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LUBRICATING OIL COMPOSITION

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ABSTRACT OF THE DISCLOSURE

Lubricating compositions comprising oil of lubricating viscosity, alkali and alkaline earth metal phenates, chlorinated hydrocarbonaceous components, sulfur-containing compounds, naphthyl amines and diamine components are disclosed. These lubricating compositions when maintained on internal combustion engine components requiring lubrication, exhibit improved resistance to wear caused to both silver and bronze engine components. The compositions of the present invention also have outstanding resistance to deterioration by oxidation.

This invention relates to new and improved lubricating oil compositions. More particularly, it releates to lubricating oil compositions which exhibit improved wear resistance toward metals such as both silver and bronze. The invention also relates to lubricating compositions having improved resistance to deterioration by oxidation.

Mineral oil lubricating compositions which are used in severe service, for example, as lubricants for railroad diesel engines, are advantageously alkaline in nature. The alkalinity is desired to neutralize certain acids which are formed in the engine during operation. Typical among the conventional sources of alkalinity are the normal alkali metal and alkaline earth metal phenates. The incorporation of these phenates and other additives into engine lubricants, however, can cause excessive wear in silver engine components such as, for example, silver wrist pin bushings in railroad engines and the silver bearing surfaces in aircraft engines.

Many internal combustion engines have bronze engine components which may be susceptible to excessive wear. Therefore, in order to be completely acceptable for use in a wide variety of internal combustion engines, lubricating oil compositions should impart wear resistance to both silver and bronze.

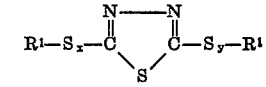
Another problem involved in producing a lubricating oil composition is the necessity of protecting the composition from deterioration by oxidation. Conventional additives are known to give a degree of protection against oxidation. However, as the lubricating oil technology develops, oils having the ability for longer engine service are required. Therefore, the need for improved oxidation resistance in lubricating oil compositions manifests itself.

Therefore, one of the objects of the present invention is to provide a lubricating oil composition which imparts improved wear properties to engine components of metals such as silver, bronze and the like.

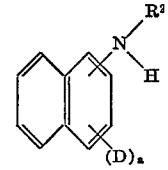
Another object of the present invention is to provide a lubricating oil composition having improved resistance toward deterioration by oxidation. Other objects and advantages of the present invention will become apparent hereinafter.

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 a least one phenate selected from the group consisting of alkali metal phenate, alkaline earth metal phenate and mixtures thereof, said phenate being present in an amount

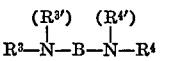
sufficient to contribute alkalinity to said lubricating oil composition; at least one chlorinated hydrocarbonaceous component which comprises at least about 5%, preferably at least about 20%, by weight of chlorine, said chlorinated hydrocarbonaceous component being present in an amount sufficient to improve the wear properties of said lubricating oil composition toward bronze; at least one sulfur-containing compound having the following structure:



wherein each R^1 is a monovalent hydrocarbon radical containing from 1 to about 30 carbon atoms, x and y each are integers from 1 to 9, the sum of x and y being at least 2, said sulfur-containing compound being present in an amount sufficient to improve the wear properties of said lubricating oil composition toward silver; at least one naphthyl amine having the following structure:



wherein R^2 is selected from the group consisting of hydrogen and monovalent hydrocarbon radicals containing from 1 to about 30, preferably from about 6 to about 18 carbon atoms, a is an integer from zero to 7, preferably zero to 1 inclusive and D is a monovalent hydrocarbon radical containing from 1 to about 30, preferably from about 1 to about 18 carbon atoms; at least one diamine component having the following structure:



wherein R^3, $R^{3'}$, R^4 and $R^{4'}$ are independently selected from the group consisting of hydrogen, alkyl having from 1 to about 12 carbon atoms, and aryl, aralkyl, alkaryl having from 6 to about 22 carbon atoms, and B is selected from the group consisting of divalent aromatic-containing hydrocarbon radicals and substituted divalent aromatic-containing hydrocarbon radicals containing 6 to about 30, preferably from about 6 to about 24, carbon atoms, said naphthyl amine and diamine component each being present in an amount sufficient to improve the resistance to oxidation of said lubricating oil composition.

In order to supply the proper amount of alkalinity to the compositions of the present invention, it is preferred that the phenate (expressed in terms of active ingredients) be present in an amount from about 1% to about 10%, more preferably from about 2% to about 7%, by weight of the total compositions. The preferred concentration of the chlorinated hydrocarbonaceous component is from about 0.05% to about 2.0%, more preferably from about 0.05% to about 0.5%, by weight of the total composition. The preferred concentration of the sulfur-containing compound is from about 0.02% to about 10%, more preferably from about 0.05% to about 2.0%, by weight of the total composition.

In addition, it has been found that the incorporation of a combination of at least one naphthyl amine and diamine component into a lubricating oil composition provides the lubricating oil composition with outstanding resistance to deterioration by oxidation. It is preferred that the naphthyl amine be present in a concentration of at least about 0.05%, more preferably at least about 0.10%, by weight of the total composition. For economic reasons, it is preferred that the naphthyl amine be present in a

concentration from about 0.05% to about 2.0%, more preferably from about 0.1% to about 1.0%, by weight of the total composition. The concentration of the diamine component is preferably at least about 0.01% by weight of the total composition. Again, for economic reasons, the diamine component concentration is preferably within the range from about 0.01% to about 2%, more preferably from about 0.01% to about 0.5%, by weight of the total composition.

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 prsent 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.

The alkali metal and alkaline earth metal phenates which can be incorporated into the compositions of the present invention may be monomeric or polymeric in nature, with the polymeric phenates being preferred. The phenate may be polymerized, for example, by reaction with elemental sulfur to form sulfurized phenates. Other polyphenates, for example, carbon bridged polyphenates, are also suitable for use in the present invention. In order to minimize the deleterious effect that the phenates have on silver engine components, it is preferred that sulfurized phenates containing only mono-sulfide linkages be used when these phenates are used to contribute alkalinity to the compositions of the present invention. The preferred phenates for use in the present invention are the alkaline earth metal, more preferably calcium, phenates.

One method for preparing sulfurized phenates is given in U.S. Pat. 2,680,096. This patent also discloses a description of the calcium phenates, both sulfurized and unsulfurized, which are suitable for use in the present invention. The unsulfurized calcium phenates have the following formula:

$$[(R)_bAO]_2Ca$$

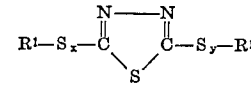
wherein A is an "essentially hydrocarbon" aromatic radical, preferably a benzene radical, R is a cyclic, straight-chained or branched-chained, saturated, essentially hydrocarbon radical having from 4 to 30 carbon atoms, O represents oxygen, *b* is an integer having a value of 1 to 5. An analogous structural formula for other phenates, i.e., phenates associated with metals other than calcium, can be drawn taking into account the valance state of the metal cation.

By "essentially hydrocarbon" (i.e., hydrocarbonaceous) radical is meant those radicals which are composed mainly of hydrogen and carbon, and include such radicals which contain, in addition, minor amounts of substituents, such as chlorine, bromine, oxygen, sulfur, nitrogen and the like, which do not substantially affect their hydrocarbon character. Examples of suitable hydrocarbonaceous radicals include alkyl radicals such as butyl, hexyl, octyl, decyl, dodecyl, hexadecyl, eicosyl, triacontyl, etc.; radicals derived from petroleum hydrocarbons, such as white oil, wax, olefin polymers (e.g., polypropylene and polybutylene), etc.; aryl radicals such as phenyl, naphthyl, etc.; aralykyl radicals such as benzyl, phenylethyl, phenyloctyl, phenyldecyl, phenyloctadecyl, etc.; alkaryl radicals such as amylphenyl, octylphenyl, nonylphenyl, cetylphenyl, etc.; and cyclic non-benzenoid radicals, such as cyclohexyl, bornyl, etc.

Examples of calcium phenates include the calcium salts of octyl phenol, nonyl phenol, dodecyl phenol, tetradecyl phenol, hexadecyl phenol, triacontyl phenol, dioctyl phenol, dinonyl phenol and the like.

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 bronze.

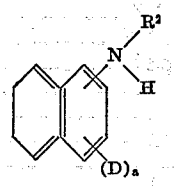
The general formula for the suitable sulfur-containing compounds is:



wherein each R^1 is the same or different monovalent hydrocarbon radicals, *x* and *y* each are integers from 1 to about 9 and the sum of *x* and *y* is at least 2, and preferably 4 to about 16. The radicals R^1 can be aliphatic or aromatic including acyclic, alicyclic, aralkyl, aryl and alkaryl radicals and mixtures of such radicals. The hydrocarbon radicals can contain from 1 to about 30 carbon atoms, and preferably from about 1 to about 18 carbon atoms. The most preferred sulfur containing compounds are those in which each R^1 is alkyl having from 1 to about 18 carbon atoms and *x* and *y* each are integers from 1 to 3. Examples of suitable monovalent hydrocarbon radicals are ethyl, propyl, butyl, hexyl, octyl, nonyl, decyl, dodecyl, tridecyl, hexadecyl, octadecyl, cyclo-hexyl, phenyl, tolyl, benzyl, naphthyl, styryl and the like. These sulfur-containing compounds and methods for their preparation are described in U.S. Pat. 2,719,126.

The sulfur-containing compound may be present in the compositions of the present invention in an amount sufficient to improve the wear properties of the composition toward silver. The preferred concentration of these sulfur-containing compounds is from about 0.02% to about 10.0%, more preferably from about 0.05% to about 2.0%, by weight of the total composition.

The naphthyl amines suitable for use in the present invention comprise a broad class of compounds. The general structural formula for these compounds is as follows:



wherein R^2 is selected from the group consisting of hydrogen and monovalent hydrocarbon radicals containing from 1 to about 30, preferably from about 6 to about 18 carbon atoms, *a* is an integer from zero to 7, preferably zero to 1 inclusive, D is a monovalent hydrocarbon radical containing from 1 to about 30, preferably from about 1 to about 18 carbon atoms. Included among the monovalent hydrocarbon radicals contemplated by the present invention are, for example, alkyl, aryl, aralkyl, alkaryl and substituted counterparts of these radicals. Included among the suitable amines are phenyl alpha- or beta-naphthylamine, octylphenyl alpha- or beta-naphthylamine, alpha-alpha, alpha-beta or beta-beta dinaphthylamines, various phenanthryl-anthryl-naphthylamines, xylyl naphthylamines, dodecyl phenyl naphthylamines, biphenyl naphthylamines and phenyl naphthylamines alkylated with olefins containing from about 8 to about 24 carbon atoms per molecule. Specific examples of these olefins include pinene, α-methylstyrene, and the like. The naphthylamines in which R^2 is a radical selected from the group consisting of aryl and alkaryl containing from 6 to about 18 carbon atoms, are of particular usefulness in the present invention and are, therefore, the more preferred class of compounds for use in the present invention.

In choosing the diamine component, it is preferred that R^3 and R^4 be H, i.e., hydrogen. Examples of the alkyl groups from which R^3, $R^{3'}$, R^4 and $R^{4'}$ may be selected include methyl, ethyl, isopropyl, sec-butyl, cyclohexyl, octyl, nonyl, decyl and the like. Examples of the aryl, aralkyl and alkaryl groups from which R^3, $R^{3'}$, R^4, and $R^{4'}$ may be selected include phenyl, benzyl, phenyl ethyl, phenyl isopropyl, phenyl octyl, phenyl decyl, tolyl, isopropyl phenyl, octyl phenyl, decyl phenyl and the like. Examples of the divalent aromatic-containing hydrocarbon radicals from which B may be selected, include phenylene, alkylene diphenylene and phenylene dialkylene wherein the alkylene groups contain from 1 to about 12 carbon atoms, and the like radicals. These divalent hydrocarbon radicals may be substituted with minor amounts of oxygen, sulfur and the like. Examples of the suitable substituted divalent aromatic-containing hydrocarbon radicals include divalent diphenyl ethers, and diphenyl sulfides and the like.

Because of their outstanding performance in the compositions of the present invention, the following diamine components are among those preferred: Bis-(N-sec-butyl-p-amino phenyl) methane, N-isopropyl-N'-phenyl-p-phenylene diamine, N-cyclohexyl-N'-phenyl-p-phenylene diamine, 2,2-bis (p-N,N-dimethylaminophenyl) propane and mixtures thereof.

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. Among 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-naphthylsulfide-sulfonic acids, diphenyl amine-sulfonic acids, phenylnaphthylsulfide 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. patents: 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.

In many instances, the components comprising the compositions of the present invention are available as solutions or mixtures in mineral oil or other solvent carriers. The proportion ratios given in this application refer to the active components rather than the mixtures or solutions.

It is preferred that the lubricating compositions of the present invention include at least one detergent in addition to the phenates and sulfonates described above. Both the ash-containing detergents, such as the conventional metal based detergents, and the ashless detergents are suitable for use. However, it is preferred to use the ashless detergents in the compositions of the present invention. When these detergents are included in the compositions of this invention, they comprise from about 1% to about 6% by weight of the total composition.

In general, the ashless detergents preferred for use are compounds which comprise an oil solubilizing tail and a polar detergent head. Many ashless detergents fitting this general description are known to the art and are commercially available. For example, basic polyamines substituted with long chain hydrocarbons having from about 30 to about 250 carbon atoms to provide oleophilic character are suitable for use in the present invention. Specific examples of this type of ashless detergent include the polyamines-polyalkylene alkenyl succinimides in which the alkenyl group contains from about 30 to about 250 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. 1,265,085 and U.S. Pat. 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 detergent 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. 3,003,964; and British Pat. 815,810; also U.S. Pats. 3,256,189 and 3,256,194, which patents are hereby incorporated by reference into the present application. All of these suitable ashless detergents may be generally characterized as compounds comprising a hydrocarbon portion of sufficient size to render the compound oil soluble and at least one nonmetallic polar portion which provides a substantial part of the detergent 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 and/or bronze 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 and bronze 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 lubrication and/or wear improvement results in obtaining substantial benefifits from the present invention. In addition, the compositions of the present invention which contain a combination of naphthyl amine and diamine components 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 following examples illustrate more clearly the compositions of the present invention. However, these illustrations are not to be interpreted as specific limitations on this invention.

EXAMPLE 1

This example illustrates the deleterious effect that alkali and alkaline earth metal phenates may have on silver components of diesel engines.

A lubricating oil composition was 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. The final compositions were as follows.

Component:	Weight percent
Mineral oil, 890 SUS at 100° F.	89.7
Sulfurized calcium phenate [1]	5.5
Ashless detergent [2]	3.0
Calcium sulfonate [3]	1.7

[1] A mixture of about 50% by weight of active material in a mineral oil carrier. The active material comprises monosulfide linked phenate derived from dodecyl phenol. The mixture has a total base number (ASTM Test D-664) of about 85.

[2] A mixture of about 50% by weight of detergent in a mineral carrier. The detergent comprises, as an oil solubilizing portion, a hydrocarbon olefin polymer which is believed to contain an average of about 75 to about 100 carbon atoms and, to provide a substantial part of the detergency action, a polar portion containing basic nitrogen. This detergent has a molecular weight of about 7860. This commercially available detergent mixture contains about 1.5% by weight of nitrogen and has a total base number of from about 30 to about 40.

[3] 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.

This lubricating oil composition was used in an EMD 2–567 test engine to determine the effect the lubricating composition had on the wear of the silver engine components. This engine utilizes a D–1 type power assembly. Each new test involves using various new components. Among these new components are the silver piston pins and special unleaded pin insert bearings. These components are installed at the beginning of each test. Each engine test includes 9 hours and 20 minutes of pre-run and 25 hours on test. Below is a table of typical conditions for the engine test.

Typical 25 hour operating conditions

Engine type	EMD 2–567
Cylinders, No.	2
Bore, in.	8.50
Stroke, in.	10.0
Compression ratio	20.1
Test duration, hr.	25
Engine load, BHP	208.8
Engine speed, r.p.m.	835
Fuel sulfur content, wt. percent	1.0
Oil temp. to bearings, ° F.	238
Oil temp. to engine, ° F.	210
Coolant temp. (out), ° F.	184
Engine oil pressure, p.s.i.	55
Inlet air temp., ° F.	95
Airbox temp., ° F.	160
Airbox pressure, in. Hg	6.8
Exhaust temp., ° F.	905
Exhaust pressure, in. Hg	0.5

EMD engine bearing rating of the anti-wear properties of the lubricating oil are done on a numerical basis as prescribed by EMD with the following relationships.

EMD silver bearing rating system

0–20	Excellent oil.
20–40	Good oil.
40–75	Borderline oil.
>75	Failure.

The results of this test using the above composition are as follows:

Silver bearing condition

EMD rating	22.
Surface condition	Extensive pitting.

EXAMPLE 2

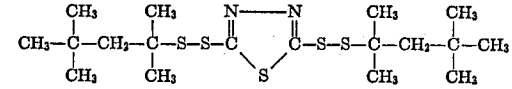
This example illustrates that the compositions of the present invention which contain alkali and/or alkaline earth metal phenates have improved wear resistance toward silver.

A lubricating oil composition was prepared and tested in a manner similar to the composition of Example 1, and except as noted below, comprising the same components as those making up the composition of the previous example. The final lubricating oil composition was as follows.

Component:[1]	Weight percent
Mineral oil, 890 SUS at 100° F.	88.75
Sulfurized calcium phenate	6.0
Ashless detergent	3.0
Calcium sulfonate	1.7
Sulfur-containing compound [2]	0.1
Chlorinated hydrocarbonaceous component [3]	0.1
Phenyl-α-naphthyl amine	0.25
Diamine component [4]	0.1

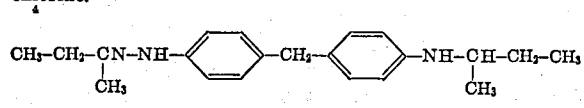
[1] This composition, as well as those of succeeding examples, contains about 0.001% by weight of Dow Corning silicon antifoam agent.

[2] Comprising primarily:



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

[4]



The results of using this lubricating oil composition is the EMD 2–567 test engine were as follows:

EMD rating	11.0.
Surface condition	No pitting.

This test demonstrates that the silver wear which is apparent when engine lubricating oil compositions containing alkali and/or alkaline earth metal phenates are used can be substantially reduced by using the compositions of the present invention.

EXAMPLE 3

This example illustrates the improved wear resistance the compositions of the present invention have toward bronze.

A composition identical to that of Example 2 was tested for bronze wear resistance using a modified Four Ball Wear Tester as incorporated in the Roxanna Test Machine, according to a procedure developed by General Electric Co. to study bronze-steel, ball is rotated under a 20 kg. load at 600 r.p.m. against 3 bronze discs which are covered by the lubricating oil composition being tested. Before the test is started, the discs are preconditioned with one revolution of the steel bar under a 60 kg. load. The pre-dent scar is measured, the load reduced to 20 kg. and fresh oil applied to the discs. Heat is applied and when the temperature reaches 200° F., the steel ball is rotated at the above-noted conditions for 5 minutes and then shut down. The temperature is then raised to 300° F. at which time the steel ball is again rotated against the disc for 5 minutes and then shut down. This procedure is repeated at 50° F. intervals through 450° F. At the end of the 6th test cycle, the disc wear scar diameter is measured and the average value obtained.

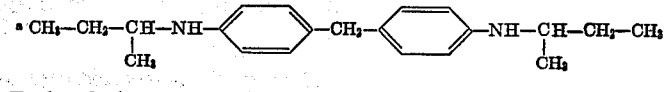
The lubricating oil composition tested gave an average scar diameter of 1.15 mm. This result, when compared to wear data obtained using other, commercially available lubricating oil compositions, indicated the compositions of the present invention provide substantial wear resistance toward bronze.

EXAMPLES 4–6

These examples illustrate the significant and unexpected improvement in oxidation resistance obtained by the compositions of the present invention.

Three additional lubricating oil compositions were prepared in a manner similar to that used in Examples 1 and 2, and except as noted below, comprising similar components to those making up the compositions of the previous examples.

Component	Weight percent of—		
	Ex. 4	Ex. 5	Ex. 6
Mineral oil, 890 SUS at 100° F.	89.1	89.0	88.85
Sulfurized calcium phenate	6.0	6.0	6.0
Ashless detergent	3.0	3.0	3.0
Calcium sulfonate	1.7	1.7	1.7
Chlorinated hydrocarbonaceous component	0.1	0.1	0.1
Sulfur-containing component	0.1	0.1	0.1
Phenyl-naphthyl amine			0.25
Diamine component *		0.10	

* 

Each of these compositions along with a composition identical to that of Example 2 was tested using a bench procedure known as the Sinclair Railroad Oil Oxidation Test. This procedure has been used to screen railroad diesel lubricating oils for oxidation resistance, and the results of this test give a reasonably true indication of the composition's oxidation properties in engine lubrication service.

This bench test procedure involves bubbling five liters of oxygen per hour through 300 ml. of test oil at 285° F. in the presence of a 1 in. by 3 in. steel backed copper-lead specimen. Fifty ml. samples of the oil composition are withdrawn at 48 hour intervals with fresh oil being added to maintain a volume of 300 ml. The test is run for a total of 144 hours at which time the viscosity and percent n-pentane insolubles of the used oil are determined. Each of these determinations give an indication of the extent of oxidative deterioration experienced by the oil during the test period. For example, both the viscosity increase of the test oil over the test period and the amount of n-pentane insolubles in the used oil are indications of

the extent to which the oils have experienced chemical reaction involving oxygen, e.g., polymerization, during the test period.

The results of these oxidation tests are as follows:

Property	Example—			
	4	5	6	2
Viscosity, SUS at 100° F.:				
New oil	944.6	994.6	994.6	994.6
Used oil	2,361	2,099	1,783	1,268
Percent viscosity increase	137	111	79.3	27.5
n-Pentane insolubles, wt. percent of used oil	3.69	3.24	2.06	0.44

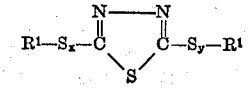
The lubricating oil compositions containing either none (Example 4) or only one (Examples 5 and 6) oxidation inhibitor, i.e., the naphthyl amine or diamine component disclosed herein, experienced substantially higher viscosity increases and n-pentane insoluble production over the test period than did the composition containing the combination of oxidation inhibitors (Example 2). The improvement in oxidation resistance obtained by the composition containing a combination of additives is unexpectedly greater than the additive effect of each inhibitor alone. These results illustrate the improved oxidation resistance of the compositions of the present invention, which include such a combination of oxidation inhibitors.

In summary, the preceding examples have demonstrated that the lubricating oil compositions of the present invention have improved wear properties toward both silver and bronze. Thus these compositions can be used in an increased number of engines, for example, in engines which have silver components and/or bronze components.

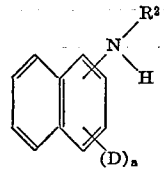
In addition, it has been discovered that the compositions of the present invention, which contain a combination of oxidation inhibitors, have an unexpectedly high resistance to deterioration by oxidation. This discovery, although quite distinct from the improved wear properties of the compositions of the present invention, is advantageously used in conjunction with wear resistant oil compositions since the combination of these properties allows for a longer useful lubricant life.

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

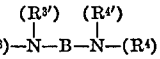
1. A lubricating oil composition which comprises a major proportion of oil of lubricating viscosity; a minor amount of at least one phenate selected from the group consisting of alkali metal phenate, alkaline earth metal phenate and mixtures thereof, said phenate being present in an amount sufficient to contribute alkalinity to said lubricating oil composition; at least one chlorinated hydrocarbonaceous component which comprises at least about 5% by weight of chlorine, said chlorinated hydrocarbonaceous component being present in an amount sufficient to improve the wear properties of said lubricating oil composition toward bronze; at least one sulfur containing compound having the following structure:



wherein each R^1 is a monovalent hydrocarbon radical containing from 1 to about 30 carbon atoms, x and y are each integers from 1 to 9, the sum of x and y being at least 2, said sulfur containing compound being present in an amount sufficient to improve the wear properties of said lubricating oil composition toward silver; at least one naphthyl amine having the following structure:



wherein R^2 is selected from the group consisting of hydrogen and monovalent hydrocarbon radicals containing from 1 to about 30 carbon atoms, a is an integer from zero to 7 and D is a monovalent hydrocarbon radical containing from 1 to about 30 carbon atoms; at least one diamine component having the following structure:



wherein R^3, $R^{3'}$, R^4 and $R^{4'}$ are independently selected from the group consisting of hydrogen, alkyl having from 1 to about 12 carbon atoms, and aryl, aralkyl, alkaryl having from 6 to about 22 carbon atoms, and B is selected from the group consisting of divalent aromatic-containing hydrocarbon radicals and substituted divalent aromatic-containing hydrocarbon radicals containing from 6 to about 30 carbon atoms, said naphthyl amine and diamine component each being present in an amount sufficient to improve the resistance to oxidation of said lubricating oil composition.

2. The composition of claim **1** wherein said naphthyl amine is present in an amount of at least about 0.05% by weight of the total composition, said diamine component is present in an amount of at least 0.01% by weight of the total composition, R^2 contains from about 6 to about 18 carbon atoms, a is an integer from 0 to 1 inclusive, D contains from about 1 to 18 carbon atoms, and R^3 and R^4 are H.

3. The composition of claim **2** wherein said chlorinated hydrocarbonaceous component is selected from the group consisting of chlorinated paraffins, chlorinated olefins, chlorinated polyolefins, chlorinated cycloaliphatic compounds, chlorinated aromatics, chlorinated esters of fatty acids, chlorinated esters of naphthenic acids, chlorinated esters of resin acids and mixtures thereof, said chlorinated hydrocarbonaceous component containing less than about 70 carbon atoms per molecule.

4. The composition of claim **3** wherein said phenate is present in an amount from about 1% to about 10% by weight of the total composition; said chlorinated hydrocarbonaceous component is present in an amount from about 0.05% to about 2.0% by weight of the total composition; and said sulfur-containing compound is present in an amount from about 0.02% to about 10.0% by weight of the total composition.

5. The composition of claim **4** wherein the chlorinated hydrocarbonaceous component comprises at least 20% by weight of chlorine.

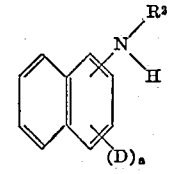
6. The composition of claim **5** wherein said phenate is selected from the group consisting of alkaline earth metal phenate and mixtures thereof, said naphthyl amine is present in a concentration of from about 0.05% to about 2% by weight of the total composition, and said diamine component is present in a concentration from about 0.01% to about 2.0% by weight of the total composition.

7. The composition of claim **6** wherein R^2 is a radical selected from the group consisting of aryl and alkaryl containing from 6 to about 18 carbon atoms and said diamine component is selected from the group consisting of bis-(N-sec-butyl-p-amino phenyl) methane, N-isopropyl-N'-phenyl-p-phenylenediamine, N - cyclohexyl-N'-phenyl-p-phenylene diamine, 2,2-bis (p-N,N'-dimethyl-aminophenyl) propane and mixtures thereof.

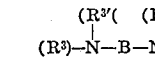
8. The composition of claim **7** wherein said chlorinated hydrocarbonaceous component contains from about 10 to about 40 carbon atoms.

9. The composition of claim **8** wherein said phenate is selected from the group consisting of calcium phenate and mixtures thereof, said naphthyl amine is present in a concentration of from about 0.10% to about 1.0% by weight of the total composition and said diamine component is present in a concentration of from about 0.01% to about 0.5% by weight of the total composition.

10. A lubricating oil composition which comprises a major proportion of oil of lubricating viscosity; at least one naphthyl amine having the following structure:



wherein R^2 is selected from the group consisting of hydrogen and monovalent hydrocarbon radicals containing from 1 to about 30 carbon atoms, a is an integer from zero to 7 and D is a monovalent hydrocarbon radical containing from 1 to about 30 carbon atoms; at least one diamine component having the following structure:



wherein R^3, $R^{3'}$, R^4 and $R^{4'}$ are independently selected from the group consisting of hydrogen, alkyl having from 1 to about 12 carbon atoms, and aryl, aralkyl, alkaryl having from 6 to about 22 carbon atoms, and B is selected from the group consisting of divalent aromatic-containing hydrocarbon radicals and substituted divalent aromatic-containing hydrocarbon radicals containing from 6 to about 30 carbon atoms, said naphthyl amine and diamine component each being present in an amount sufficient to improve the resistance to oxidation of said lubricating oil composition.

11. The composition of claim **10** wherein said naphthyl amine is present in an amount of at least about 0.05% by weight of the total composition, and said diamine component is present in an amount of at least about 0.01% by weight of the total composition.

12. The composition of claim **11** wherein R^2 contains from about 6 to about 18 carbon atoms, a is an integer from 0 to 1 inclusive, D contains from about 1 to 18 carbon atoms and R^3 and R^4 are H.

13. The composition of claim **12** wherein said naphthyl amine is present in an amount from about 0.05% to about 2% by weight of the total composition and said diamine component is present in an amount from about 0.01% to about 2.0% by weight of the total composition.

14. The composition of claim **1** wherein said composition contains from about 1% to about 6% by weight of at least one ashless detergent, said ashless detergent being a compound which comprises a hydrocarbon portion of sufficient size to render said compound oil soluble and at least one non-metallic polar portion which provides a substantial portion of the detergent action.

15. The composition of claim **4** wherein said composition contains from about 1% to about 6% by weight of at least one ashless detergent, said ashless detergent being a compound which comprises a hydrocarbon portion of sufficient size to render said compound oil soluble and at least one non-metallic polar portion which provides a substantial portion of the detergent action.

16. The composition of claim **6** wherein said composition contains from about 1% to about 6% by weight of at least one ashless detergent, said ashless detergent

being a compound which comprises a hydrocarbon portion of sufficient size to render said compound oil soluble and at least one non-metallic polar portion which provides a substantial portion of the detergent action.

17. The composition of claim **9** wherein said composition contains from about 1% to about 6% by weight of at least one ashless detergent, said ashless detergent being a compound which comprises a hydrocarbon portion of sufficient size to render said compound oil soluble and at least one non-metallic polar portion which provides a substantial portion of the detergent action.

18. The composition of claim **1** wherein said composition contains from about 0.1% to about 10% by weight of at least one sulfonate selected from the group consisting of alkali metal sulfonate, alkaline earth metal sulfonate and mixtures thereof, said sulfonate being present in an amount sufficient to improve the lubricating qualities of said composition.

19. The composition of claim **6** wherein said composition contains from about 0.1% to about 5% by weight of at least one alkaline earth metal sulfonate, said sulfonate being present in an amount sufficient to improve the lubricating qualities of said composition.

20. The composition of claim **9** wherein said composition contains from about 0.1% to about 5% by weight

of at least one calicum sulfonate, said sulfonate being present in an amount sufficient to improve the lubricating qualities of said composition.

21. The composition of claim **17** wherein said composition contains from 0.1% to about 5.0% by weight of at least one calcium sulfonate derived from a sulfonic acid having from about 12 to about 200 carbon atoms per molecule, said sulfonate being present in an amount sufficient to improve the lubricating qualities of said composition.

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