valent metal the thioethers of alkyl phenolate may have a formula such as the following:



As these substituted phenolates are generally made by reacting the corresponding phenols with a metal oxide or hydroxide (either the one desired, or the sodium or potassium compound to be converted into the one desired), the amount of metal in the phenolate product will depend on the proportions of reactant used, and if products having different proportions are possible, the products will usually consist of a mixture, which may be used as such or may be separated into several constituents. For instance, as will be seen from the experimental data given later, nickel derivatives of tertiary amyl phenol thioethers have been prepared which contain 3 different proportions of nickel. It is probable that the normal compound containing 1 nickel atom per thioether molecule, which should contain 18% NiO, should have the following graphic formula:

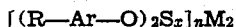


On the other hand, if only enough metal is reacted with the phenolic compound to combine with one of the hydroxyl groups it is likely that the resultant product will have the following graphic formula:



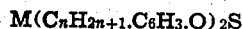
Finally, by using an excess of the metal, in using the cobalt or like salt for the double decomposition it is possible to make compounds containing even more metal than 1 atom per dihydroxy thioether molecule.

As seen from the above description, the metal compound preferably has the general formula:



where M is a metal selected from the group consisting of cobalt, nickel and iron, R represents one or more alkyl groups having enough carbon atoms (preferably a total of at least 10) to insure solubility of the total compounds in mineral oil, Ar is an aromatic nucleus, preferably a ben-

zene nucleus, x is 1 or 2, and n is the valency of the metal. More particularly, compounds having the following general formula are preferred:



where M is cobalt, nickel or iron, n is at least 4, and preferably 5 or more, and where the group C_nH_{2n+1} is preferably a branched alkyl group.

For the objects stated, the metal phenolates have been preferably prepared from phenolic compounds readily obtainable by alkylation of the simple phenols or by extraction from high boiling petroleum oils.

Suitable synthetic alkyl phenols for preparing the desired phenolates are principally of the secondary and tertiary types, because alkylation of a simple phenol occurs more readily with branched aliphatic reactants. Commonly, the alkylation reaction involves a condensation of olefins with the simple phenols, the reaction being catalyzed by anhydrous metal halides, sulfuric acid, phosphoric acid, or certain activated clays. As olefinic reactants, refinery gases containing propylene, butylenes, amylenes, etc., are economically useful, although individual olefins, e. g., isobutylene, iso-amylene, diisobutylene, triisobutylene, etc., or olefin-containing mixtures from other sources may be used. The reaction temperature is usually controlled to avoid side reactions. In employing sulfuric acid, a liquid phase reaction at relatively low temperatures is preferred; with phosphoric acid the reaction may be carried out in the vapor phase.

As starting materials for conversion into the metal phenolates, the phenols may contain one or more substituents which provide a desired number of saturated carbon atoms in groups having the form of straight chains, branched chains, or even rings. Monoalkyl or polyalkyl phenols are synthesized conveniently by alkylating a phenol with branched chain olefin polymers, such as diisobutylene, di-tert-amylene, or other suitable agents, such as alcohols, alkyl sulfates, alkyl phosphates, or alkyl halides, thereby forming carbon-to-carbon bonds between the aromatic nuclei and the alkyl groups.

Petroleum phenols which qualify for the present purpose are considered to contain polymethylene or cycloalkyl side chains, as evidenced by their hydrogen and carbon analysis. The petroleum phenols are obtained by extraction of various stocks, chiefly from cracking process heating oil stocks, with caustic soda, and acidification of the alkaline extract with a weak mineral acid, followed by a non-destructive distillation if desired.

By using the described methods or any other well known method for preparing alkyl phenols, the following alkylated phenols may be procured for preparing the phenolates, e. g., tert-amyl phenol, iso-hexyl phenol, tert-octyl phenol, di-tert-butyl phenol, di-tert-amyl phenol, di-normal amyl phenol, etc.

Inorganic substituents are introduced into alkyl phenols by well known methods. For example, an alkyl phenol, e. g., tert-amyl phenol, is reacted with sulfur mono-chloride, S_2Cl_2 in about 1:1/2 mole ratio and preferably in a solvent such as dichlor-ethane, to produce the alkyl phenol disulfide. Using substantially the same procedure but substituting sulfur dichloride, SCl_2 , for the mono-chloride, the alkyl phenols are given a thioether linkage substituent. Alkyl chlorophenols are obtained by chlorination, preferably controlled to replace nuclear hydrogen by a chloro

group. This may be accomplished by chlorinating the phenol before alkylation. In such a manner, for example, 2-chlor-4-tert-amyl phenol can be produced. Nitro substituents are introduced readily into the aromatic nucleus by direct nitration, and nitro substituents can be reduced to amino groups. It is to be understood, however, that the preparation of substituted phenolic compounds which have been described does not form part of this invention and that any of the well known methods for their production may be used.

The following experimental data illustrate the preparation of some cobalt and nickel derivatives of the substituted phenolic compounds according to this invention.

EXAMPLE 1

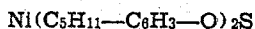
Cobalt salt of tertiary amyl phenol sulfide

7.7 grams ($\frac{1}{3}$ mole) of sodium were dissolved in 150 ccs. of absolute ethyl alcohol. 60 grams ($\frac{1}{6}$ mole) of tertiary amyl phenol sulfide, dissolved in 100 ccs. of absolute ethyl alcohol, were added. 23 grams (21.7 equals $\frac{1}{6}$ mole) of cobalt chloride, CoCl_2 (anhydrous) were dissolved in 250 ccs. of absolute ethyl alcohol and added to the above mixture with agitation. The solution turned brown. The alcohol was stripped off and the brown residue was agitated with 54 naphtha¹ in which the cobalt salt of tertiary amyl phenol sulfide dissolved very readily, the sodium chloride resulting from the double decomposition remaining insoluble. The solution was filtered free of sodium chloride and then distilled to strip off the naphtha. 70 grams of a dark chocolate colored product were obtained. This product, which was cobalt tertiary amyl phenol sulfide, dissolved readily in a naphthenic base lubricating oil having a Saybolt viscosity of about 55 seconds at 210° F., such as is suitable for use as a crankcase lubricant for Diesel engines. Analysis indicated that this cobalt salt contained 17.65% of Co_3O_4 (theoretical 19.36).

EXAMPLE 2

Nickel salt of tertiary amyl phenol sulfide

Some tertiary amyl phenol sulfide was converted into the corresponding sodium salt by treating with a solution of sodium in absolute ethyl alcohol, using $\frac{1}{3}$ mole of sodium and $\frac{1}{6}$ mole of the tertiary amyl phenol sulfide. 21.6 grams ($\frac{1}{6}$ mole) of nickel chloride, NiCl_2 , were suspended in 200 ccs. of absolute alcohol, and the resulting suspension was added to the alcohol solution of the sodium tertiary amyl phenol sulfide. The mixture was refluxed for 4 hours and gradually turned a dark green color. After refluxing for 24 hours more the solution was filtered free from insoluble materials (mostly sodium chloride and some unreacted nickel chloride), and the alcohol was stripped off the filtrate yielding 67 grams of a green solid which was readily soluble in the naphthenic oil base stock referred to in Example 1. Analysis of the product indicated a content of 6.40% of nickel oxide expressed as NiO . Based on the formula

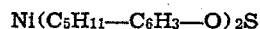


the reaction did not go to completion because the calculated content of NiO should be 18.0%.

This experiment was repeated using absolute methyl alcohol instead of ethyl alcohol as the

solvent for the nickel chloride, a better reaction took place, and this time a green solid product was obtained which was found to have a content of 21.6% nickel oxide (NiO), which is slightly above the theoretical amount calculated for the formula given above. This product is also soluble in the naphthenic oil referred to.

In another experiment using methyl alcohol, 60 grams ($\frac{1}{6}$ mole) of tertiary amyl phenol sulfide were dissolved in 100 ccs. of absolute methyl alcohol and added to a solution of 7.7 grams ($\frac{1}{3}$ gram-atom) of sodium dissolved in 150 ccs. of methyl alcohol. 28 grams (21.6 grams equal $\frac{1}{6}$ mole) of anhydrous nickel chloride (NiCl_2) were dissolved in 300 cc. of absolute methyl alcohol by refluxing, and after cooling this solution was added to the alcohol solution of sodium tertiary amyl phenol sulfide prepared first. A precipitate formed and another 60 cc. of alcohol were added and the mixture was permitted to stand over night. After recovering the precipitate, dissolving it in 54 naphtha, filtering off the residual sodium chloride and evaporation of the naphtha, a yellow-colored product was obtained which had a nickel oxide content of 17.9% NiO , which corresponds closely with the theoretical 18.0% for the compounds having the formula



This product is also soluble in the naphthenic oil referred to.

EXAMPLE 3

Nickel methoxo salt of tertiary amyl phenol sulfide

15.5 grams ($\frac{2}{3}$ gram-atom) of sodium were dissolved in 300 cc. of absolute methyl alcohol. 60 grams ($\frac{1}{6}$ mole) of tertiary amyl phenol sulfide dissolved in 100 cc. of methyl alcohol were added. 44 grams (23.2 grams equal $\frac{1}{3}$ mole) of anhydrous nickel chloride (NiCl_2) were dissolved in 400 cc. of dry methyl alcohol by refluxing. The nickel chloride solution was added to the above with agitation. A precipitate formed, and after standing for several hours the solution was filtered off, the precipitate being air-dried and the alcohol being stripped off from the filtrate. 30 grams of green solid were obtained from the filtrate and 114 grams of light-green solid from the precipitate. The two solids were combined and warmed with 54 naphtha, cooled and then filtered after standing over night. The naphtha was stripped off from the solution and a yield of 91 grams of an oil-soluble green solid was obtained which had a content of 27.45% of nickel oxide (NiO), which corresponds closely to the theoretical 27.90% calculated for the formula $(\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_3-\text{O}-\text{Ni}-\text{O}-\text{CH}_3)_2\text{S}$, the nickel methoxo salt of tertiary amyl phenol sulfide.

EXAMPLE 4

Nickel salt of tertiary amyl phenol disulfide

7.7 grams ($\frac{1}{2}$ gram-atom) of sodium were dissolved in 150 cc. of pure methyl alcohol. 65 grams ($\frac{1}{6}$ mole) of tertiary amyl phenol disulfide (obtained by treating tertiary amyl phenol with sulfur monochloride (S_2Cl_2), dissolved in 100 cc. of methyl alcohol, were added to the first solution to form the sodium salt of tertiary amyl phenol disulfide. 25 grams (21.6 grams equal $\frac{1}{6}$ mole) of nickel chloride (NiCl_2) were dissolved in methyl alcohol by refluxing and the resulting solution was slowly added to the solution of sodium

¹A light solvent naphtha having a boiling range of 160-240° F.

tertiary amyl phenol disulfide with agitation. After standing, the precipitate which formed was filtered off and dried. The yield equalled 68 grams.

The filtrate was stripped free of alcohol, leaving a residue of 39 grams. These two residues were combined and refluxed with 54 naphtha for a few minutes, cooled, settled for a day and the supernatant liquid was drawn off and stripped free of naphtha, leaving a residue of 75 grams of greenish-yellow solid which dissolved readily in the naphthenic oil referred to in Example 1 on heating. This product contained 15.49% of nickel oxide (NiO), which corresponds fairly well with the theoretical 16.72% calculated for the formula $\text{Ni}(\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_5-\text{O})_2\text{SS}$, the nickel salt of tertiary amyl phenol disulfide.

EXAMPLE 5

Cobalt salt of tertiary amyl phenol sulfide

This is the laboratory method of preparation which was subsequently adopted for the commercial manufacture of cobalt tertiary amyl phenol sulfide.

71.6 grams of tertiary amyl phenol sulfide were dissolved in 300 cc. of 98% isopropyl alcohol by warming and agitation. 16 grams of flake caustic soda were added and the mixture warmed to about 150° F. and agitated until the caustic soda was completely reacted to give a yellowish-brown solution of sodium tertiary amyl phenol sulfide in the alcohol. A solution of 27.6 grams of cobalt chloride hexahydrate in 150 cc. of isopropyl alcohol, prepared by warming the alcohol to about 125° F. and stirring, was then added, with stirring, to the alcoholic sodium tertiary amyl phenol sulfide solution, producing a brownish paste of cobalt tertiary amyl phenol sulfide suspended in alcohol. 320 grams of a Coastal naphthenic lubricating oil base stock having a viscosity of about 55 seconds Saybolt at 210° F. (a sufficient quantity to give a 20% solution of the cobalt salt) was then added and the alcohol was removed by stripping in vacuum. In order to assist in removing the last portion of the solvent, the product was blown with air. The finished product was filtered through paper and the filtered 20% concentrate of cobalt tertiary amyl phenol sulfide in the naphthenic lubricating oil base stock was found upon analysis to contain 3.42% of cobalt oxide (Co_3O_4) (which checks satisfactorily with the theoretical amount of 3.33%).

Corresponding cobalt, nickel or iron salts of other alkyl phenol sulfides may be prepared, for instance, by substituting polysulfide or polymers, such as the dimers, trimers, and tetramers of the alkyl phenol thio-ethers used in the above examples. Also, the corresponding metal salts of the corresponding selenides and tellurides may be prepared, although the sulfur compounds are preferred.

The various products obtained may be purified, if desired, by fractional crystallization, extraction, precipitation with selective solvents, etc. Also, impurities may be removed by treatment with suitable adsorptive agents such as clay.

While these compounds or mixtures thereof, alone or in admixture with corresponding alkyl phenol sulfides, may be added in any desired concentration within their solubility limits to lubricating oils, they are preferably used in concentrations of about 0.01 to 2.02%, about 0.1 to 1.0% being generally sufficient to impart sludging-re-

sistant properties to the majority of lubricating oils. Larger amounts up to 5% or more may be used to improve the lubricating or oiliness characteristics of the lubricating oils.

These metal compounds may also be used as improving agents in other hydrocarbon oils or products, such as waxes, fuel oils, Diesel fuels, naphthas, gasoline, burning oil, and the like.

These metal compounds may also be used as improving agents in products derived from petroleum oils or in different types of products such as fatty oils, soaps, aldehydes, resins, rubber, paper, and various synthetic products which tend to deteriorate by oxidation either alone or in accompaniment with other chemical phenomena.

The metal compounds of this invention are especially useful for improving mineral lubricating oils, particularly those used for crankcase lubrication of internal combustion engines. These oils may be obtained from various types of crudes such as paraffinic, naphthenic, asphaltic, or mixed crudes, and they may be either plain distillates or fractions obtained by treating or refining by various methods known to the art, such as acid treating, clay treating, solvent extraction, dewaxing, etc., or they may be synthetic oils resulting from various types of chemical reactions such as cracking, polymerization, condensation, and the like.

In preparing finished lubricants according to this invention as described above, other known addition agents may also be used such as other known effective anti-oxidants, dyes, soaps, pour inhibitors, sludge dispersers, etc.

Although the invention is of primary importance for preparing Diesel engine lubricants, it is also useful for other types of crankcase lubricants, steam cylinder oils, greases, upper cylinder lubricants, sludging oils, etc.

The invention has numerous advantages, some of which are apparent from the preceding discussion, but it should also be pointed out that these derivatives of cobalt, nickel and iron cause very remarkable improvement in the performance of such internal combustion engines, particularly when contrasted with materials used heretofore in such engines when operated under severe testing conditions, such as at high speed and high temperature, etc. Another very important feature of this invention is that the metal compounds disclosed herein, especially the cobalt compounds, are particularly valuable for their anti-corrosion enhancing properties. The formation of acid compounds on the part of lubricating oils through oxidation in service causes corrosion of alloy bearing metals, e. g. copper-lead; such corrosion is also caused or accelerated by certain compounding agents frequently added to mineral oils to improve the engine performance. Hence, the present invention finds particular application by incorporating these novel metal compounds in a lubricating oil or other hydrocarbon composition which is normally corrosive to metals such as alloy bearing metals, etc.

Another advantage of this invention is that these metal compounds, especially the nickel compounds such as the nickel salt of tertiary amyl phenol thio-ether, have exceptionally high solubility in mineral oils, particularly in paraffinic oils in which many other types of metal compounds are relatively insoluble. Also, these novel mineral compounds are especially good for keep-

ing piston rings clean in an internal combustion engine and due to their non-corrosive or anti-corrosive properties, they can be used in oils containing substantial amounts of sulfur, either in the mineral oil itself or in some additive such as tertiary amyl phenol sulfide or corresponding disulfide, where other metal compounds would cause staining of copper and other metals. The nickel compounds of this invention are both non-corrosive and highly oil soluble, by reason of which properties lubricants to which these nickel compounds are added have new and unexpected properties and are adapted to obtain results never heretofore obtained.

These and other advantages of the invention will be still better understood from an examination of the following engine test data.

0.25% solution of various metal derivatives of tertiary amyl phenol thio-ethers such as prepared above under Examples 1 to 5, dissolved in mineral lubricating oil base stock were subjected to a number of oxidation and sludging tests and were subjected to a number of tests in the C. F. R. (Cooperative Fuel Research) engine for 15 hours at 390° F. After each run, the engine was taken down, inspected and rated by demerit (the lower, the better) according to the condition of the piston parts, valves, and cylinder. The demerit rating of the blank oil is represented as 100 and the reference rating of the blend is expressed as "per cent of reference" and is calculated as follows:

$$\text{Per cent of reference} = \frac{\text{Blend demerit times 100}}{\text{Blank oil demerit}}$$

The lower the "per cent of reference" the better is the oil according to this engine test. The results of these tests are reported in Table I.

TABLE I

	Test						
	1	2	3	4	5	6	7
	Blank	Nickel tertiary amyl phenol sulfide Cal. % NiO=18.0			Nickel methoxy tertiary amyl phenol sulfide	Nickel tertiary amyl phenol disulfide	Cobalt
		A	B	C			
Percent NiO.....		6.4	17.85	21.6			
Oxid. rate.....	56 74	16	86	114	145	32	48
	46 40	47	35	238	36	32	80
	30 35	18	28		27	18	48
	26 28	16	26		24	22	40
Average.....	40 44	24	44	176	58	26	54
C. F. R. eng. demerits:							
Percent ref.	100		28	13	30		9
Piston overall ..	3.51		1.44	0.57	1.54		0.41
Rings stuck	2		0	0	0		0
Carbon formed ..	4.2			0.56	1.41		0.17
Almen wts. carried	2	13					14

The blank oil used in the above test was an extracted paraffinic fraction obtained from a Mid-Continent crude, and was a lubricating oil base stock, the representative inspection of which is:

Gravity.....°A. P. I. 29
Flash point.....°F. 470
Fire point.....°F. 525
Vis./100° F.....68
Vis./210° F.....77
Carbon residue......24

The oxidation test referred to above comprises bubbling oxygen through a 10 gm. sample of the oil at a temperature of 200° C. (392° F.) and at a rate of 700 cc. per min. and determining the

amount of oxygen (measured in cubic centimeters) absorbed in successive 15-minute intervals.

The results of Table I show, most important of all, that in regard to the C. F. R. engine demerits, the nickel and cobalt compounds of this invention cause a very substantial improvement in the blank oil, tests 3, 4, 5 and 7 showing respectively a per cent of reference of 28, 13, 30 and 9, compared to 100 for the blank oil. As will be noted from the table, the improved results are attributable both to the prevention of ring sticking and reduction of carbon formation, thereby resulting in a much lower piston overall demerit rating than in the case of the blank oil. It will also be noted from the above table that, in spite of the fact that the metal additives used are compounds of metals which are well known to be great oxidation accelerators, the oxidation rate of the blank oil was not substantially raised in any case except in test 4 where the nickel compound used contained a substantial excess of nickel over the stoichiometric amount required to combine with the two hydroxyl groups in the tertiary amyl phenol thio-ether. It is also significant, on the other hand, that the oxidation rate of the blank oil was not lowered in any of the blends having a lower C. F. R. engine demerit rating than the blank oil (demerit ratings being lacking for the only two blends which showed a slight reduction in oxidation rate). Consequently, it is evident that the oxidation rate bears little if any relationship to the actual engine performance of a lubricating oil as measured by the engine demerit rating, and so this oxidation rate is relatively unimportant.

It should also be noted in the above Table I that both nickel and cobalt derivatives of tertiary amyl phenol thio-ether (tests 2 and 7) possess the property of increasing the load carrying capacity of the blank oil, since blends containing the nickel and cobalt compounds carry 13 and 14 weights, respectively, whereas the blank oil only carries 2 weights (the Almen test is made on the Almen pin test machine as described by Mougey and Almen in the Proceedings of A. P. I., 1931, page 277).

As explained previously, the invention has been found particularly useful for preparing Diesel engine lubricants by adding small amounts of the novel metal compounds of this invention to a Diesel engine lubricating oil base stock.

Such base stocks should, in general, have the following general characteristics:

	Limits	Preferred limits
Gravity.....°A. P. I.	1 15	1 19
Flash.....°F.	1 350	1 370
Fire.....°F.	1 400	1 420
Viscosity.....seconds Saybolt at 210° F.	40-95	50-80

¹ Minimum.

Inasmuch as the different types of Diesel engines operate under somewhat different conditions of speed, temperature, etc. and have different lubricating oil requirements owing to the different designs of the engine, some tests were made on a Caterpillar single cylinder Diesel engine and also on a Hercules Diesel engine.

In the Caterpillar Diesel engine test, four runs were made, No. 1 on a plain naphthenic oil A (Grade SAE 30), No. 2 a blend of that oil plus 0.5% of nickel tertiary amyl phenol sulfide, No. 3 the same oil base stock plus 0.5% of cobalt tertiary amyl phenol sulfide, and No. 4, another run somewhat similar to No. 3 but made at a later date and with the engine in somewhat different condition than during run No. 3. The results of these four tests run on the Caterpillar Diesel engine are recorded in Table II.

TABLE II

Test No.	Oil	Hours	Overall piston demerit	Demerits				
				Ring zone cleanliness grooves	Carbon	Skirt and liner	Varnish on skirt	Oil filter
1.....	Naphthenic oil A, S. A. E. 30.....	110	1.45	3.10	3.40	2.17	1.5	2.0
		242	1.96	4.33	3.87	2.92	2.0	4.0
		539	2.45	4.90	4.60	4.08	3.0	7.0
		109	1.20	3.10	3.40	1.08	1.0	1.0
2.....	Oil A+0.5% nickel salt ¹	246	1.33	3.10	3.30	1.33	1.0	3.0
		349	1.40	3.50	3.40	1.00	1.0	4.0
		113	1.07	2.70	3.30	0.80	0.6	1.0
		266	1.36	3.40	3.80	0.90	0.3	1.5
3.....	Oil A+0.5% cobalt salt ¹	515	1.61	4.40	4.00	0.90	1.0	3.0
		707	1.74	4.70	3.50	1.30	0.7	5.0
		985	2.04	5.80	3.70	1.30	1.5	6.0
		111	0.95	1.90	3.30	0.92	0.75	1.0
4.....	Oil A+0.5% cobalt salt ¹	267	1.33	3.40	3.40	1.21	1.00	1.5
		496	1.45	3.90	3.00	1.33	1.00	2.0

¹ Salt of tertiary amyl phenol sulfide.

The inspection record of the plain naphthenic oil base stock A used in test 1 and the blends containing the metal compounds used in tests 2, 3 and 4 are shown in Table IV further on.

In Table II the most important results are shown in column 2, namely, the overall piston demerit which is a single figure calculated to summarize the various demerits estimated for the different parts of the pistons, several of the more important of which are recorded in columns 3, 4, 5 and 6. Column 1 shows the number of hours of running of the engine up to the time when the particular observations recorded in columns 2 to 7 were made by stopping the engine and taking it all apart and examining the different parts. The great value of the invention will readily be seen by comparing the overall piston demerit of the blend used in tests 2, 3 and 4 with the overall piston demerit of the blank oil in test 1 for any particular corresponding number of hours of running. For example, it will be noted in column 1 that under tests 1, 2, 3 and 4 the first observations were made at 110, 109, 113 and 111 hours, respectively, and that these times of duration are very close together or substantially identical, and yet whereas

the plain oil had an overall piston demerit of 1.45 at the end of the first 110-hour running period, the blend containing the nickel salt (test 2) had an overall demerit of only 1.20 (83% of reference) and the two cobalt blends had overall demerits of 1.07 (74% of reference) and 0.95 (66% of reference), respectively, after the same period of running. This shows that the nickel and cobalt salts produce a marked improvement in the engine performance. That this improvement was not merely a temporary coincidence but was a true characteristic of the blend which persisted throughout the engine test, even after long running periods, is indicated by a comparison of other figures in column 2 for the different tests. For instance, after 539 hours of running, the plain oil in test 1 had an overall demerit of 2.45, whereas the blend containing the cobalt salts (test 3) had a demerit of only 2.04 after 985 hours (almost twice as long) and the cobalt salt blend in test 4 had an overall demerit of only 1.45 after 496 hours (almost equivalent to the 539 on the plain oil). For comparison with the nickel salt blend in test 2, after 349 hours of running, producing an overall piston demerit of 1.40, the overall demerit of the blank oil (test 1) for a corresponding length of time is found by interpolation (graphically from the rest of the data on test 1) to be about 2.20,

thus showing that also the nickel salts of the tertiary amyl phenol sulfide caused big improvement in the performance of this naphthenic oil base stock in the Caterpillar Diesel engine. For the sake of exact comparison, the overall piston demerit for each of the four tests, 1 to 4, at exactly the same number of hours of running, namely, 500, was estimated graphically by interpolation or extrapolation from the results in columns 1 and 2 of the above Table II, and are found to be as follows:

	Overall demerit at 500 hrs. ¹	Per cent of reference
1 Plain oil.....	2.40	100
2 Plain oil+nickel salt.....	1.50	62
3 Plain oil+cobalt salt.....	1.59	66
4 Plain oil+cobalt salt.....	1.46	61

¹ As estimated graphically by interpolation or extrapolation.

Thus it is apparent that the superiority of the blends prepared according to this invention becomes relatively even greater where the engine tests are continued for a longer period of time.

In the Hercules Diesel engine tests, two runs

were made, No. 1 being a plain naphthenic oil B (S. A. E. 40) and No. 2 a blend of that same oil containing 0.5% of cobalt tertiary amyl phenol sulfide. These Hercules Diesel engine tests were both run for 84 hours and the results are reported in Table III.

TABLE III
84 hour Hercules Diesel engine tests

Oil	Test run No.—	
	1 Naphthenic oil B (S. A. E. 40)	2 Oil B+0.5% cobalt tertiary amyl phenol sulfide
Demerits of engine:		
Overall demerit.....	2.06	1.71
Sludge.....	1.92	1.86
Valves.....	1.64	1.64
Piston skirts.....	1.91	0.50
Crankshaft.....	1.50	0.50
Rings and grooves (composite rating).....	2.45	1.85
Compression rings.....	2.75	2.56
Oil rings.....	1.83	0.42
Oil filter.....	7.0	7.0
Bearing corrosion loss (gm.) ¹	0.066	0.061

¹ Total weight loss (gm.) from six copper-lead connecting-rod bearings.

Table III shows that after 84 hours of running in the Hercules Diesel engine the plain naphthenic oil B had an overall demerit of 2.06, whereas the blend containing 0.5% of cobalt tertiary amyl phenol sulfide according to the present invention (test 2) had an overall demerit of only 1.71, which shows a very distinct improvement in engine performance. It will also be noticed from the last line in this Table III that the addition of the cobalt salt to the naphthenic oil did not cause any increase in the bearing corrosion loss. This is a very important fact, because usually heretofore practically all addition agents which were effective in improving the engine performance of lubricants for Diesel engines caused a very serious increase in the bearing corrosion loss of copper-lead connecting rod bearings as well as other alloy bearings.

The inspection record of the naphthenic oil B alone and together with the addition of 0.5% of cobalt tertiary amyl phenol sulfide used in these two Hercules engine tests, are shown in Table IV.

TABLE IV

Type of sample	Inspection record of—				
	Caterpillar tests			Hercules tests	
	Naphthenic oil A S. A. E. 30	Oil A+0.5% nickel salt ¹	Oil A+0.5% cobalt salt ¹	Naphthenic oil B S. A. E. 40	Oil B+0.5% cobalt salt ¹
Grav.....°A. P. I.....	22.8	22.7	22.0	21.9	21.7
Flash.....°F.....	405	405	410	420	420
Fire.....°F.....		480	455		
Vis./100° F.....	514.0	537.5	527.5	774	773.5
Vis./210° F.....	55.7	56.6	55.6	62.6	63.3
V. I. (viscosity index).....	39	41	33	25	30
Pour.....°F.....	-10	-10	-5	-15	-15
Carbon residue.....per cent.....	0.05	0.30	0.27	0.07	0.38
Sulfur.....do.....	0.25				
Neutralization No.....	0.05	0.14	0.17		
Saponification No.....	0.07	0.56	0.69		

¹ Salt of tertiary amyl phenol sulfide.

Oils compounded with nickel and cobalt derivatives of tertiary amyl phenol sulfide were also tested in a Caterpillar engine equipped with a copper-lead connecting rod bearing, to determine

their suitability for use in engines equipped with such sensitive alloy metal bearings. In this test very severe conditions were imposed (atmospheric temperature 125° F., bearing temperature 210° F., and oil temperature 195–210° F.) to simulate the most severe conditions which could be encountered in regular field operations. Neither the nickel tertiary amyl phenol sulfide blend nor the corresponding cobalt salt blend showed any greater tendency to corrode copper-lead bearings than did the uncompounded oil. The results of these tests are recorded in Table V.

TABLE V

15 High temperature Caterpillar engine copper-lead bearing corrosion tests

Oil	Hours	Weight loss (grams) from copper-lead bearing weighing approx. 650 grams
Naphthenic oil A (S. A. E. 30).....	60	0.037
Oil A+0.5% cobalt salt ¹	60	0.029
Oil A+1.0% nickel salt ¹	60	0.018
Oil A+1.0% nickel soap of a fatty acid.....	60	5.689

¹ Salt of tertiary amyl phenol sulfide.

Similar tests were made on an oil compounded with 0.5% of the same cobalt salt in a Caterpillar engine equipped with a cadmium-silver connecting rod bearing. Again no corrosion was experienced; the results are recorded in Table VI.

TABLE VI

35 High-temperature Caterpillar engine cadmium-silver bearing corrosion tests

Oil	Hours	Weight loss (grams) from cadmium-silver bearing weighing approx. 650 gms.
Naphthenic oil A (S. A. E. 30).....	60	0.011
Oil A+0.5% cobalt salt ¹	120	0.021
Oil A+1.0% nickel soap of a fatty acid.....	60	0.014
	120	0.027
	60	4.143

¹ Salt of tertiary amyl phenol sulfide.

² Total.

For the sake of comparison with the valuable

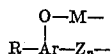
and significant result discussed above in connection with Tables V and VI, corresponding results are also shown for a blend of the same lubricating oil base stock containing 1.0% of a nickel

fatty acid soap. As indicated in Tables V and VI, these nickel soap blends caused an exceedingly great corrosion loss of both the copper-lead and the cadmium-silver bearings. This emphasizes the extreme value of the present invention which provides nickel and cobalt salt, which effects a great improvement in engine performance of Diesel engine lubricants, but without at the same time causing any substantial increase in bearing corrosion loss.

This invention is not to be limited to any of the specific examples presented herein, which were given solely for the purpose of illustration, nor by any theory as to the mechanism of the operation of the invention, but only by the following claims in which it is desired to claim all novelty inherent in the invention as far as the prior art permits.

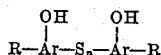
We claim:

1. A lubricant comprising a major proportion of mineral lubricating oil and a small amount of a compound containing at least one grouping having the general formula:



wherein M is a metal of group VIII, series 4, of the Mendeleeff Periodic Table, Ar is an aromatic nucleus, R is an aliphatic hydrocarbon substituent having a sufficient number of carbon atoms to insure solubility of the compound in mineral oils, Z is an element of the sulfur family and n is an integer of 1 to 5.

2. A lubricant comprising a major proportion of a viscous oil and a small amount of an oil-soluble compound selected from the group consisting of cobalt and nickel derivatives of organic compounds having the general formula:



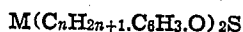
Ar is an aromatic nucleus, R is an alkyl of at least four carbon atoms, n is an integer of from 1 to 5 and in which the metal replaces at least part of the hydroxyl hydrogen.

3. A lubricant comprising a major proportion of mineral lubricating oil and a small amount of a compound having the general formula:



in which M is a metal selected from the group consisting of cobalt and nickel, R is an alkyl substituent in the aromatic nucleus, Ar, containing at least 4 carbon atoms per alkyl radical, S is also substituted in the aromatic nucleus, and n is an integer of 1 to 5 and in which the sulfur is linked directly to two aryl nuclei and in which M is linked directly to the oxygen atoms.

4. A lubricating comprising a major proportion of a mineral lubricating oil and a small amount of a compound having the general formula:



where M is a metal of group VIII, series 4 of the Mendeleeff Periodic Table and n is an integer of at least 4, and in which the said sulfur atom (S) is directly linked to each of the two said aryl nuclei (C_6H_3) and in which the two said oxygen atoms (O) are both linked directly to the said metal atom (M).

5. A lubricating comprising a major proportion

of a mineral lubricating oil and a small amount of an oil-soluble cobalt salt of compounds having the general formula $(\text{C}_n\text{H}_{2n+1}\text{C}_6\text{H}_3\text{O})_2\text{S}$, where n is an integer of at least 4.

6. A lubricant comprising a major proportion of a mineral lubricating oil and a small amount of an oil-soluble nickel salt of compounds having the general formula $(\text{C}_n\text{H}_{2n+1}\text{C}_6\text{H}_3\text{O})_2\text{S}$, where n is an integer of at least 4.

7. A lubricant comprising a major proportion of a mineral lubricating oil and a small amount of an oil-soluble compound selected from the group consisting of cobalt and nickel salts of alkyl phenol sulfide said alkyl radicals each containing at least four carbon atoms.

8. Lubricant according to claim 7, in which the compound is a cobalt salt of an alkyl phenol sulfide.

9. A lubricant comprising a mineral oil base stock and a small amount of an oil-soluble metal salt whose metal is of group VIII, series 4, of the Mendeleeff Periodic Table of the reaction product of a sulfur halide with an alkylated aryl compound having a hydroxy group attached directly to the aryl nucleus.

10. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil miscible sulfide of an alkyl substituted aryl metal oxide in which the oxygen of the metal oxide group is directly attached to the aryl nucleus and in which at least two alkyl substituted aryl nuclei are interconnected by at least one atom of sulfur, and in which said metal is a metal of group VIII, series 4, of the Mendeleeff Periodic Table.

11. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil miscible sulfide of an alkyl substituted aryl cobalt oxide in which the oxygen of the cobalt oxide group is directly attached to the aryl nucleus and in which at least two alkyl substituted aryl nuclei are interconnected by at least one atom of sulfur.

12. An improved mineral oil composition comprising a mineral oil having admixed therewith a minor proportion of an oil miscible sulfide of an alkyl substituted aryl nickel oxide in which the oxygen of the nickel oxide group is directly attached to the aryl nucleus and in which at least two alkyl substituted aryl nuclei are interconnected by at least one atom of sulfur.

13. A lubricant comprising a mineral lubricating oil and a small amount of an oil-soluble sulfide of a metal alkyl phenolate in which a plurality of phenol groups are attached to a single metal atom and in which said metal is a metal of group VIII, series 4, of the Mendeleeff Periodic Table.

14. A lubricant composition according to claim 13 in which the said metal is cobalt.

15. A lubricant composition according to claim 13 in which the said metal is nickel.

16. A lubricating oil composition comprising a major amount of a hydrocarbon lubricating oil and a minor amount of the metal salt of an oil-soluble aliphatic substituted phenol sulfide, each aliphatic radical containing at least four aliphatic carbon atoms, the metal being of group VIII, series 4, of the Mendeleeff Periodic Table.

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