

[54] LUBRICATING OIL COMPOSITION

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[58] Field of Search ..... 252/51.5 R, 392, 252/33, 33.4, 42.7

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[57] ABSTRACT

The incorporation of at least one of certain nitrogen-oxygen containing compounds into lubricating oil compositions comprising mineral oil of lubricating viscosity and at least one alkali metal and/or alkaline earth metal carbonate overbased sulfonate and/or phenate improves the wear properties of the lubricating composition toward metals, in particular silver. These lubricating oil compositions may be used by maintaining a lubricating amount of the composition on the components of an internal combustion engine, in particular a railroad diesel engine having silver components, requiring lubrication.

32 Claims, No Drawings

## LUBRICATING OIL COMPOSITION

This invention relates to new and improved lubricating compositions. More particularly, it relates to mineral oil lubricating compositions which have improved wear properties toward metals such as, for example, silver, alloys of silver and the like.

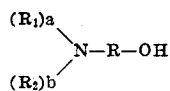
Mineral oil lubricating compositions which are used in severe service, for example, as lubricants for railroad diesel engines are advantageously alkaline in nature. The alkalinity is desired to neutralize certain acids which are formed in the engine during operation. The alkalinity can be supplied to these lubricating compositions from various sources. Typical among these sources are, for example, normal alkali metal and alkaline earth metal phenates.

Other possible sources of alkalinity for these lubricating compositions are the alkali metal and alkaline earth metal carbonate overbased sulfonates and phenates. However, the incorporation of these overbased components into the lubricating compositions, while being an efficient and economical source of alkalinity, can cause unacceptable wear to certain engine components; for example, silver wrist pin bushings in railroad diesel engines and the silver bearing surfaces in aircraft engines. It, therefore, would be advantageous to use these overbased materials to provide at least a portion of the desired alkalinity to lubricating oil compositions without causing undue wear to metal components, and in particular to silver components.

Therefore, one of the objects of the present invention is to provide a lubricating oil composition which includes alkali metal and/or alkaline earth metal carbonate overbased sulfonates and/or phenates and which have improved wear properties toward metals, in particular silver and silver alloys. Other objects and advantages of the present invention will become apparent hereinafter.

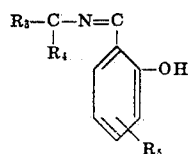
It has now been discovered that the incorporation of at least one of certain nitrogen-oxygen containing compounds into lubricating oil compositions containing at least one alkali metal and/or alkaline earth metal carbonate overbased sulfonate and/or phenate improves the wear properties of the lubricating composition toward silver. In one aspect, the present invention is a lubricating oil composition which comprises a major proportion of oil of lubricating viscosity; at least one carbonate overbased salt present in an amount sufficient to contribute alkalinity to the lubricating composition, said carbonate over-based salt being selected from the group consisting of alkali metal sulfonate, alkaline earth metal sulfonate, alkali metal phenate, alkaline earth metal phenate, and mixtures thereof, and overbased as the corresponding carbonate; and at least one oil-miscible compound selected from the group consisting of

(I)

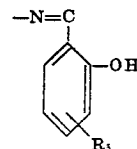


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(II)



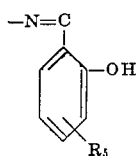
and mixtures of I and II, wherein the total number of carbon atoms contained in I is between one and about 100, preferably between about two and about 30, and the total number of carbon atoms contained in II is between eight and about 100, preferably between about eight and about 35;  $a$  is an integer from 1 to 3 and  $b$  is from zero to 1, provided that the number of valance bonds to N always totals 3; R contains from one to about four carbon atoms and is selected from the group consisting of a di-valent hydrocarbon radical and a substituted di-valent hydrocarbon radical;  $R_1$  and  $R_2$  each have from zero to about 100 carbon atoms and are independently selected from the group consisting of H, R-OH, a mono- and di-valent hydrocarbon radical, a substituted mono- and substituted di-valent hydrocarbon radical, said di-valent and substituted di-valent radical having both valance bonds on the carbon atom which is attached to N; and when  $a$  and  $b$  are both 1,  $R_1$  and  $R_2$  in combination with N can form a ring structure having at least one cyclic portion, said ring structure being selected from the group consisting of a heterocyclic ring and a substituted heterocyclic ring, said cyclic portion comprising from four to six total atoms, from three to five carbon atoms and from one to three hetero-atoms, said hetero-atoms in addition to N being independently selected from the group consisting of N, O and S, said substituents of the substituted heterocyclic ring being independently selected from the group consisting of a monovalent hydrocarbon radical, a non-hydrocarbon substituted mono-valent hydrocarbon radical, OH and  $NH_2$ , said total ring structure comprising from three to about 100, preferably from about four to about 30, carbon atoms; and when  $a$  is 1, R and  $R_1$  in combination with N can form a ring structure having at least one cyclic portion including N, said ring structure selected from the group consisting of a heterocyclic ring, a substituted heterocyclic ring, a condensed aromatic heterocyclic ring and a substituted condensed aromatic heterocyclic ring, said cyclic portion comprising from four to six total atoms, from three to five carbon atoms and from one to three hetero-atoms, said hetero-atoms in addition to N being independently selected from the group consisting of N, O and S, said substituents of the substituted heterocyclic ring and substituted condensed aromatic heterocyclic ring being selected from the group consisting of a mono-valent hydrocarbon radical, a non-hydrocarbon substituted mono-valent hydrocarbon radical, OH and  $NH_2$ , said total ring structure comprising from three to about 100, preferably from about five to about 25, carbon atoms;  $R_3$  has from zero to about 30 carbon atoms and is selected from the group consisting of H, a mono-valent hydrocarbon radical, a substituted mono-valent hydrocarbon radical, and



wherein  $R_4$  and  $R_5$  each individually have from zero to about 30 carbon atoms and are independently selected from the group consisting of H, a mono-valent hydrocarbon radical and a substituted mono-valent hydrocarbon radical said oil-miscible compound being pres-

ent in an amount sufficient to improve the wear properties of the lubricating composition toward metal, in particular silver. In each of the above structural formulas it is preferred that the N and OH be separated by from one to four, more preferably two to three, carbon atoms.

When  $a$  and  $b$  are both 1, and  $R_1$  and  $R_2$  are not combined with N into a ring structure, it is preferred that  $R_1$  and  $R_2$  be independently selected from the group consisting of H and R-OH where R is an alkyl radical having from one to four, more preferably two to three carbon atoms. Thus, the nitrogen-oxygen containing wear modifiers include the lower alkanol-amines. When either R and  $R_1$  or  $R_1$  and  $R_2$  are combined with N to form a ring structure, it is preferred that the cyclic portion of said ring structure containing N comprise from five to six total atoms and that all hetero-atoms be N. When the wear modifier is defined by structure (II) above, it is preferred that  $R_3$  be



and that  $R_3$  be selected from the group consisting of H and alkyl radical, said alkyl radical having between 1 and about 18 carbon atoms.

Typical examples of di-valent hydrocarbon radicals represented by R which are suitable include alkylene such as ethylene, propylene, butylene and the like radicals; alkylidene such as ethylidene, propylidene, butylidene and the like radicals; alkenylene such as propenylene, butenylene and pentenylene and the like radicals; alkenylidene such as propenylidene, butenylidene, pentenylidene and the like radicals; arylene such as phenylene, naphthylene and the like radicals; aralkylene such as phenyl ethylene and the like radicals; aralkylidene such as phenylpropylidene and the like radicals; alkarylene such as ethyl phenylene and the like radicals. In choosing the hydrocarbon radicals to be used, the proviso that the number of valance bonds to N always total 3 must be adhered to. For example, if  $b$  is zero and R and  $R_1$  are not combined with N into a ring structure, then either R or  $R_1$  must be alkylidene, alkenylidene or their substituted analogs. Similarly, if  $a$  and  $b$  are 1 and  $R_1$  and/or  $R_2$  is a hydrocarbon radical, these radicals cannot be di-valent.

Typical examples of the mono-valent hydrocarbon radicals represented by  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ , and  $R_5$  which are suitable include alkyl such as methyl, ethyl, propyl, lauryl, stearyl and the like radicals; alkenyl such as ethylenyl, propenyl, butenyl, oleyl, linoleyl and the like radicals; aryl such as phenyl, naphthyl and the like radicals; alkaryl such as methyl phenyl, ethyl phenyl, propyl phenyl and the like radicals; aralkyl such as phenyl methyl, phenyl ethyl, phenyl propyl and the like radicals. In each instance in which a substituted radical is called for, it is contemplated to include all those substituents which do not materially interfere with the wear improving properties of the compound. Included among these non-interfering substituents are OH,  $NH_2$ , CL, SH and the like radicals.

Compounds which are particularly preferred for improving the wear properties of the lubricating compositions of the present invention toward silver are those

selected from the group consisting of 8-hydroxyquinoline; disalicylal propylene diimine; 1-hydroxyethyl, 2-alkenyl imidazoline; 1-hydroxyethyl, 2-alkyl imidazoline and mixtures thereof, wherein the alkenyl and alkyl groups contain between about seven and about 29 carbon atoms.

The nitrogen-oxygen containing compounds defined above are present in the lubricating oil compositions in an amount sufficient to improve the wear properties of the lubricating oil compositions toward metal, in particular toward silver. It is preferred to utilize concentrations of at least about 0.01 percent by weight of these nitrogen-oxygen containing compounds in the lubricating oil compositions. In order to obtain the maximum benefits from the present invention, it is more preferred to use at least about 0.05 percent by weight and still more preferably at least about 0.1 percent by weight of these compounds. For economic reasons, it is preferred to limit the concentration of these compounds to about 2.0 percent by weight of the total lubricating composition. Therefore, these nitrogen-oxygen containing compounds should preferably comprise from about 0.01 percent to about 2.0 percent, more preferably from about 0.05 percent to about 2.0 percent and optimally from about 0.1 percent to about 2.0 percent, by weight of the total composition. It is, of course, understood that more than one effective nitrogen-oxygen containing compound may be used in combination in a single lubricating composition and such a composition is within the scope of the present invention. The proportions given above apply to the total amounts of these compounds regardless of how many are used.

The oils used in the compositions of the present invention are those conventionally used in lubricant manufacture. The suitable lubricating oils include those having a viscosity within the range of about 50 SUS to about 2000 SUS at 100°F. These oils may be refined or otherwise processed to produce an oil having the desired quality. Although mineral oils are preferred, the oil may be synthetic in nature. Typical of the oils used in the present invention is a mineral oil having a viscosity of about 1000 SUS at 100°F. Combinations of two or more different oils in a single lubricating composition are within the scope of the present invention. The lubricating oil comprises a major proportion, preferably at least about 70 percent, still more preferably at least about 90% by weight, of the total composition.

The carbonate overbased sulfonates and phenates contribute at least a portion of the alkalinity to the lubricating compositions of the present invention. Although the degree of alkalinity of these compositions may vary widely and is, therefore, not critical, it is preferred that the lubricating oil compositions of the present invention have a positive Total Base Number (TBN) of less than about 15, more preferably less than about 10. The term "Total Base Number" or "TBN" as used herein refers to a measure of alkalinity. The TBN is determined through the use of test procedure ASTM D-664 which involves titrating a sample containing the lubricating oil composition being tested to a pH of 4. The overbased salts are normally present in the lubricating oil compositions of the present invention in a minor amount, preferably in an amount from about 0.1 percent to about 8 percent and more preferably from about 0.25 percent to about 5 percent, by weight of the total composition. These overbased materials can be added to the lubricating oil as a dispersion in oil or

other fluid. The above-noted proportion range is based on the active overbased sulfonate and phenate. More than one overbased salt may be used in the lubricating compositions of the present invention. The proportions given above apply to the total amount of these salts regardless of how many are used.

The alkali metal (i.e., sodium, potassium and lithium) and alkaline earth metal (i.e., magnesium, strontium, barium and calcium) carbonate overbased alkali metal and alkaline earth metal sulfonates which may be incorporated into the compositions of the present invention comprise: (1) alkali and alkaline earth metal salts of sulfonic acids; and (2) dispersed solid particles of alkali metal and alkaline earth metal carbonates.

Sulfonates derived from sulfonic acids having about 12 to about 200 carbon atoms per molecule are of particular usefulness in the present invention. Among the sulfonic acids are the following: mahogany sulfonic acids, petrolatum sulfonic acids, mono- and polywax substituted naphthalene sulfonic acids, phenol sulfonic acids, diphenyl ether sulfonic acids, diphenyl ether disulfonic acids, naphthalene disulfide-sulfonic acids, naphthalene disulfide disulfonic acids, diphenyl amine disulfonic acids, cetyl-phenol mono-sulfide sulfonic acids, cetoxycapryl-benzene sulfonic acids, di-cetyl thianthrene sulfonic acids, such as cethyl chlorobenzene sulfonic acids, cetyl-phenol sulfonic acids, cetyl-phenol disulfide sulfonic acids, cetyl-phenol mono-sulfide sulfonic acids, cetoxycapryl-benzene sulfonic acids, di-cetyl thianthrene sulfonic acids, di-lauryl betanaphthol sulfonic acids and di-capryl nitronaphthalene sulfonic acids, aliphatic sulfonic acids such as paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy substituted paraffin wax sulfonic acids, tetraisobutylene sulfonic acids, tetra-amylenesulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitroso paraffin wax sulfonic acids, etc., cycloaliphatic sulfonic acids, such as petroleum naphthene sulfonic acids, cetyl-cyclopentyl sulfonic acids, laurylcyclohexyl 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 products. 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 more preferred class of carbonate overbased sulfonates are the calcium sulfonates overbased with calcium carbonate. Calcium sulfonates overbased with calcium carbonate can be obtained by passing carbon dioxide through a mixture of neutral calcium sulfonates, mineral oil, lime and water. The formation of the overbased sulfonates can be aided through the use of "promoters," such as phenols, aromatic amines, sucrose and lower aliphatic alcohols. Many patents have been issued which disclose processes for making calcium carbonate overbased sulfonates. Among these are

U.S. Pat. Nos. 2,865,956 and 2,956,018. The other overbased sulfonates useful in the present invention can be prepared by methods analogous to that given above for the overbased calcium sulfonates.

The alkali metal and alkaline earth metal carbonate overbased alkali metal and alkaline earth metal phenates which may be incorporated into the compositions of the present invention comprise: (1) alkali and alkaline earth metal phenates; and (2) dispersed solid particles of alkali metal and alkaline earth metal carbonates. The preferred overbased phenates for use in the present invention are the calcium phenates overbased with calcium carbonate. The phenates may be polymerized, for example, by reaction with elemental sulphur to form sulphurized phenates. The sulphurized phenates, as well as poly phenates prepared by other methods, for example, carbon bridged poly phenates, when overbased, are suitable for use in the present invention.

One method for preparing sulphurized phenates is given in U.S. Pat. No. 2,680,096. This patent also discloses a description of the calcium phenates, both sulphurized and unsulphurized, which are suitable for use in the present invention. The unsulphurized calcium phenates have the following formula:



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 four to 30 carbon atoms, O represents oxygen, a is a number having a value of 1 to 5.

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, eicoxyl, triacontyl radicals; 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.; aralkyl radicals such as phenyloctyl, phenyldecyl, phenyloctadecyl, etc.; alkaryl radicals such as amylphenyl, cetylphenyl, etc.; and cyclic non-benzenoid radicals, such as cyclohexyl, bornyl, etc.

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

Both the unsulphurized and the sulphurized phenates can be overbased with carbonate by treating the phenate with carbon dioxide such as disclosed in U.S. Pat. No. 3,036,971.

It is preferred that the lubricating compositions of the present invention include at least one detergent. 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 detergent in the compositions of the present invention. Although the detergents are not effective by themselves to satisfactorily reduce the wear characteristics of the lubricating compositions toward silver, they may enhance the silver anti-wear properties of the

compositions containing the nitrogen-oxygen containing compounds of the present invention. When these detergents are included in the compositions of this invention, they comprise from about 1 percent to about 6 percent by weight of the total composition.

In general, the ashless detergents suitable for use are compounds which comprise an oil solubilizing tail and 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 hydro-carbons having from about 30 to about 200 carbon atoms to provide oleophilic character are suitable for use in the present invention. Specific examples of this type of ashless detergent are the N-dialkylaminoalkyl alkenyl succinimides, wherein the alkenyl group contains from about 30 to about 200 carbon atoms, and the di-valent alkylene radical along with the two alkyl radicals contain a total of less than about 10 carbon atoms. See U.S. Pat. No. 3,018,291, which is hereby incorporated by reference into the present application. The required polarity may be supplied by groups containing, for example, oxygen, halogen, sulfur, phosphorous as well as nitrogen and mixtures thereof. For example, an ashless detergent can be derived by reacting hydrocarbon polymer containing from about 30 to about 200 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 detergents 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 detergent action.

In addition to the additives already described, lubricating oil compositions contemplated herein may contain other agents, such as pour point depressants, oiliness agents, blooming agents, compounds for enhancing the viscosity index of the lubricating oil, peptizing agents, 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 operation 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 benefits from the present invention.

The lubricating oil compositions of the present invention were tested following the two procedures given below. The first procedure is a laboratory test which has been 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, Texas, on November 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 termination of rubbing. The silver pins which are to be tested are attached to the rider and have conical ends. The included angle of the cone is 120 deg. 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 delineated, wear measurements sensitive to  $2 \times 10^{-5}$  inches as scar diameter (or  $3 \times 10^{-6}$  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 discs. 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 7,500 psi., 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  $10 \times 10^{-8}$  inches per foot rubbed indicate that the lubricant being tested has satisfactory anti-wear properties.

The second testing procedure involves using the various lubricants in an EMD 2-567 test engine. 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, rpm. — 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, psi. — 55  
 Inlet air temp., °F. — 95  
 Airbox temp., °F. — 160  
 Air box pressure, in. Hg. — 6.8  
 Exhaust temp., °F. — 905  
 Exhaust pressure, in. Hg. — 0.5

EMD Engine bearing ratings of the anti-wear properties of the lubricating oil are done on a numerical basis as prescribed by EMD with the following relationship.

#### EMD Silver Bearing Rating System

0 - 20 — Excellent oil  
 20 - 40 — Good Oil  
 40 - 75 — Borderline Oil  
 > 75 — Failure

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

A lubricating oil composition was prepared by blending together a mineral oil of lubricating viscosity (about 900 SUS at 100°F.) with a calcium carbonate overbased calcium sulfonate-oil mixture having a TBN of about 280. The sulfonate was derived from petroleum sources and contained about 25 carbon atoms per molecule. Lubricating oil compositions having a total base number of 3 (containing 1.05 percent by weight of the overbased sulfonate mixture) and 6 (containing 2.1 percent by weight of the overbased sulfonate mixture) were prepared.

Each lubricating oil composition was evaluated according to the bench procedure described previously. The table below gives the average wear rate based on a series of three tests with each composition.

| Total Base Number | Bench Test Wear Rate<br>at 7500 psi. and 20 fpm.,<br>in./ft. $\times 10^{-8}$ |
|-------------------|-------------------------------------------------------------------------------|
| 3                 | 27                                                                            |
| 6                 | 39                                                                            |

#### EXAMPLE 2

The lubricating oil composition of Example 1 having a total base number of 6 was further modified to include about 3 percent by weight of an ashless detergent. The detergent comprises as an oil solubilizing portion, a hydrocarbon olefin polymer containing an average of about 75 carbon atoms and to provide a substantial part of the detergency action, a polar portion containing basic nitrogen. This commercially available detergent contains 1.2 percent nitrogen and has a total base number of about 30 to about 40. The bench test procedure resulted in a wear rate of  $16 \times 10^{-8}$  in./ft. using the composition including this ashless detergent. This result when compared to Example 1 indicates that the ashless detergent does act to improve somewhat the wear properties of the lubricating composition toward silver.

#### EXAMPLE 3 to 14

Lubricating oil compositions were prepared according to the manner of Example 1 with alkalinity being supplied by the same calcium carbonate overbased calcium sulfonate-oil mixture. Each of the compositions included nitrogen-oxygen containing wear modifiers. Each composition was tested by means of the bench test procedure and the resulting wear rates are reported below.

| Example | Total base No. | Wear modifier and concentration, wt. percent    | Bench test wear rate, in./ft. $\times 10^{-8}$ |
|---------|----------------|-------------------------------------------------|------------------------------------------------|
| 1       | 3, 6           | None                                            | 27, 39                                         |
| 2       | 6              | do.                                             | 16                                             |
| 3       | 6              | 1.0% triethanolamine                            | 2.0                                            |
| 4       | 3              | 0.5% diisopropanolamine                         | 11.1                                           |
| 5       | 3              | 0.5% 8-hydroxyquinoline                         | 1.0                                            |
| 6       | 5              | 0.1% 8-hydroxyquinoline                         | 0.8                                            |
| 7       | 6              | 0.5% 1-hydroxyethyl, 2-heptadecenyl imidazoline | 3.8                                            |
| 8       | 6              | 1.0% 1-hydroxyethyl, 2-heptadecenyl imidazoline | 8.3                                            |
| 9       | 6              | 0.6% disalicylal propylene diimine              | 4.6                                            |
| 10      | 6              | 0.3% 1,3,5-tris (2-hydroxyethyl) s-triazine     | 6.0                                            |
| 11      | 6              | 0.3% salicylideneaminoquandine taltate          | 1.0                                            |
| 12      | 6              | 0.3% 3-hydroxypyridine                          | 7.5                                            |
| 13      | 6              | 0.3% 2-hydroxypyridine                          | 1.4                                            |
| 14      | 6              | 0.4% o-aminophenol                              | 5.0                                            |

Each of the nitrogen-oxygen containing compounds used as wear modifiers can be characterized as fitting one of the structural formulas given previously. The results of these tests demonstrate that all these compounds substantially improve the wear properties of lubricating oil compositions containing carbonate overbased salts toward silver.

#### EXAMPLE 15

A lubricating oil composition was prepared by blending together a mineral oil of lubricating viscosity (about 900 SUS at 100°F.) with a mixture of oil and a sulfurized calcium alkyl phenate overbased with calcium carbonate. The phenate included an alkyl group having about 18 carbon atoms and the oil-over-based phenate mixture had a TBN of about 155. The final lubricating oil composition had a TBN of 6 (containing 4 percent by weight of the oil-overbased phenate mixture) and when tested according to the bench procedure previously described gave a wear rate of  $105 \times 10^{-8}$  in./ft.

#### EXAMPLE 16 and 17

Two lubricating oil compositions were prepared according to the procedure of Example 15 except that one composition included 1.0 percent by weight of triethanolamine and the other composition included 0.4 percent by weight monoethanolamine. The addition of these additives gave the following bench test results:

| Example | TBN | Nitrogen-Oxygen Containing Additive | Bench Test Wear Rate, in./ft. $\times 10^{-8}$ |
|---------|-----|-------------------------------------|------------------------------------------------|
| 15      | 6   | None                                | 105                                            |
| 16      | 6   | 1.0% Triethanolamine                | 10.8                                           |
| 17      | 6   | 0.4% Monoethanolamine               | 1.6                                            |

## EXAMPLE 18 to 22

Lubricating oil compositions were prepared according to the manner in Example 1. Each composition, with the exception of that used in Example 18, include 3 percent by weight of the ashless detergent described in Example 2. Each of the compositions were tested using the EMD Engine Test described previously. Results of these tests are presented below.

| Example | Total base No. | Ashless detergent, wt. percent | Wear modifier and concentration, wt. percent    | Average bearing rate |
|---------|----------------|--------------------------------|-------------------------------------------------|----------------------|
| 18..... | 5              | None                           | 0.5% 1-hydroxyethyl-2-heptadecenyl imidazoline. | 42                   |
| 19..... | 5              | 3                              | 0.5% 1-hydroxyethyl-2-heptadecenyl imidazoline. | 24                   |
| 20..... | 5              | 3                              | 0.1% 8-hydroxyquinoline.                        | 9                    |
| 21..... | 5              | 3                              | 0.5% 1-hydroxyethyl-2-heptadecenyl imidazoline. | 19                   |
| 22..... | 5              | 3                              | 0.25% disalicylal propylene diimine.            | 25                   |

A lubricating oil composition containing no ashless detergent and wear modifier when engine tested results in severely damaged (i.e., wiped out) bearings. Examples 18 and 19 indicate that the use of an ashless detergent may enhance the silver wear properties of the composition.

Aside from the bearing wear measurements noted above, the oil compositions in Examples 18 to 22 were effective lubricating oils and, therefore, were acceptable lubricants.

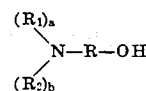
The preceding examples demonstrate the outstanding effectiveness of the nitrogen-oxygen containing wear modifiers defined herein. Not only have lubricating oil compositions which include these wear modifiers been shown to be effective diesel engine lubricants, but also these lubricating compositions have outstanding wear properties when applied to metal, in particular silver, engine components.

Examples 1, 2 and 15, when analyzed in view of the other examples, demonstrate that the oil compositions which do not include the nitrogen-oxygen containing wear modifiers have substantially poorer wear properties toward silver than do the compositions of the present invention. Although oil compositions which include ashless detergents show an improvement in silver wear over oils not containing the ashless detergents, a still more enhanced silver wear improvement is obtained using the ashless detergent in combination with the nitrogen-oxygen containing additives defined herein.

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

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity; at least one carbonate overbased salt present in an amount sufficient to contribute alkalinity to said lubricating oil composition, said carbonate overbased salt being selected from the group consisting of alkali metal sulfonate, alkaline earth metal sulfonate, alkali metal phenate, alkaline earth metal phenate and mixtures thereof and overbased as the corresponding carbonate and mixtures thereof; and at least one oil-miscible compound selected from the group consisting of

(I)



5 and

(II)

disalicylalpropylenediimine

and mixtures of I and II, wherein the total number of carbon atoms contained in I is between 1 and about 100a is an integer from 1 to 3 and b is from zero to 1, provided that the number of valence bonds to N always totals 3; R contains from one to about four carbon atoms and is selected from the group consisting of a divalent hydrocarbon radical and a substituted di-valent hydrocarbon radical; R<sub>1</sub> and R<sub>2</sub> each have from zero to about 100 carbon atoms and independently selected from the group consisting of H, R-OH, a mono- and divalent hydrocarbon radical, a substituted mono- and substituted di-valent hydrocarbon radical, said divalent and substituted di-valent radical having both valence bonds on the carbon atoms which is attached to N; and when a and b are both 1, R<sub>1</sub> and R<sub>2</sub> in combination with N can form a ring structure having at least one cyclic portion, said ring structure being selected from the group consisting of a heterocyclic ring and a substituted heterocyclic ring, said cyclic portion comprising from four to six total atoms, from three to five carbon atoms and from one to three hetero-atoms, said hetero-atoms in addition to N being independently selected from the group consisting of N, O and S, said substituents of the substituted heterocyclic ring being independently selected from the group consisting of a monovalent hydrocarbon radical, a non-hydrocarbon substituted mono-valent hydrocarbon radical, OH and NH<sub>2</sub>, said total ring structure comprising from three to about 100 carbon atoms; and when a is 1, R and R<sub>1</sub> in combination with N can form a ring structure selected from the group consisting of a heterocyclic ring, a substituted heterocyclic ring, a condensed aromatic heterocyclic ring and a substituted condensed aromatic heterocyclic ring, said cyclic portion comprising from 4 to 6 total atoms, from three to five carbon atoms and from one to three hetero-atoms, said hetero-atoms in addition to N being independently selected from the group consisting of N, O and S, said substituents of the substituted heterocyclic ring and substituted condensed aromatic heterocyclic ring being selected from the group consisting of a mono-valent hydrocarbon radical, a non-hydrocarbon substituted mono-valent hydrocarbon radical, OH and NH<sub>2</sub>, said total ring structure comprising from three to about 100 carbon atoms; said oil-miscible compound being present in an amount sufficient to improve the wear properties of the lubricating composition toward silver.

2. The composition of claim 1, wherein the total number of carbon atoms contained in I is between about two and about 30, when R<sub>1</sub> and R<sub>2</sub> in combination with N form a ring structure, said total ring structure comprises from about four to about 30 carbon atoms; when R and R<sub>1</sub> in combination with N form a ring structure, said total ring structure comprises from about five to about 25 carbon atoms; and the N and OH are separated by from one to four carbon atoms.

3. The composition of claim 1 wherein R<sub>1</sub> and R<sub>2</sub> are independently selected from the group consisting of H and R-OH where R is an alkyl radical having from one to four carbon atoms, said cyclic portions of said ring structures containing N comprise from five to six total

atoms, said hetero-atoms being N; said oil-miscible compound being present in an amount of at least about 0.01 percent by weight of the total composition.

4. The composition of claim 1 wherein said oil-miscible compound is selected from the group consisting of 8-hydroxyquinoline; disalicylal propylene diimine; 1-hydroxyethyl, 2-alkenyl imidazoline; 1-hydroxyethyl, 2-alkyl imidazoline and mixtures thereof, wherein the alkenyl and alkyl groups contain between about seven and about 29 carbon atoms.

5. The composition of claim 1 wherein said oil-miscible compound is present in an amount of at least about 0.01 percent by weight of the total composition.

6. The composition of claim 2 wherein said oil-miscible compound is present in an amount of at least about 0.01 percent by weight of the total composition.

7. The composition of claim 4 wherein said oil-miscible compound is present in an amount of at least about 0.01 percent by weight of the total composition.

8. The composition of claim 7 wherein said oil-miscible compound is present in an amount from about 0.01 percent to about 2.0 percent by weight of the total composition.

9. The composition of claim 1 wherein said carbonate overbased salt is present in an amount from about 0.1 percent to about 8 percent by weight of the total composition.

10. The composition of claim 6 wherein said carbonate overbased salt is present in an amount from about 0.1 percent to about 8 percent of the total composition.

11. The composition of claim 8 wherein said carbonate overbased salt is present in an amount from about 0.1 percent to about 8 percent of the total composition.

12. The composition of claim 1 wherein said carbonate overbased salt is selected from the group consisting of calcium sulfonate, calcium phenate and mixtures thereof, and overbased as calcium carbonate.

13. The composition of claim 6 wherein said carbonate overbased salt is selected from the group consisting of calcium sulfonate, calcium phenate and mixtures thereof, and overbased as calcium carbonate.

14. The composition of claim 11 wherein said carbonate overbased salt is selected from the group consisting of calcium sulfonate, calcium phenate and mixtures thereof, and overbased as calcium carbonate.

15. The composition of claim 1 wherein said composition contains from about 1 percent to about 6 percent 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 5 wherein said composition contains from about 1 percent to about 6 percent 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 6 wherein said composition contains from about 1 percent to about 6 percent 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 7 wherein said composition contains from about 1 percent to about 6 percent 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.

19. The composition of claim 18, wherein said carbonate overbased salt is selected from the group consisting of calcium sulfonate, calcium phenate and mixtures thereof and overbased as calcium carbonate, said carbonate overbased salt being present in an amount from about 0.1 percent to about 8 percent by weight of the total composition, said composition containing from about 1 percent to about 6 percent 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.

20. The composition of claim 19 wherein said oil-miscible compound is present in an amount from about 0.01 percent to about 2.0 percent by weight of the total composition.

21. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 1 on the components of said engine requiring lubrication.

22. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 2 on the components of said engine requiring lubrication.

23. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 3 on the components of said engine requiring lubrication.

24. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 4 on the components 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 5 on the components of said engine requiring lubrication.

26. The method of claim 25 wherein said engine comprises silver components requiring lubrication.

27. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of claim 10 on the components of said engine requiring lubrication.

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

29. In a method for lubricating an internal combustion engine, the improvement which comprises maintaining a lubricating amount of the composition of



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claim 19 on the components of said engine requiring lubrication.

30. The method of claim 29 wherein said engine is a railroad diesel engine and comprises silver components requiring lubrication.

31. In a method for lubricating an internal combustion engine which comprises silver components requir-

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ing lubrication, the improvement which comprises maintaining a lubricating amount of the composition of claim 20 on the components of said engine requiring lubrication.

5 32. The method of claim 31 wherein said engine is a railroad diesel engine.

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