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DeVries et al.

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[45] **Sept. 30, 1975**

[54] **COMPOSITION AND METHOD**

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[52] **U.S. Cl.** ..... **252/42.7;** 123/196; 252/50; 252/51.5 A

[51] **Int. Cl.²** **C10M 1/54**

[58] **Field of Search** ..... 252/42.7, 50, 51.5 A; 123/196

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[57] **ABSTRACT**

A composition useful for lubricating components of internal combustion engines requiring lubrication comprising a major proportion of oil of lubricating viscosity, a minor amount of at least one metal carbon linked phenate and a minor amount of at least one of certain nitrogen-containing components wherein the combination of the phenate and the nitrogen-containing component is present in an amount to improve the oxidation stability of the composition. These compositions may also include at least one chlorinated hydrocarbonaceous component in an amount sufficient to improve the wear properties of the lubricating oil composition toward silver.

28 Claims, No Drawings

COMPOSITION AND METHOD

This invention relates to new and improved lubricating compositions. More particularly, it relates to lubricating oil compositions which have improved resistance to deterioration by oxidation and may have improved wear resistance toward metal engine components, such as silver engine components.

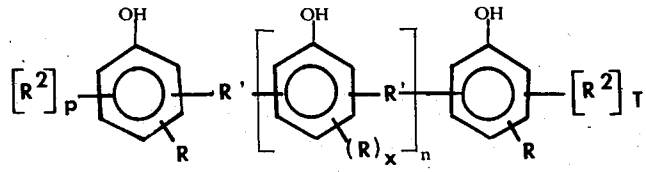
One problem involved in using lubricating oil compositions in severe service, for example, as lubricants for railroad diesel engines, is the necessity of protecting the lubricating composition from deterioration by oxidation. Conventional additives are known to give a degree of protection against oxidation. However, as lubricating oil requirements are increased, oils having the ability for longer engine service are required. Therefore, there is a need for improved oxidation resistance in lubricating oil compositions.

An additional problem which may occur in lubricating internal combustion engines which contain silver engine components which require lubrication such as, for example, silver wrist pin bushings in railroad engines and the silver bearing surfaces in aircraft engines, is excessive wear of these components. It is, therefore, important to provide a lubricating oil composition having improved wear characteristics towards metals such as silver.

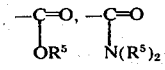
Therefore, one of the objects of the present invention is to provide a lubricating oil composition having improved resistance toward deterioration by oxidation.

Another object of the present invention is to provide a lubricating oil composition which exhibits improved wear properties toward silver engine components. Other objects and advantages of the present invention will become apparent hereinafter.

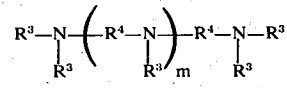
It has now been discovered that the above-noted objects are accomplished by the compositions of the present invention. In one aspect, the present invention is a lubricating oil composition which comprises a major proportion of oil of lubricating viscosity, a minor amount of at least one metal phenate compound of a phenolic component having the following structure



wherein each R is independently selected from the group consisting of monovalent essentially hydrocarbon radicals containing from about 3 to about 20, preferably from about 8 to about 20, carbon atoms, each R' is independently selected from the group consisting of divalent essentially hydrocarbon radicals containing from 1 to about 5 carbon atoms and a carbonyl group, each R^2 is independently selected from the group consisting of non-interferring monovalent essentially hydrocarbon radicals containing up to about 20 carbon atoms, non-interferring non-hydrocarbon radicals,



wherein R^5 is selected from the group consisting of hydrogen and monovalent essentially hydrocarbon radicals containing up to about 5 carbon atoms and mixtures thereof, n is an integer from 1 to about 6, and P, T and X are each integers from zero to 3; and a minor amount of at least one nitrogen-containing component selected from the group consisting of



wherein each R^3 is independently selected from the group consisting of hydrogen, monovalent essentially hydrocarbon radicals having a molecular weight from about 400 to about 5000, preferably from about 750 to about 3000 and acyl radicals having a molecular weight from about 400 to about 5000, preferably from about 750 to about 3000, provided that at least one R^3 has a molecular weight of at least about 400, and preferably at least about 750, each R^4 is independently selected from the group consisting of divalent essentially hydrocarbon radicals containing from 1 to about 8, preferably from 1 to about 3 and more preferably 2 or 3 carbon atoms, and *m* is an integer from 1 to about 10, preferably from 1 to about 6, provided that an essentially hydrocarbon radical R^3 may be combined with at least one entity selected from the group consisting of a nitrogen atom, R^4, an essentially hydrocarbon radical R^3 and mixtures thereof to form at least a portion of the nitrogen-containing component into a heterocyclic ring; wherein the combination of said metal phenate compound and said nitrogen-containing component is present in an amount sufficient to improve the oxidation stability of said composition.

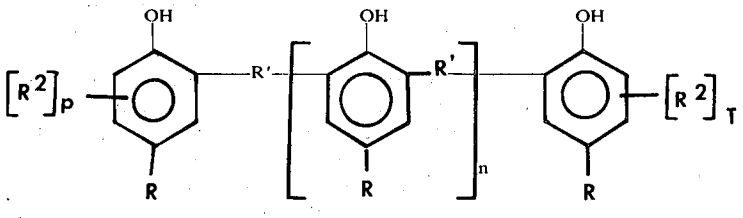
The compositions of the present invention may also include at least one chlorinated hydrocarbonaceous component which comprises at least about 5%, preferably at least about 20%, by weight of chlorine. The chlorinated hydrocarbonaceous component is present in the lubricating compositions in an amount sufficient to improve the wear properties of the lubricating oil composition toward silver.

In order to achieve improved benefits of the present invention, it is preferred that the metal phenate compound be present in an amount from about 1 to about 10%, more preferably from about 2 to about 7%, by weight of the total composition. The preferred concentration of the nitrogen-containing component is from about 0.5 to about 10%, more preferably from about 1 to about 6%, by weight of the total composition. When the chlorinated hydrocarbonaceous components are employed, the preferred concentration of the chlorinated hydrocarbonaceous component is from about 0.5 to about 2.0%, more preferably from about 0.05 to about 0.5%, by weight of the total composition.

The metal phenate compounds useful in the compositions of the present invention are preferably oil-soluble. The metals which may be used to form the metal phenate compounds suitable for the present compositions include the alkaline earth metals such as barium, calcium, strontium, and magnesium; the alkali metals such as sodium, potassium and lithium; and polyvalent metals such as lead, tin, zinc, aluminum, copper, mercury, vanadium, chromium, molybdenum, manganese, iron, cobalt and nickel. The alkali and, particularly, the alkaline earth metals are preferred. The most preferred metal for use in the phenate compounds is calcium.

The metal phenate compounds useful in the present invention may be referred to as carbon linked poly-phenate metal compounds. Although the carbon link between phenyl groups can contain as many as about 5 carbon atoms, it is preferred that this carbon link contain only one carbon atom.

It is preferred that the phenolic component comprise the following structure



wherein each R, R′ and R^2 and n are as previously defined. The monovalent essentially hydrocarbon radicals from which each R is independently selected include alkyl and alkenyl groups containing from about 3 to about 20, preferably from about 8 to about 20, carbon atoms; aryl, aralkyl, alkaryl, aryl alkenyl and alkenyl aryl groups containing from about 6 to about 20, preferably from about 8 to about 20 carbon atoms. The divalent essentially hydrocarbon radicals from which each R′ is independently selected include alkylene groups containing from 1 to about 5 carbon atoms.

Typical examples of suitable alkyl groups include propyl, butyl, pentyl, octyl, decyl, dodecyl, tetradecyl, stearyl and the like. Suitable alkenyl groups include propenyl, butenyl, pentenyl, octenyl, decenyl, dodecenyl, tetradecenyl, oleic and the like. Suitable aryl, aralkyl, alkaryl, aryl alkenyl and alkenyl aryl groups include phenyl, naphthyl, phenyl ethyl, phenyl hexyl, phenyl octyl, phenyl tetradecyl, naphthyl hexyl, naphthyl octyl, ethyl phenyl, hexyl phenyl, octyl phenyl, tetradecyl phenyl, hexyl naphthyl, octyl naphthyl, phenyl ethenyl, phenyl hexenyl, phenyl octenyl, phenyl tetradecenyl, naphthyl hexenyl, naphthyl octenyl, ethenyl phenyl, hexenyl phenyl, octenyl phenyl, tetradecenyl phenyl, hexenyl, naphthyl octenyl naphthyl and the like. Included among the suitable alkylene groups are methylene, ethylene, propylene, butylene, pentylene and the like.

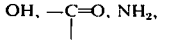
The above-described essentially hydrocarbon radicals may include non-hydrocarbonaceous substituents thus forming substituted monovalent and divalent essentially hydrocarbon radicals. Suitable substituents include those which do not materially interfere with the effectiveness, e.g., oil solubility and oxidation inhibition properties, of the metal phenate compound. Typical examples of such non-interferring substituents include OH,



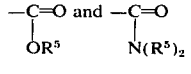
NH_2, halide, SH and the like radicals.

It is preferred that each R be an alkyl group, more preferably the same alkyl group, containing from about 8 to about 20 carbon atoms, and that each R′ contain 1 carbon atom. At least one R′ may contain a carbonyl carbon atom or itself be a carbonyl group. The carbonyl functionality can result from oxidation of a hydrocarbon radical R′. For example, if R′ is methylene, oxidation will produce a carbonyl group.

In addition, at least one of the terminal phenyl groups of the metal phenate compound may be further substituted with non-interferring radicals both monovalent essentially hydrocarbon radicals containing from about 8 to about 20 carbon atoms and non-hydrocarbon radicals, i.e., radicals which do not materially interfere with the effectiveness of the phenate compound in the compositions of the present invention. Groups including, for example, R and non-hydrocarbon radicals such as



halide, SH and the like radicals, may be substituted on the terminal phenyl groups. In addition, a radical selected from the group consisting of



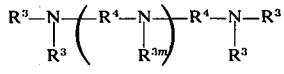
may form at least part of a substituent on at least one of the terminal phenyl groups.

The metal phenate compound preferably contains at least one carbonyl carbon atom per molecule. This carbonyl group can be present as R′, or as part of R, R′ or R^2. For example, the carbonyl group can be on one of the terminal phenyl groups of the phenate compound.

The carbon linked poly-phenate metal compounds suitable for use in the present invention may be prepared by conventional procedures well known in the art. For example, see U.S. Pat. No. 2,736,701. These phenate metal compounds can be prepared by condensing an alkylated phenol with a low molecular weight aldehyde, preferably formaldehyde, in the presence of a basic compound, e.g., hydroxide, of the desired metal. This basic compound may act both to catalyze the condensation, although other condensation catalysts such as sulfuric acid and other strong mineral acids may be used, and to react with the phenolic hydroxy groups to form the desired poly-phenate metal compound. The condensation may be catalyzed by one

basic compound and the phenolic hydroxy groups reacted with a different basic compound. However, it is preferred to use the same basic compound to perform both functions. It may be necessary to add additional basic compound after the condensation has stopped in order to form the desired metal phenate compound. The condensation and phenolic hydroxy group reaction conditions are well known in the art.

Included among the nitrogen-containing components useful in the present invention are those compounds comprising the following structure:

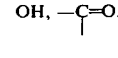


wherein R^3, R^4 and m are defined previously. When R^3 is an essentially hydrocarbon radical, it may be combined with at least one other essentially hydrocarbon radical, e.g., R^3 or R^4, and/or a nitrogen atom to form at least a portion of the nitrogen-containing component into a heterocyclic ring.

Included among the divalent essentially hydrocarbon radicals from which each R^4 may be independently selected are methylene, ethylene, ethenylene, propylene, propenylene, octylene, octenylene and the like. The saturated divalent radicals are preferred. Also, it is preferred that each R^4 be the same divalent radical.

Included among the monovalent essentially hydrocarbon radicals from which each R^3 may be independently selected include those radicals derived from principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of mono- olefins having from 2 to about 30 carbon atoms per molecule. Included among these mono-olefins are ethylene, propene, 1-butene, 2-butene, isobutene, 3-pentene, 1-hexene, 1-octene, 4-octene 2 methyl-1-heptene, 3-cyclohexyl-1-butene, 2-methyl-5-propyl-1-hexene and the like. Also useful are radicals derived from interpolymers of these mono-olefins with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins. Another source of these monovalent essentially hydrocarbon radicals comprises saturated aliphatic hydrocarbons such as highly refined high molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of high molecular weight olefin polymers illustrated above or higher molecular weight olefinic substances.

These monovalent and divalent essentially hydrocarbon radicals from which each R^3 and R^4 may be independently selected may contain substituents which do not materially interfere with the effectiveness of the nitrogen-containing component. Typical examples of such non-interferring substituents include



NH_2 halide, SH and the like radicals.

Included among the acyl radicals from which each R^3 may be independently selected are those acyl radicals derived from the monovalent essentially hydrocarbon radicals illustrated above.

In order to provide the nitrogen-containing component with oil solubility it is necessary that at least one R^3 have a molecular weight from about 400 to about 5000, preferably from about 750 to about 3000. The nitrogen-containing components suitable for use in the present invention may be prepared by conventional procedures.

The base oils used in the compositions of the present invention are those conventionally used in lubricant manufacture. Typical examples of the suitable lubricating oils include those having a viscosity within the range of about 50 SUS to about 2000 SUS, preferably from about 500 SUS to about 1200 SUS, at 100°F. These oils may be refined or otherwise processed to produce the desired quality. Although mineral oils are preferred, the base oil may be synthetic in nature. A specific example of the oils used in the present invention is a mineral oil mixture having a viscosity of about 900 SUS at 100°F. Combinations or mixtures of two or more different base oils in a single lubricating composition are often used to provide the desired physical properties and these mixtures are, therefore, within the scope of the present invention. The base oil comprises a major portion, preferably at least about 70%, still more preferably at least about 85%, by weight of the total composition.

In order to improve the detergent qualities of the compositions of the present invention, it is preferred to include from about 0.1 to about 10%, more preferably from about 0.1 to about 5%, by weight of at least one sulfonate selected from the group consisting of alkali metal sulfonate, alkaline earth metal sulfonate and mixtures thereof. The preferred sulfonates for use in the compositions of the present invention are the alkaline earth metal sulfonates, more preferably the calcium sulfonates.

Sulfonates derived from sulfonic acids having about 12 to about 200 carbon atoms per molecule are of particular usefulness in the present invention. Amone these sulfonic acids are mono- and polyalkyl substituted naphthalene sulfonic acids, phenol sulfonic acids, diphenyl ether sulfonic acids, diphenyl ether disulfonic acids, diphenyl sulfide-sulfonic acids, di-napthylsulfide-sulfonic acids, diphenyl amine-sulfonic acids, phenyl-naphthylsulfide sulfonic acids, cycloaliphatic sulfonic acids, such as petroleum naphthene sulfonic acids, cetylcyclopentyl sulfonic acids, lauryl-cyclohexyl sulfonic acids, bis-(Diisobutyl)- cyclohexyl sulfonic acids, mono- and poly-wax substituted cyclohexyl sulfonic acids, etc.

With respect to the sulfonic acids, it is intended herein to employ the term "petroleum sulfonic acids" to cover all sulfonic acids which are derived at least in part from petroleum sources. Additional examples of sulfonic acids and/or the alkali and alkaline earth metal salts thereof which can be employed as starting materials are disclosed in the following U.S. Pat. Nos. 2,174,110; 2,174,560; 2,174,508; 2,193,824; 2,197,800; 2,020,791; 2,212,786; 2,213,360; 2,228,598; 2,233,676; 2,239,974; 2,263,312; 2,276,090; 2,276,097; 2,315,514; 2,319,121; 2,321,022; 2,333,568; 2,333,788; 2,335,259; 2,337,552; 2,346,568; 2,366,027; 2,374,193 and 2,383,319.

The chlorinated hydrocarbonaceous components suitable for use in the present invention may vary widely in structure and composition provided that the chlorine content of these components is at least about 5%, preferably at least about 20%, by weight. Included among the suitable chlorinated components are the

chlorinated paraffins (including paraffin wax, kerosene and the like), chlorinated olefins and chlorinated polyolefins, Chlorinated cycloaliphatic compounds, chlorinated aromatics (including chlorinated biphenyls and chlorinated naphthenes), chlorinated esters of fatty, naphthenic and resin acids and the like and mixtures thereof which contain less than about 70 carbon atoms per molecule. Of course, more than one chlorinated component may be used in a single composition, and such a composition is within the scope of the present invention. It is preferred to use chlorinated paraffins, chlorinated olefins and polyolefins, chlorinated cycloaliphatic compounds, chlorinated esters of fatty, naphthenic and resin acids and mixtures thereof which contain less than about 70, preferably from about 10 to about 40, carbon atoms per molecule. Still more preferably, chlorinated paraffin containing from about 10 to about 40 carbon atoms per molecule can be used. The chlorinated components useful in the present invention may be prepared in any conventional manner, such as, for example, contacting molecular chlorine with the hydrocarbonaceous material to be chlorinated. By "hydrocarbonaceous material" is meant those materials (e.g., paraffins, waxes, olefins, polyolefins and the like) which are composed mainly of hydrogen and carbon, and include such materials which contain, in addition, minor amounts of substituents, such as oxygen, sulfur, nitrogen, etc., which do not substantially affect their hydrocarbon character. As the data presented hereinafter demonstrate, the addition of these chlorinated compounds to the compositions of the present invention gives these compositions an unusually strong ability to impart wear resistance to metals such as silver.

It is preferred that the lubricating compositions of the present invention include at least one dispersant in addition to the sulfonates described above. The nitrogen-containing component described previously may be used in the compositions of the present invention in an amount sufficient to improve the dispersant properties of the composition. In any event, additional dispersants, such as the conventional ash-containing metal-based dispersants and other ashless dispersants may be used. It is preferred that any additional dispersant used in the compositions of the present invention be ashless in nature and comprise from about 1% to about 6% by weight of the total composition.

In general, the additional ashless dispersants preferred for use are compounds which comprise an oil solubilizing tail and a polar detergent head. Many ashless dispersants fitting this general description are known to the art and are commercially available. Specific examples of this type of ashless dispersant include the polyamines-polyalkylene alkenyl succinimides in which the alkenyl group contains from about 30 to about 200 carbon atoms, the divalent alkylene radicals, which number from about 2 to about 6, each contain from about 1 to about 3 carbon atoms; and the N-dialkylaminoalkyl alkenyl succinimides in which the alkenyl group contains from about 30 to about 250 carbon atoms and the divalent alkylene radical along with the two alkyl radicals contain a total of less than about 10 carbon atoms. See French Pat. No. 1,265,085 and U.S. Pat. No. 3,018,291, which are hereby incorporated by reference into the present application. The required polarity may be supplied by groups containing, for example, oxygen, sulfur, phosphorous as well as nitrogen and mixtures thereof. For example, an ashless dispersant can be derived by reacting a hydrocarbon polymer containing from about 30 to about 250 carbon atoms with P_2S_5. See U.S. Pat. No. 3,003,964; and British Pat. No. 815,810; also U.S. Pat. Nos. 3,256,189 and 3,256,194, which patents are hereby incorporated by reference into the present application. All of these suitable ashless dispersants may be generally characterized as compounds comprising a hydrocarbon portion of sufficient size to render the compound oil soluble and at least one non-metallic polar portion which provides a substantial part of the dispersant action.

In addition to the additives already described, lubricating oil compositions contemplated herein may contain other agents such as antifoam agents, corrosion inhibitors, metal deactivators, pour point depressants, oiliness agents, compounds for enhancing the viscosity index of the lubricating oil, etc.

The lubricating oil compositions of the present invention can be used to lubricate internal combustion engines, and in particular, engines having silver components, such as, for example, many railroad diesel engines. More specifically, the lubricating oil compositions of the present invention can be used to reduce the wear of metal, in particular, silver engine components which normally occurs during the operating of the engine. Maintaining (or causing to be maintained) a lubricating amount of the oil compositions of the present invention on internal combustion engine components such as bearing surfaces, wrist pin bushings and the like requiring lubricating and/or wear improvement results in obtaining substantial benefits from the present invention. In addition, the compositions of the present invention which contain a combination of carbon linked metal phenate compound and defined nitrogen-containing component can be used to lubricate internal combustion engines in the manner noted above to give longer lubricant life because of the substantially improved oxidation resistance of these compositions.

The oxidation stability of the lubricating oils of the present invention were tested by the following procedure. This procedure is presented in detail in a paper by T. S. Chao, M. Kjonaas and B. C. Vitchus entitled "Oxygen Adsorption Test for Evaluation of Oxidation Stability of Lubricating Oils." This paper was presented before the National Combined Fuels and Lubricants and Transportation Meetings of the Society of Automotive Engineers in Philadelphia, Pa., Nov. 4 – 6, 1970. This procedure in known to give results which may be reasonably correlated with the true oxidation stability of lubricating oils.

In brief, the above test procedure involves the circulation of oxygen in a closed system through a definite quantity of oil at a controlled temperature and flow rate until a definite volume of 0_2 is consumed. As 0_2 is being consumed, the pressure in the system drops. This pressure drop which is directly proportional to the volume of 0_2 absorbed by the oil is monitored by a pressure transducer. A potentiometer recorder plots a curve relating the volume of 0_2 absorbed with time.

The test apparatus involves three basic parts. The first part is an oxidation cell which includes a pyrex test tube and a thermocouple well extending to the bottom of the test tube. The test tube is fitted with a gas inlet tube equipped with a three-way stopcock and extending also to the bottom of the test tube. The test tube is fitted with a gas inlet tube equipped with a three-way

stopcock and extending also to the bottom of the test tube. The three-way stopcock permits the feeding of sample at the beginning of the test from a funnel. The cell may be inserted in an electrically heated aluminum block packed with insulation in a stainless steel beaker. The temperature of the aluminum block may be controlled by a temperature controller through a thermocouple placed in a well drilled in the block.

The second part of the test apparatus is a gas purification train. Oxygen, after bubbling through the oil, carrys with it oil fumes, CO_2, water, and other volatile oxidation products. Most of the liquids and condensable products are returned to the oil phase by means of an aircooled condenser. A very small portion which passes through the condenser is absorbed by conventional means such as active charcoal in an adsorption tube. Water vapor, CO_2 and other acidic gases may be removed by Drierite and Ascarite. Organic materials and CO, if any, are converted in a catalytic tube furnace into H_2O and CO_2 which are removed by Drierite and Ascarite in another adsorption tube. The gas stream which then contains only unused O_2 is recirculated through the oil. Any O_2 consumed through the cycle is replenished with fresh O_2 from an O_2 source.

The third part of the test apparatus is the O_2 source and measuring device. The oxygen storage tanks connect to the inlet of the oxidation cell. These tanks also connect to one side of the diaphragm of a D/P transducer. The other side of the diaphragm is connected to an enclosed space of about 600 ml. which is used as the reference side. The system is balanced initially by opening a by-pass valve across the diaphragm allowing O_2 to feed into the reference cell. When the test starts, the by-pass valve is closed. Any loss of O_2 in the operating side will move the diaphragm and will generate a potential difference which will be indicated by a recorder which can be calibrated to record directly any loss of O_2 from the system.

In performing the oxidation test, 75 grams of oil composition to be tested were used in the oxidation cell and the oil temperature was maintained at 360°F. until 1200 ml. of O_2 (measured at 78° ± 2°F. and 1 atmosphere) was absorbed. A catalyst mixture was prepared from copper naphtheneate, iron naphate, lead naphthenate and a light base oil (150 SUS at 100°F., solvent treated neutral), such that 0.16% by weight of this mixture furnished 24 ppm. each of copper, iron and lead. The catalyst mixture was added to the oil sample before the test, care being taken to have adequate mixing and to avoid oxidation, during mixing. The aluminum block was heated to the operating temperature and the apparatus was evacuated to remove all the air. With the bypass valve across the transducer open, oxygen was fed into the evacuated system and the tubing pump was turned on to insure adequate circulation. This procedure was repeated twice more. After the third evacuation, the sample was fed into the oxidation cell through the heating funnel and the three-way stopcock. After pressuring the system with oxygen to approximately atmospheric pressure, the pump was turned on and the rate of oxygen flow was adjusted to 1 $Ft.^3$ per hour. The by-pass valve across the transducer was closed and the test was begun.

After a predetermined amount of oxygen had been absorbed into the oil, e.g., 1200 ml., the test was ended. The time required to absorb a given amount of oxygen is a measure of the oxidation stability of the composition being tested. Oxidation stability increases as time required to absorb a given volume of oxygen increased

EXAMPLES 1 to 6

These examples illustrate the outstanding oxidation resistance of the present compositions. The following lubricating oil compositions were prepared by blending together individual components, noted below, at a slightly elevated temperature, i.e., from about 100°F. to about 130°F., to insure complete mixing.

EXAMPLE	1	2	3	4	5	6
Mineral Oil, 890 SUS at 100°F.	88.7	84.0	93.0	88.3	94.0	89.3
Carbon Bridged Compound Calcium Phenate[1]	11.3	11.3				
Carbon Bridged Compound Calcium Phenate[2]			7.0	7.0		
Sulfurized Compound Calcium Phenate[3]					6.0	6.0
Nitrogen-Containing Component (I)[4]		3.0		3.0		3.0
Calcium Sulfonate[5]		1.7		1.7		1.7

1. Prepared by condensing substantially paradodecyl phenol and formaldehyde in equal molar amounts in the presence of excess calcium hydroxide. This condensation product was contained in a mineral oil carrier and the excess calcium hydroxide filtered. The calcium phenate compound amounted to approximately 50% by weight of the total mixture.

2. A commercially available mixture of about 50% by weight of active material in a mineral oil carrier. This carbon bridged calcium phenate compound is derived from the condensation of alkyl phenol with formaldehyde. The material contained 2.4% by weight of calcium. Infra-red spectrometry indicates the phenate salt contains carbonyl functionality which may be located at either or both a carbon bridge or as part of a substituent on a terminal phenyl group. Based upon molecular weight considerations and elemental analysis, the phenate compound comprises 6 aromatic nuclei with single carbon atoms bridges in between.

3. A mixture of about 50% by weight of active material in a mineral oil carrier. The active material comprises mono-sulfide linked calcium phenate compounds derived from dodecyl phenol.

4. A mixture of about 50% by weight of a nitrogen-containing component in a mineral oil carrier. This mixture contains about 1.2% by weight of nitrogen and has a total base number (ASTM Test D-664) of about 40. The nitrogen-containing component of this mixture comprises a polyamine which contains about 3 to 5 basic nitrogen atoms bridged by hydrocarbon radicals

containing about 2 to 4 carbon atoms per radical, and hydrocarbon portions having an average molecular weight of about 1000 so that the average molecular weight of the nitrogen-containing component is believed to be about 7000. The nitrogen-containing component includes at least one carbonyl group between the polyamiine portion and a hydrocarbon portion. The nitrogen-containing component of this polyamine is essentially free of imide functionality.

5. A mixture of about 45% by weight of active calcium sulfonate in a mineral oil carrier. The calcium sulfonate is derived from petroleum sources and has about 25 carbon atoms per molecule.

Using the oxidation test procedure described previously, each of these six compositions was tested to determine oxidation stability. The results of these tests were as follows:

Composition	Time Required for Composition To Adsorb 1200 ml. of oxygen
Example 1	96 minutes
Example 2	145 minutes
Example 3	105 minutes
Example 4	204 minutes
Example 5	159 minutes
Example 6	148 minutes

These results indicate that the carbon-linked phenate compounds of the present invention when used in combination with the nitrogen-containing components of the present invention yield compositions having improved resistance to deterioration by oxidation. This improvement in oxidation stability using the carbon linked phenate compounds is in contrast to the sulfur-linked calcium phenate compounds which show no improvement in oxidation stability when used in combination with the nitrogen-containing component. In addition, these results show a greater improvement in oxidation stability for a composition which includes a carbon linked phenate compound containing carbonyl functionability.

EXAMPLE 7

This example shows that the addition of calcium sulfonate to lubricating oil compositions has very little, if any, effect on the oxidation stability of the compositions. The following composition was prepared and tested in a manner similar to the composition of Examples 1 to 6:

Composition[6]	Wt.%
Mineral Oil, 890 SUS at 100°F.	91.3
Carbon Bridged Calcium Phenate Compound II	7.0
Calcium Sulfonate	1.7
Test Results	
Time Required For Composition to Absorb 1200 ml. of Oxygen	107 Minutes

[6]The components used to prepare this composition are the same as the components used to prepare the compositions of Examples 1 to 6.

Comparing these results with those of Examples 3 and 4, it becomes clear that a substantial improvement in oxidation stability is achieved through the use of a carbon-linked phenate compound and a defined nitrogen-containing component.

EXAMPLES 8 and 9

These examples illustrate the need to use proper nitrogen-containing components in the compositions of the present invention. These compositions were prepared and tested in a manner similar to those of Examples 1 to 6. The compositions and test results were as follows:

Compositions[7]	Wt.% 8	9
Mineral Oil, 890 SUS at 100°F.	88.3	88.3
Carbon Bridged Calcium Phenate Compound II	7.0	7.0
Calcium sulfonate	1.7	1.7
Nitrogen-Containing Component I	3.0	
Imide-Containing[8] Ashless Dispersant		3.0
Test Results		
Time Required For Composition to Absorb 1200 ml. of Oxygen, Min.	204	183

[7]Unless otherwise noted, the components used to prepare these compositions are the same as the components used to prepare the compositions of Examples 1 to 6.

[8]A commercially available mixture of about 50% by weight of ashless dispersant in a mineral oil carrier. The dispersant is believed to comprise, as an oil solubilizing portion, a hydrocarbon olefin polymer which contains an average of about 75 to about 100 carbon atoms per molecule and, to provide a substantial part of the dispersant properties, a polar portion containing basic nitrogen. Infra red spectrometry indicates that this mixture includes imide, as well as amide, functionality. The mixture contains 1.9% by weight of nitrogen and has a total base number (ASTM Test D-664) of about 49.

These results show that the nitrogen-containing components defined herein when used in combination with defined phenate salts, provide lubricating compositions having improved oxidation stability. It is particularly significant in comparing Example 8 with Example 9 to note that the nitrogen-containing component (and, therefore, the composition) of Example 8 contained less nitrogen and had a lower total base number than did the composition of Example 9. However, the composition containing the nitrogen-containing component of the present invention (Example 8) provides improved oxidation stability relative to the corresponding composition (Example 9) containing an imide-containing ashless dispersant.

EXAMPLE 10

This example illustrates the improved silver wear properties of the present compositions.

The lubricating compositions of this example were tested using a laboratory procedure developed to study silver lubrication. This test is described in detail in a paper given at the National Combined Fuels and Lubricants and Transportation Meetings in Houston, Tex., on Nov. 4, thru 7, 1969. The title of the paper is "A Bench Test for the Evaluation of Silver-Steel Lubrication Properties of Railroad Diesel Oil", by B. W. Turnquest, P. G. Culliney, R. J. Danehy and R. D. Fullman. Results from this bench test procedure correlate quite well with actual engine test results and, therefore, provide a reasonable indication of the true utility of the lubricating oil composition being tested.

This procedure utilizes the Sinclair Pin and Disc Machine. Basically, this apparatus is of the pin-on-disc type, in which a loaded rider rubs against the flat surface of a rotating disc. Contact of the rider against the disc is effected by means of a lever and cam arrangement which permits split-second initiation and termina-

tion of rubbing. The silver pins which are to be tested are attached to the rider and have conical ends. The included angel of the cone is 120° so that the measured increase in the diameter of the work wear scar is 3.46 times the axial depth of wear. In a wear experiment the primary observation is the increase in the diameter of the truncated area of the cone. Provided the perimeter of the scar is clearly elineated, wear measurements sensitive to 2×10^{-5} inches as scar diameter (or 3×10^{-6} inches as wear scar depth) are feasible.

Using this apparatus and measuring procedure, the lubricants of the present invention are tested as follows. The lubricant is supplied to the rubbing zone by allowing it to flow onto the disc from a reservoir. The supply tube is positioned so that the lubricant stream impinges upon the leading edge of the rider with reference to the motion of the disc. Band heaters are fitted to the lubricant reservoir and the receiving bath for experiments carried out at elevated temperatures. Alternately, the disc may be submerged in the test oil. The conically ended silver pins were used on mirror finished steel disc. The same break-in procedure is followed in all cases. In the first stage of the break-in procedure, the silver pins are run on ground steel discs until rubbing surfaces of appropriate size are established. A 100 gram load is applied in all cases during the first stage of the break-in procedure and white oil is used as the lubricant. In the final stage of the break-in, the pins are run for approximately 15 minutes in the test lubricant and on the mirror finished surface of the disc. A 800 gram load is applied in the final break-in stage.

The actual test is run at the following conditions: pressure of 7500 psig., rubbing speed of 20 feet per minute (fpm) and a constant temperature of 200°F. The test is continued for a sufficient length of time to allow an accurate measurement of the increase in the diameter of the truncated area of the pin. Depending on the wear rate observed, the operating time per experiment can vary from about 280 to about 500 minutes. Bench test wear rates of less than about 10×10^{-8} inches per foot rubbed indicate that the lubricant being tested has satisfactory anti-wear properties.

Three lubricating compositions were tested for silver wear using the above procedure. These compositions were (1) the composition of Example 7, (2) the composition of Example 4 and (3) a composition, i.e., the composition of Example 10, prepared in a manner similar to the composition of Example 1. The three compositions tested are as follows:

Composition[9]	Wt.% 7	4	10
Mineral Oil, 890 SUS at 100°F.	91.3	88.3	88.2
Carbon Bridged Calcium Phenate Compound II	7.0	7.0	7.0
Nitrogen-Containing Component I		3.0	3.0
Calcium Sulfonate	1.7	1.7	1.7
Chlorinated Hydrocarbonaceous Component[10]			0.1

[9]Unless otherwise noted, the components used to prepare these compositions are the same as the components used to prepare the compositions of Examples 1 to 6.

[10]A chlorinated hydrocarbon paraffin containing about 12 carbon atoms per molecule and about 60% by weight of chlorine.

The silver wear test results for each of these compositions are as follows:

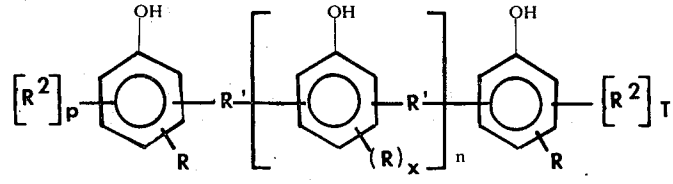
Wear Rate 10^{-8} in./ft.	Composition of Example 7	4	10
	17.5	7.9	2.0

These results clearly show that the compositions of the present invention have improved silver wear properties. Further, hte incorporation of a chlorinated hydrocarbonaceous component into the present compositions provides still more improved silver wear properties.

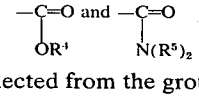
While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

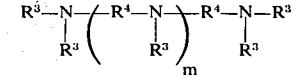
1. A lubricating oil composition which comprises a major amount of oil of lubricating viscosity; a minor amount of at least one metal phenate compound of a phenolic component having the following structure:



wherein each R is independently selected from the group consisting of monovalent essentially hydrocarbon radicals containing from about 3 to about 20 carbon atoms, each R′ is independently selected from the group consisting of divalent essentially hydrocarbon radicals containing from 1 to 5 carbon atoms and a carbonyl group, each R^2 is independently selected from the group consisting of non-interferring hydrocarbon radicals containing up to about 20 carbon atoms, non-interferring, non-hydrocarbon radicals



wherein R^5 is selected from the group consisting of hydrogen and monovalent essentially hydrocarbon radicals containing up to about 5 carbon atoms and mixtures thereof, *n* is an integer from 1 to about 6 and P, X and T are each integers from zero to 3, said metal being selected from the group consisting of alkali metal and alkaline earth metal; and a minor amount of at least one nitrogen-containing component selected from the group consisting of

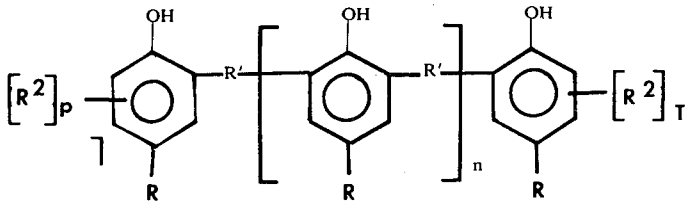


wherein each R^3 is independently selected from the group consisting of hydrogen, monovalent essentially hydrocarbon radicals having a molecular weight from

about 400 to about 5000, and acyl radicals having a molecular weight from about 400 to about 5000, provided that at least one R^3 has a molecular weight of at least about 400, and each R^4 is independently selected from the group consisting of divalent essentially hydrocarbon radicals containing from 1 to about 8 carbon atoms, and m is an integer from 1 to about 10 provided that an essentially hydrocarbon radical R^3 may be combined with at least one entity selected from the group consisting of a nitrogen atom, R^4, an essentially hydrocarbon radical R^3 and mixtures thereof to form at least a portion of the nitrogen-containing component into a heterocyclic ring, provided that said nitrogen-containing component includes at least one carbonyl group; wherein the combination of said metal phenate compound and said nitrogen-containing component is present in an amount sufficient to improve the oxidation stability of said composition.

2. The composition of claim **1** wherein said metal phenate compound is present in an amount from about 1% to about 10% by weight of the total composition of said nitrogen-containing component is present in an amount from about 0.5 to about 10% by weight of the total composition.

3. The composition of claim **2** wherein said phenolic component has the following structure



4. The composition of claim **3** wherein each R contains from about 8 to about 20 carbon atoms, each R' contains 1 carbon atom, and at least one R^3 has a molecular weight from about 750 to about 3000.

5. The composition of claim **4** wherein said metal phenate compound is a compound of an alkaline earth metal, and said phenate compounnd contains at least one carbonyl carbon atom.

6. The composition of claim **5** wherein said phenate compound is present in an amount from about 2 to about 7% by weight of the total composition and said nitrogen-containing component is present in an amount from about 1 to about 6% by weight of the total composition.

7. The composition of claim **6** wherein said metal phenate compound is a compound of calcium.

8. The composition of claim **1** wherein at least one chlorinated hydrocarbonaceous component which comprises at least about 5% by weight of chlorine is present in an amount sufficient to improve the wear properties of said composition toward silver.

9. The composition of claim **2** wherein at least one chlorinated hydrocabonaceous component which comprises at least about 5% by weight of chlorine is present in an amount from about 0.05 to about 2.0% by weight of the total composition sufficient to improve the wear properties of said composition toward silver.

10. The composition of claim **4** wherein at least one chlorinated hydrocarbonaceous component which comprises at least 20% by weight of chlorine is present in an amount from about 0.05 to about 2.0% by weight of the total composition sufficient to improve the wear properties of said composition toward silver.

11. The composition of claim **7** wherein at least one chlorinated hydrocarbonaceous component which comprises at least about 20% by weight of chlorine is present in an amount from about 0.05 to about 0.5% by weight of the total composition sufficient to improve the wear properties of said composition toward silver.

12. The composition of claim **1** which comprises from about 0.1 to about 10% by weight of the total composition of at least one sulfonate selected from the group consisting of alkali metal sulfonate, alkaline earth metal sulfonate and mixtures thereof.

13. The composition of claim **8** which comprises from about 0.1 to about 10% by weight of the total composition of at least one sulfonate selected from the group consisting of alkali metal sulfonate, alkaline earth metal sulfonate and mixtures thereof.

14. The composition of claim **10** which comprises from about 0.1 to about 10% by weight of the total composition of at least one sulfonate selected from the group consisting of alkali metal sulfonate, alkaline earth metal sulfonate and mixtures thereof.

15. The composition of claim **11** which comprises from about 0.1 to about 5% by weight of the total composition of at least one calcium sulfonate.

16. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim **1** on at least one component of said engine requiring lubrication.

17. In a method for lubricating an internal combustion engine having at least one component requiring lubrication, the improvement which comprises maintaining a lubricating amount of the composition of claim **2** on at least one component of said engine requiring lubrication.

18. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim **4** on at least one component of said engine requiring lubrication.

19. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim **7** on at least one component of said engine requiring lubrication.

20. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim **8** on at least one component of said engine requiring lubrication.

21. The method of claim **20** wherein said engine is a railroad diesel engine and said engine component comprises silver.

22. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim **11** on at least one component of said engine requiring lubrication.

23. The method of claim 22 wherin said engine is a railroad diesel engine and said engine component comprises silver.

24. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 12 on at least one component of said engine requiring lubrication.

25. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 13 on at least one component of said engine requiring lubrication.

26. The method of claim 25 wherein said engine is a railroad diesel engine and said engine component comprises silver.

27. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 15 on at least one component of said engine requiring lubrication.

28. The method of claim 27 wherein said engine is a railroad diesel engine and said engine component comprises silver.

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