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3,236,772

LUBRICATING COMPOSITIONS

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This invention relates to lubricating compositions of improved stability, their methods of preparation and uses. Particularly, the invention relates to lubricating oil compositions of improved oxidation stability, which compositions include oil-soluble organo-tin compounds containing at least one carbon-tin bond per molecule, in combination with metal alkyl phenate sulfide detergent additives.

Metal phenates and thiophenates are well-known additive materials for lubricating oils, particularly crankcase oils. These materials improve various properties of internal combustion engine lubricants, particularly from the standpoint of detergency properties to promote engine cleanliness. Such additives have also met with particular success in railway diesel engine lubricants where other conventional additives, which may be satisfactory for other applications, have not proved successful, partly because of the relatively high operating temperatures. In addition, one major problem is that the steel-backed silver bearings customarily used in railway diesel engines are highly susceptible to wear and corrosion. The metal alkyl phenate sulfide additives which have been developed for utilization in heavy duty diesel engine lubrication provide acceptable limits for silver corrosivity and lubricity.

However, while the metal alkyl phenate sulfide additives are generally effective in promoting engine cleanliness and in reducing wear and corrosion, various other factors are also to be considered in an evaluation of heavy duty lubricants. Among such factors may be included viscosity and alkalinity retention, which factors are generally directly related to the oxidation stability of the lubricant. Optimization of the above-mentioned factors will generally determine customer acceptance of the additive and the lubricant. Ordinarily, there are predetermined criteria, such as oil viscosity, pH, base number, etc., which criteria generally indicate when the oil is to be replaced and discarded. There is, therefore, a constant demand for lubricants of increased oxidation stability which will exhibit higher viscosity and alkalinity retention and, at the same time, satisfy the stringent requirements for engine cleanliness, wear reduction, and corrosion protection. In this regard, the conventional antioxidants, such as phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, 4,4'-methylene bis (2,6-ditertiary butyl phenol), and octylated diphenylamines, which have generally proved successful in conventional lubricating compositions for automotive, aviation and stationary engine applications, exhibit little, if any, antioxidant properties in lubricating compositions containing a metal alkyl phenate sulfide as a major additive.

It has now been surprisingly discovered that the inclusion of an oil-soluble organo-tin compound containing at least one carbon-tin bond per molecule, preferably at least two per molecule, either used alone or in combination with other antioxidants, will substantially improve the oxidation stability of metal alkyl phenate sulfide-containing lubricating compositions.

It should be understood that the present invention does not contemplate the use of such oil-soluble organo-tin compounds as the sole additives, or in combination with other additives in lubricating oil compositions which do not contain the metal alkyl phenate sulfide type additives. It is realized that organo-tin compounds have been used previously in lubricating oil compositions. For example, British Patent 833,873 discloses a lubricating oil composition containing an oil-soluble halogen-containing organic compound and an oil-soluble organo-tin compound having at least one carbon-tin bond in the molecule, which composition exhibits improved corrosion resistance to ferrous surfaces due apparently to the absorption of excess chlorine by the carbon-tin bond. The present invention, however, is primarily concerned with the surprising interaction between such organo-tin compounds and metal alkyl phenate sulfide type compounds in lubricating oil compositions, which interaction markedly improves the oxidation stability of said compositions.

The lubricating oil compositions of this invention are, as hereinbefore indicated, particularly suitable for the lubrication of railway diesel engines. However, they are equally applicable for use in other internal combustion engines, such as aviation, automotive, marine, stationary and auxiliary power engines, as well as in other applications wherein the metal alkyl phenate sulfide type additives may be advantageously utilized. Among such other applications may be included extreme pressure lubricants, engine flushing oils, industrial oils, general machinery oils, process oils, rust preventive compositions, greases, etc.

In general, the compositions of the present invention will comprise a major proportion of a lubricating oil base stock; a minor proportion of the metal alkyl phenate sulfide additive, e.g., about 0.5 to 20, preferably about 1.0 to 15 wt. percent, more preferably 1.0 to 10 wt. percent, based on the weight of the total composition; and an amount of the organo-tin compound sufficient to improve the oxidation stability of the lubricating composition. Particularly, the organo-tin compound may be present in an amount within the range of 0.2 to 25 wt. percent of said metal alkyl phenate sulfide, corresponding to a range of 0.01 to 5 wt. percent based on the weight of the total composition. A particularly preferred range for the organo-tin compound will be 0.1 to 1.0 wt. percent, based on the weight of the total composition. While the amount of the organo-tin compound will usually be within the range of 0.2 to 25 wt. percent of the metal alkyl phenate sulfide additive, it should be understood that larger amounts of the additive may be used for some purposes. Thus, the exact amounts of the two principal additives will depend upon the particular compounds utilized, the nature of the lubricating oil base stock and the general operating conditions of the engine in which the lubricant is to be employed.

It is often convenient to prepare concentrates of the additives in oil, with the concentrate later being added to a suitable base oil to give a final composition containing the above percentages of additive. Suitable concentrates will contain about 25 to 74.5 wt. percent oil, about 25 to 74.5 wt. percent of the metal alkyl phenate

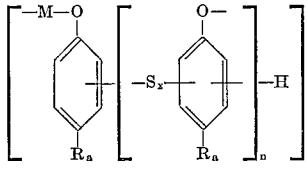
sulfide additive, and about 0.5 to 35 wt. percent of the organo-tin compound.

The lubricating oil base stocks used in the compositions of this invention may be mineral lubricating oils. For the lubrication of certain low and medium speed diesel engines, the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 75. In other types of diesel service, particularly with high speed diesel engines, and in aviation engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index. For railroad diesel engines, a lubricating base stock will generally have a viscosity within the range of 75 to 85 SUS at 210° F. and a viscosity index within the range of 55 to 80.

In addition to the materials to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat-thickened fatty oils, sulfurized fatty oils, other organometallic compounds, metallic or other soaps, sludge dispersants, detergents (e.g., petroleum sulfonates), antioxidants, thickeners, silver corrosion inhibitors, viscosity index improvers, oiliness agents, etc.

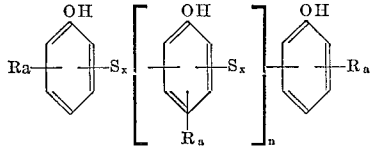
The preparation of the above-described compositions may be generally accomplished by simple admixture of the ingredients into the lubricating oil in the desired proportions.

The metal alkyl phenate sulfides used as oil additives and their preparation are well known to the art. They have been described in numerous patents, for example, U.S. 2,451,345 and U.S. 2,362,289–93. The more important of these materials are typified by the following formula:



wherein M represents the metal, R the alkyl group, x is generally 1 to 5, a is 1 to 4, and n is generally 1 to 6. The metal may be aluminum, cobalt, chromium, magnesium, sodium, tin, etc., or the alkaline earth metals as calcium, barium, strontium and magnesium. The alkyl portion generally contains 5 to 20, e.g., 7 to 12 carbon atoms, either straight or branched chain. Specific examples of these materials include barium tertiary octyl phenol sulfide, calcium tertiary octyl phenol sulfide, barium-calcium tertiary octyl phenol sulfide, barium tertiary amyl phenol sulfide, calcium tertiary amyl phenol sulfide, barium nonyl phenol sulfide, calcium nonyl phenol sulfide, etc.

It should be understood that generally, throughout this specification and the appended claims, the term "metal alkyl phenate sulfide" is meant to include not only the metal derivatives of the monosulfides but also of the di- and polysulfides, as well as the polymers of alkyl phenol sulfides. The polymers of alkyl phenol sulfides may be represented structurally by the formula:



wherein R, a, n and x have the meanings given above. Although the reaction of an alkylated phenol with a sulfurizing agent such as sulfur dichloride (SCl_2) will give essentially an alkyl phenol monosulfide, varying amounts of polysulfides and of polymeric materials of the above type will also be formed.

The metal alkyl phenate sulfides are readily prepared by (1) treating an alkyl phenol, e.g., nonyl phenol, with sulfur dichloride according to the teachings of U.S. Patent 2,362,289–93 or by other methods familiar to those skilled in the art, to form a branched alkyl phenol having the above general formula; and (2) reacting the resulting branched alkyl phenol with a desired metal base to form the metal salt. Nonyl phenol sulfide is particularly preferred because of its easy availability and the fact that the length of the alkyl chain seems to be the optimum for detergency and inhibitor effects. Useful metal bases may be in the form of a metal oxide, hydroxide, sulfide, alkoxide, hydride, or carbide of calcium, barium, strontium, magnesium, and the like. The alkaline earth metal compounds are particularly preferred, and of these the calcium and barium compounds are most useful.

In general, while the use of a barium base in the above-described procedure easily accomplishes an essentially complete conversion to the barium metal salt, it has proved difficult to prepare satisfactory salts of sulfur bridged alkyl phenols containing solely calcium metal. Thus, it has been observed that the reaction with barium base goes easily to completion converting essentially about 100% of the phenol groups into the barium metal derivatives. However, for some unknown reason it is extremely difficult to convert all the phenolic groups into the calcium metal derivative using the above-described procedure. This phenomenon is disadvantageous since for many additive uses, such as detergents and detergent-inhibitors, a high ratio of metal to bridged alkyl phenol is particularly desirable. In order to obtain suitable salts containing at least some calcium, one procedure has been to react the bridged phenol with a calcium base to convert as many of the phenolic groups into the metal derivatives as possible, followed by completion of the reaction with a barium metal base. This type of combination barium-calcium metal salts of alkyl bridged phenols has found great acceptance for use as additives, particularly for use in formulating lubricants for diesel engines, especially railroad diesel engines.

It has furthermore been recently discovered that by utilizing a modified procedure with certain reactants and conditions, calcium salts of bridged alkyl phenols may be obtained in which essentially 100% of the phenolic groups have been converted into calcium derivatives. Such salts are to be desired from an economical standpoint in that the calcium is less expensive than barium. Additionally it has been found that calcium-containing additives have lower ash contents, and, in some engines, result in decreased deposit conditions as compared to barium-containing additives.

Briefly, an all-calcium salt of a bridged phenol may be prepared by reacting a reaction product of a calcium base, e.g., $Ca(OH)_2$ and hydrogen sulfide, with the bridged alkyl phenol. The reaction between the reaction products and the bridged alkyl phenol is generally carried out at temperatures of about 0° to 150° F., e.g., 50° to 150° F., for about 10 to 120 minutes, e.g., 20 to 80 minutes. It is believed that the major reaction product obtained in the reaction between $Ca(OH)_2$ and H_2S is $Ca(SH)_2$. When the product is crystallized, the formula is $Ca(SH)_2.6H_2O.Ca(SH)_2$ tends to decompose upon exposure to air but is quite soluble in water or alcohol. The preferred method of carrying out the reaction between $Ca(SH)_2$ and an alkyl phenol is, therefore, to employ a polar solvent containing hydroxy substituents such as water or a C_1–C_6, e.g., C_1–C_3, aliphatic monohydroxy alcohol or a mixture of water and the aforementioned alcohols. The solvent can be removed by suitable methods, such as distillation, at the end of the reaction and the product can be further thoroughly dried by blowing with an inert gas at an elevated temperature. It is not essential that all the solvent be removed. As much as 10 wt. percent can remain, but it is preferred that the solvent concentration be reduced

to 2 wt. percent or below. Such inert gases may be argon, neon, light hydrocarbon gases, CO and preferably N_2. After blowing, the product may be further purified by filtration with conventional filter aids such as Hyflo (a diatomite).

The calcium hydrosulfide ($Ca(SH)_2$) can be conveniently prepared by bubbling H_2S in a solution of the hydroxy-containing polar solvent and $Ca(OH)_2$. The $Ca(OH)_2$ may be dispersed in any quantity up to and exceeding its solubility in the hydroxy-containing polar solvent. $Ca(OH)_2$ is sparingly soluble at ambient or elevated temperatures in alcohol and water; however, solubility can be increased by lowering the temperature of the solvent. When relatively large yields of $Ca(SH)_2$ are desired a milk of lime suspension can be used. This suspension has more $Ca(OH)_2$ present than will dissolve. After the reaction mixture is H_2S saturated, it is preferably filtered, although it can be used as is, since $Ca(SH)_2$ is much more soluble than $Ca(OH)_2$.

An alternative method of obtaining $Ca(SH)_2$ is by the hydrolysis of CaS, i.e.,

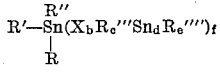
$$2CaS+2H_2O\rightarrow Ca(SH)_2+Ca(OH)_2.H_2S$$

can be bubbled through this reaction mixture to obtain a greater yield of the $Ca(SH)_2$.

Alternatively, the calcium salt of the bridged phenol can be prepared in situ. Thus, calcium base, e.g. calcium hydroxide, a polar solvent having a hydroxy substituent, e.g. methonol and a bridged alkyl phenol, may be slurried together in the desired proportions and H_2S bubbled through the slurry.

It is to be understood that the above procedures may be utilized to convert a bridged alkyl phenol having totally unreacted phenolic groups or partially reacted phenolic groups which have already been converted to a metal salt derivative. It is to be further understood that the present invention contemplates the use of metal salts of alkyl phenol sulfides wherein the penolic groups have been totally or partially converted to any of the aforementioned salts and particularly to the barium and/or calcium salts and mixtures thereof in accordance with the procedures hereinbefore described.

The organo-tin compounds which are used in accordance with the present invention are those organo-tin compounds which contains at least one carbon-tin bond per molecule, preferably at least two per molecule, and also contain a total of 3 to 90, preferably 6 to 60, and more preferably 6 to 40, carbon atoms. The above compounds will generally have structures within the following general formula:



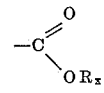
wherein the tin atoms may be either divalent or tetravalent; R, R', R'' and R'''' can be the same or different hydrocarbyl radicals of 1 to 20, e.g., 2 to 20, carbon atoms, which hydrocarbyl radicals can be substituted or unsubstituted, alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkaryl, aralkyl, etc. radicals; R and R' can also be ester groups, i.e.



wherein R_x is a C_1 to C_{30} alkyl radical identical with or different than R; R''' can be a substituted or unsubstituted C_1 to C_{30} divalent hydrocarbon radical such as methylene, ethylene, 9,10-dihydro-9,10-anthrylene, etc. radicals; R'''' can also be hydrogen, a C_1 to C_{30} acyl radical, i.e.



an ester group, i.e.,

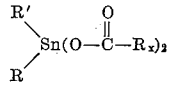


wherein R_x is a C_1 to C_{30} alkyl radical identical with or different than R, etc.; X can be oxygen or sulfur; a is 0 to 2; b, c and d are 0 to 1; e is 0 to 3; f is 0 to 2; the sum of a and f being zero when said tin atoms are divalent and two when said tin atoms are tetravalent; and when $d=1$, then $b=0$, $a+f=2$, and $c+e=4$.

Suitable substituents include ether groups, ester groups, aldehyde groups, ketone groups, oxides and halogens.

Representative classes of oil-soluble organo-tin compounds embraced by the above general formula include the following:

(1)



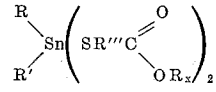
A particular example within this class is dibutyl tin dilaurate, wherein R and R' are butyl radicals and R_x is an undecyl radical.

(2)



A particular example within this class is dibutyl tin sulfide, wherein R and R' are butyl radicals.

(3)

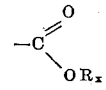


A particular example within this class is dibutyl bis (isooctyl mercaptoacetate) tin, wherein R and R' are butyl radicals, R''' is a methylene radical and R_x is an isooctyl radical.

(4)



An example within this class is stannous octoate wherein R and R' are ester groups of the form



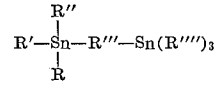
R_x being an octyl radical.

(5)



An example within this class is dibutyl (9,10-dihydro-9,10-anthrylene) tin wherein R and R' are butyl radicals, and R''' is a 9,10-dihydro-9,10-anthrylene divalent radical.

(6)

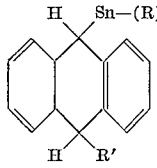


An example within this class is 9,10-bis(tributyl stannyl)-9,10-dihydroanthracene, wherein R''' is a 9,10-dihydro-9,10-anthrylene divalent radical and all other R's are butyl radicals.

Within the above general formula, and as particularly exemplified by classes 5 and 6 are included various groupings of recently discovered organo-tin compounds, which compounds are based on the 9,10-dihydro-9,10-anthryl-

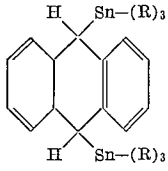
ene radical. These compounds may be represented by the following formulas:

(A)



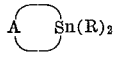
wherein R′ is selected from the group consisting of hydrogen, C_1 to C_8 alkyl radicals and C_6 to C_{10} aryl radicals; and R is a C_1 to C_{20} hydrocarbyl radical.

(B)

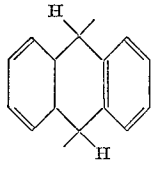


wherein R is a C_1 to C_{20} hydrocarbyl radical.

(C)

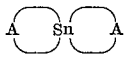


wherein A⌒ represents the 9,10-dihydro-9,10-anthrylene radical, i.e.,

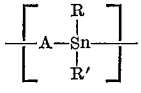


two bonds of the tetravalent tin atom are joined to the unsatisfied bonds of the anthrylene radical; and R is a C_1 to C_{20} hydrocarbyl radical.

Also included with the scope of the present invention will be compounds having the formula:



wherein A⌒ represents the 9,10-dihydro-9,10-anthrylene radical; and polymers of the above compounds having repetitive monomeric units of the formula:

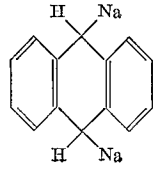


wherein A represents the 9,10-dihydro-9,10-anthrylene radical and R and R′ are selected from the group consisting of C_1 to C_{20} hydrocarbyl radicals and halogen.

Typical examples of such organo-tin compounds are 9,10-bis(tributyl stannyl)-9,10-dihydro anthracene, 9,10(dibutyl stannyl)-9,10-dihydro anthracene, dimethyl-9,10-dihydro-9,10-anthrylene tin, diphenyl-9,10-dihydro-9,10-anthrylene tin, 9,10-dihydro-9,10-anthrylene tin dichloride, bis(9,10-dihydro-9,10-anthrylene) tin, etc.

While the above classes of anthracene-tin compounds are not to be considered a subject of the present invention, their general preparation will now be described for purposes of completeness.

An alkali metal adduct of anthracene is formed by contacting an alkali metal, e.g. sodium or potassium, with anthracene under anhydrous conditions and in an oxygen-free atmosphere. The most preferred adduct is 9,10-dihydro-9,10-disodioanthrylene having the formula:



The above adduct is contacted with a Group IV–A metal halide having the general formula:

$$R_nSnX_{4-n}$$

wherein R is a hydrocarbyl radical, X is a halogen atom and *n* is an integer from 0 to 3. Preferably, the hydrocarbyl radicals are C_1 to C_{20} alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkaryl and aralkyl radicals; however, organometallic halides containing higher molecular weight hydrocarbyl radicals may similarly be employed. As to the halogen of the tin-containing reactant, either fluorides, chlorides, bromides or iodides are suitable; however, the chlorides are to be preferred since they are considerably less expensive.

The reaction is carried out with efficient mixing, and preferably under anhydrous conditions under an inert atmosphere, e.g., dry nitrogen. The reaction is exothermic and it is desirable to provide means for removing excess heat, especially during the initial stages of the reaction. In general, a reaction temperature in the range of 0° to 150° C. is suitable, the particular temperature for any given reaction being largely dependent upon the reactivity of the particular reactants and the ease of formation of the desired product. Conveniently, the temperature of the reaction is the reflux temperature of the reaction mixture, provided, of course, such temperature does not exceed the decomposition temperature of the reactants and/or products. An inert solvent, i.e., one which is not consumed during the course of the reaction, is preferably employed to aid in the control of reaction temperature. Suitable solvents include the saturated aliphatic and aromatic hydrocarbons, dialkyl ethers, cyclic ethers such as tetrahydrofuran and tetrahydropyran and polyalkylene glycol diethers. The cyclic ethers and polyalkylene glycol diethers are especially preferred solvents.

Generally, a molar ratio of the tin halide to alkali metal adduct of between 0.5 to 2:1 is used in the process; however, lesser or greater molar ratios may be employed, if so desired. Preferably, the quantity of each reactant is in accordance with the stoichiometry of the particularly reaction desired. Except where the tetrahalides are employed, the order of addition of the reactants is not important. When tetrahalide is added to an excess of the alkali metal adduct, the anthrylene derivative A⌒Sn⌒A is preferentially formed. Variations in pressure do not significantly affect the course or rate of the above reaction; hence, the process is generally carried out at substantially atmospheric pressures although this is not essential.

While the above compounds have been described with reference to the unsubstituted 9,10 - dihydroanthrylene divalent radical for purposes of simplicity, it will be apparent to those skilled in the art that the 1-, 2-, 3-, 4-, 5-, 6-, 7-, and 8-carbons of the radical may also be substituted with groups that are unreactive both with the reactants and the products of the described process. Thus, the 9,10-dihydroanthrylene radical may be substituted in the 1-, 2-, 3-, 4-, 5-, 6-, 7-, or 8-position by one or more C_1 to C_8 alkyl radicals or similarly unreactive hydrocarbon radicals, alkoxy radicals and the like without substantially affecting the character of the divalent radical. Hence, the present invention contemplates the use of such substituted radicals in place of 9,10-dihydroanthrylene radical per se.

The invention may be further understood by reference to the following examples, which are given for illustrative purposes only and are not to be construed as limiting the scope of the invention in any way.

EXAMPLE 1

Preparation of metal alkyl phenate sulfide additives

Nonyl phenol sulfide was prepared by conventionally alkylating phenol with propylene trimer and bridging by

means of sulfur dichloride as taught, for example, in U.S. 2,785,131. The nonyl phenol sulfide was obtained in the form of a 70 wt. percent active ingredient in a hydrocarbon oil having a viscosity of about 90 SUS at 100° F. This blend was further diluted with a phenol extracted paraffinic neutral oil of 150 SUS viscosity at 100° F. to a final concentration of 41 wt. percent active ingredient. The final nonyl phenol sulfide blend was then converted to a calcium nonyl phenate sulfide according to the following procedure.

Phenate additive A

Additive A was prepared by heating 169.4 parts of the above nonyl phenol sulfide oil (41 wt. percent concentration) blend to about 140° F. At this temperature, 14.6 parts of a blend of 91 vol. percent isopropanol and 9 vol. percent water was added to the nonyl phenol sulfide oil blend with stirring. 8.2 parts of calcium hydroxide $Ca(OH)_2$ was then added to the mixture over a period of about 10 minutes. The resulting mixture was then heated to about 250° F. and aged at that temperature for an additional 30 minutes to substantially remove all the alcohol/water solvent. The resulting slurry was then filtered with a filter aid to obtain about 165 parts of a calcium nonyl phenate sulfide product which contained 2.4 wt. percent Ca and 4.4 wt. percent S. The product represented about an 80% conversion of the phenolic groups to the calcium derivative. The final product was used as a 45 wt. percent active ingredient in a neutral mineral oil.

Phenate additive B

A $Ca(SH)_2$ solution was prepared by blending 9.9 parts of calcium hydroxide with 52 parts of methanol which was stirred and saturated with H_2S, and then filtered. 20 parts of the $Ca(SH)_2$ solution was mixed with 160 parts of the nonyl phenol sulfide oil blend (41 wt. percent active ingredient) at a temperature of 120° F. The resulting mixture was then refluxed at a temperature of about 150° F. The alcohol was then distilled off and the mixture dried by N_2 blowing at 300° F. The reaction mixture was then filtered to yield a final product containing 3.0 wt. percent Ca and 4.2 wt. percent S which represented about a 100% conversion of the phenolic groups to calcium. The final product was used as a 45 wt. percent active ingredient in a neutral mineral oil.

Phenate additive C

Additive C was prepared exactly like Additive A except methanol was used as the solvent and the proportions of reagents were as follows: 44.5 parts nonyl phenol sulfide oil (70% concentration), 16 parts of phenol extracted paraffinic neutral oil of 150 SUS viscosity at 100° F., 33.5 parts of methanol and 6.1 parts of calcium hydroxide $Ca(OH)_2$. The resulting calcium nonyl phenate sulfide product contained 3.4% calcium. The final product was used as a 50% active ingredient in a neutral mineral oil.

Preparation of the compositions of the invention

Various lubricating oil compositions were prepared by dissolving by simple mixing metal salt of alkyl phenol sulfide and oil-soluble organo-tin compound containing at least one carbon-tin bond, into a suitable lubricating oil base stock. These compositions included lubricating oil base stocks, X, Y, and Z, phenate additives A, B, and C, and organo-tin compounds J, K, L, M, N, and O.

Lubricating oil base stocks

Base stock X was a mildly hydrofinished phenol extracted Tia Juana oil having viscosities of 1047 SUS at 100° F. and 79.8 SUS at 210° F. It had a viscosity index (Dean-Davis) of 72, a sulfur content of 1.05 wt. percent, a specific gravity of 24.6° API, and a pour point of +20° F.

Base stock Y was a phenol extracted clay finished Tia Juana oil having viscosities of 1033 SUS at 100° F., and 79.2 SUS at 210° F. It had a viscosity index of 71, a sulfur content of 1.13 wt. percent, a specific gravity of 24.6° API and a pour point of +10° F.

Base stock Z was a severely hydrofined phenol extracted coastal distillate having viscosities of 1049 SUS at 100° F. and 78.4 SUS at 210° F. It had a viscosity index of 67.0, a sulfur content of .07 wt. percent, a specific gravity of 24.9° API, and a pour point of +15° F.

Organo-tin compounds

Compound J was dibutyl tin dilaurate.

Compound K was dibutyl tin sulfide.

Compound L was dibutyl bis (isoctyl mercaptoacetate) tin supplied by Metal & Thermit Corporation under the trade name Thermolite 31.

Compound M was dibutyl (9,10-dihydro-9,10-anthrylene) tin.

Compound N was dibutyl tin laurate-maleate supplied by Metal & Thermit Corporation under the trade name Thermolite 25.

Compound O was stannous octoate supplied by Metal & Thermit Corporation under the trade name Catalyst T-9.

Compound M, the dibutyl-(9,10-dihydro-9,10-anthrylene) tin was prepared by the following procedure.

To a tetrahydrofuran solution containing 0.25 mole of 9,10-disodioanthracene (prepared by simple mixing at room temperature of 0.25 mole of anthracene, 0.5 g. atom of sodium, and 400 ml. of tetrahydrofuran) was added 0.25 mole of dibutyl tin dichloride dissolved in 150 ml. tetrahydrofuran over a period of 5.5 hours. The mixture was heated to reflux at about 69° C., for one hour and then allowed to cool to room temperature. To destroy excess sodium, 25 ml. of isopropanol was added and then 150 ml. of water. The reaction mixture separated into an aqueous layer, a white powder, and a yellow solid. The white powder and the yellow solid were each recrystallized from benzene. The former was found to be polymeric, having a melting point in excess of 300° C. and dissolving in CCl_4 with an appreciable viscosity increase. The latter yielded yellow crystals which melted and then polymerized at 225° to 235° C. to produce a polymer. The yellow crystals were identified as dibutyl-(9,10-dihydro-9,10-anthrylene) tin by molecular weight determination and tin analysis.

The final compositions are indicated below, together with oxidation stability data.

Stability performance of the compositions of the invention

Several test lubricant compositions containing the ingredients described above were subjected to a Lubricant Stability Test and a Silver-Steel Lubricity Test. The Lubricant Stability Test involves heating the lubricant to 340° F. in the presence of a Cu-Pb oxidation catalyst while intimately mixing with air. The viscosity increases in terms of Saybolt Seconds Universal after 19 and 23 hours, and the retained pH are used to determine the stability of the lubricant to oxidation.

The Silver-Steel Lubricity Test is a laboratory test developed to measure the silver-steel lubricity characteristics of railroad diesel lubricants. The results obtained in this test are important since about 85% of all railway diesel engines in the United States use a silver-on-steel surfaced bearing. The test consists of rotating a steel ball at 600 r.p.m. on three stationary silver discs under a constantly applied load of 15 kg. in the presence of the test lubricant at 150° C., and measuring the developed torque. In this test, the lower the torque, the lower the friction and the better the silver lubricity.

The results of these tests, together with relative proportions of ingredients, are shown in Table I.

TABLE I.—BENEFICIAL EFFECT OF ORGANO-TIN COMPOUNDS IN LUBRICANTS CONTAINING PHENATE ADDITIVES

Test Lubricant	Lubricant Composition			Organo-tin Compound		Lubricant Stability Test at 340° F.			Silver-Steel Lubricity Test, grams torque
	Base Stock	Phenate Additive		Type	Wt. percent	Viscosity Increase SSU at 100° F.		pH Retained	
		Type	Wt. percent [1]			19 Hrs.	23 Hrs.		
1	X	B	6.5	None		402	500	3.2	
2	X	B	6.5	L	0.5	217	270	5.0	79
3	X	B	6.5	L	0.3	257	318	5.3	65
4	X	B	6.5	J	0.5	258	330	5.9	55
5	X	B	6.5	J	0.3	268	344	4.8	62
6	X	B	6.5	K	0.5	178	203	5.3	
7	X	A	6.5	None		452	572	2.0	87
8	X	A	6.5	J	0.5	347	439	4.3	56
9	X	C	5.3	None		456	572	4.1	64
10	X	C	5.3	N	0.5	290	363	4.8	76
11	X	C	5.3	O	0.5	193	240	5.2	87
12	X	C	5.3	M	0.5	197	256	5.0	75
13	Y	A	6.5	None		367	469	3.5	63
14	Y	A	6.5	J	0.3	239	309	5.9	60
15	Z	C	5.7	None		230	320	3.8	72
16	Z	C	5.7	J	0.3	192	280	6.5	93

[1] Weight percent of oil concentrate of phenate additive. Additives A and B were used as a 45% active ingredient in oil. Additives C was used as a 50% active ingredient in oil.

As shown in Table I, addition of the organo-tin compounds markedly improves the oxidation stability of phenate-containing lubricants. In all cases the viscosity increase at elevated temperatures was substantially reduced and pH retention of the oxidized oil was improved. Comparison is to be made with those lubricants which did not contain the organo-tin compounds, i.e., 1, 7, 9, 13 and 15. Furthermore, the Silver-Steel Lubricity Test data show about equal results for all the lubricants tested, irrespective of the inclusion of organo-tin compounds. This indicates that the inclusion of the organo-tin compounds does not adversely affect the superior silver-steel lubricity properties of phenate-containing lubricants.

Comparison between compositions of the invention and conventional antioxidants

Additional stability tests were performed according to the procedures described above, using conventional antioxidants in place of the organo-tin compounds. The results are summarized in Table II.

TABLE II.—BEHAVIOR OF CONVENTIONAL ANTIOXIDANTS IN PHENATE-CONTAINING LUBRICANTS

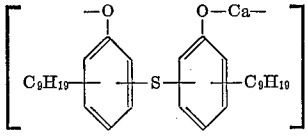
Test Lubricant	Lubricant Composition			Antioxidant		Lubricant Stability Test at 340° F.	
	Base Stock	Phenate Additive				Viscosity Increase SSU at 100° F.	
		Type	Wt. percent	Type	Wt. percent	19 hrs.	23 hrs.
17	Z	B	6.5	None		218	293
18	Z	B	6.5	Phenyl-beta naphthylamine [1]	0.4	214	269
19	Z	B	6.5	Mixture of octylated and styrenated diphenylamines.[2]	0.4	220	285
20	Z	B	6.5	Mixture of octylated diphenylamines [3]	0.4	216	274
21	Z	B	6.5	4,4'-methylene bis(2,6-ditertiary butyl phenol).[4]	0.5	201	296
22	X	B	5.2	None		340	428
23	X	B	5.2	Mixture of aryl amines [5]	0.2	377	467
24	X	B	5.2	2,-6-di-tert-butyl-alpha-dimethyl-amino-p-cresol.[6]	0.5	366	456

[1] Agerite Power, supplied by R. T. Vanderbilt Co.
[2] Agerite Stalite, supplied by R. T. Vanderbilt Co.
[3] Agerite Stalite S, supplied by R. T. Vanderbilt Co.
[4] AN-2, supplied by Ethyl Corp.
[5] DuPont 302, supplied by DuPont Chemicals Div.
[6] Ethyl 703, supplied by Ethyl Corp.

It is apparent from the preceding tables that the effectiveness of the organo-tin compounds in promoting the oxidation stability of phenate-containing lubricants is superior to a variety of conventional antioxidants which are notably effective in other applications. Thus, no significant improvement in stability was provided by any of the conventional antioxidants as shown in Table II, whereas marked improvements were provided by the organo-tin compounds as shown in Table I.

EXAMPLE 2

As a further example of the invention, a mineral lubricating oil composition consisting of 94.2 wt. percent mineral oil of 80 SUS viscosity at 210° F., 5.3 wt. percent of a phenate sulfide having the formula:

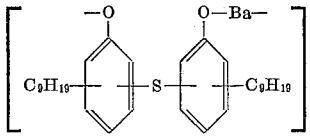


and 0.5 wt. percent of dibutyl-(9,10-dihydro-9,10-anthrylene) tin can be prepared.

EXAMPLE 3

As a further example of the invention, a mineral lubricating oil composition consisting of 93.0 wt. percent

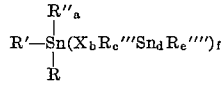
mineral oil of 80 SUS viscosity at 210° F., 6.5 wt. percent of a phenate sulfide having the formula:



and 0.5 wt. percent of dibutyl-(9,10-dihydro-9,10-anthrylene) tin can be prepared.

What is claimed is:

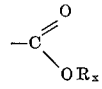
1. A lubricating composition having improved oxidation stability at high temperatures comprising a major proportion of a lubricating oil containing 0.5 to 20.0 wt. percent, based on the weight of said composition, of an oil-soluble alkaline earth metal alkyl phenate sulfide lubricating oil detergent additive, and an amount within the range of 0.2 to 25 wt. percent, based on the weight of said phenate sulfide, of an oil-soluble organo-tin compound which improves the oxidation stability of said composition and has the general formula:



wherein the tin atoms are selected from the group consisting of divalent and tetravalent tin atoms; R and R' are selected from the group consisting of C_1 to C_{20} hydrocarbyl radicals, and ester groups having the formula



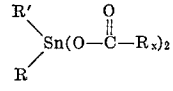
wherein R_x is a C_1 to C_{30} alkyl radical; R'' is a C_1 to C_{20} hydrocarbyl radical; R''' is a C_1 to C_{30} divalent hydrocarbon radical; R'''' is selected from the group consisting of C_1 to C_{20} hydrocarbyl radicals, C_1 to C_{30} acyl radicals, and ester groups having the formula



wherein R_x is a C_1 to C_{30} alkyl radical; X is selected from the group consisting of oxygen and sulfur; *a* is 0 to 2; *b*, *c*, and *d* are 0 to 1; *e* is 0 to 3; *f* is 0 to 2; the sum of *a* and *f* being zero when said tin atoms are divalent and two when said tin atoms are tetravalent; and when $d=1$, then $b=0$, $a+f=2$, and $c+e=4$.

2. A lubricating oil composition as defined by claim **1** wherein said composition is halogen-free and wherein said phenate sulfide is present in an amount within the range of 1.0 to 10 wt. percent based upon the weight of said composition and said organo-tin compound is present in an amount within the range of 0.1 to 1.0 wt. percent based upon the weight of said composition.

3. A composition according to claim **1**, wherein said oil-soluble organo-tin compound has the general formula:



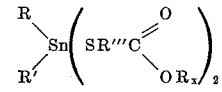
wherein R and R' are C_1 to C_{20} hydrocarbyl radicals and R_x is a C_1 to C_{30} alkyl radical.

4. A composition according to claim **1**, wherein said oil-soluble organo-tin compound has the general formula:



wherein R and R' are C_1 to C_{20} hydrocarbyl radicals and X is selected from the group consisting of sulfur and a C_1 to C_{30} divalent hydrocarbon radical, wherein both free bonds of said divalent hydrocarbon radical are joined to the tin atom.

5. A composition according to claim **1**, wherein said oil-soluble organo-tin compound has the general formula:



wherein R and R' are C_1 to C_{20} hydrocarbyl radicals, R''' is a C_1 to C_{30} divalent hydrocarbon radical, and R_x is a C_1 to C_{30} alkyl radical.

6. A composition according to claim **1**, wherein said oil-soluble organo-tin compound has the general formula:



wherein R and R' are C_1 to C_{20} hydrocarbyl radicals.

7. A composition according to claim **4**, wherein said divalent hydrocarbon radical is a 9,10-dihydro-9,10-anthylene radical.

8. A composition according to claim **2**, wherein said oil-soluble organo-tin compound is dibutyl tin dilaurate.

9. A composition according to claim **2**, wherein said oil-soluble organo-tin compound is dibutyl tin sulfide.

10. A composition according to claim **2**, wherein said oil-soluble organo-tin compound is dibutyl bis(isooctyl mercaptoacetate) tin.

11. A composition according to claim **2**, wherein said oil-soluble organo-tin compound is stannous octoate.

12. A composition according to claim **2**, wherein said oil-soluble organo-tin compound is dibutyl (9,10-dihydro-9,10-anthrylene) tin.

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