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LUBRICANT COMPOSITIONS

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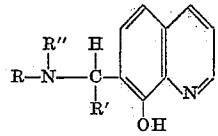
10 Claims. (Cl. 252—32.7)

This invention relates to improvements in lubricants and more particularly to hydrocarbon oil compositions which are non-corrosive and resistant to oxidative deterioration. More particularly, the present invention is directed to internal combustion engine lubricants which are resistant to the formation of gums, resinous and varnish-like materials, and which are non-corrosive to metal surfaces, especially bearings of the hard metal alloy type.

Many oils are not well suited as lubricants for use in internal combustion engines, particularly those of the type operating under severe conditions, since under such severe operating conditions the oils are susceptible to oxidative deterioration, resulting in the development of carbonaceous and/or resinous or similar varnish-like deposits in the engine and on and about the valves and rings of the engine. Furthermore, such lubricants often develop products of oxidative deterioration which are corrosive, particularly to the bearings of the hard metal alloy type, such as copper-lead bearings, cadmium-silver bearings, etc., which are frequently used in such engines.

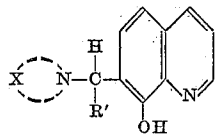
It is an object of the present invention to provide additives for oils, particularly hydrocarbon oils such as mineral oils, which will stabilize such oils against oxidative deterioration and which will render such oils non-corrosive. It is another object of the invention to provide lubricants for internal combustion engines which do not form carbonaceous deposits or resinous varnish-like materials on and about the valves, pistons and rings of such engines and which are not corrosive to metals, particularly to hard alloy bearings metals of the copper-lead and cadmium-silver type.

In accordance with the present invention, the foregoing objects can be attained by incorporating in an oleaginous material, such as for example a lubricating oil, a small, but corrosion and/or oxidation inhibiting, amount of an oil-soluble compound selected from the class of a compound having the general structural formula



(I)

and a compound having the general structural formula



(II)

in which R′ and R″ are radicals selected from the class consisting of hydrogen, a hydrocarbon radical, and a heterocyclic radical containing from 1 to about 40 carbon atoms, R is a hydrocarbon radical of from 1 to about 40 carbon atoms, and X represents the remainder of the nucleus of an N-hetero ring selected from the group consisting of 5- and 6-membered N-hetero rings in which a

hydrogen is attaced to the hetero nitrogen atom. The hydrocarbon radical can be acyclic, alicyclic, or an aryl mono- or poly-nuclear radical. When R′ and/or R″ is a heterocyclic radical, it may contain an S-, N-, or O-hetero-atom. The hydrocarbon and heterocyclic radicals can contain substituent groups such as alkyl, aryl, alkoxy, aryloxy, halogen, hydroxy, amino, cyano, etc. groups.

The oil-soluble compounds of the type I above described can be obtained by reacting 8-quinolinol with an azomethine having the general formula

R′—CH=N—R

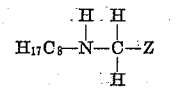
in which R and R′ are as above described in molar proportion of 1:1 at a temperature of from about 50° C. to about 110° C. for 0.5 to about 18 hours.

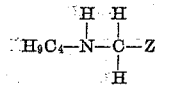
The azomethines are readily prepared by well known means by reacting in mole ratio of 1:1 an aliphatic, cycloaliphatic, aromatic or heterocyclic amine of from 1 to about 40 carbon atoms with an aliphatic, cycloaliphatic, aromatic or heterocyclic aldehyde of from 1 to about 18 carbon atoms.

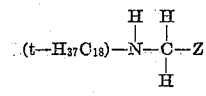
The oil-soluble compounds of the type II above described are obtainable by reacting 8-quinolinol with a nitrogen heterocyclic compound, having a hydrogen atom attached to the N-hetero atom and an aldehyde as above described. Examples of suitable N-heterocyclic compounds are piperidine, tetrahydropyrrole, py-tetrahydroquinoline, and py-tetrahydroisoquinoline.

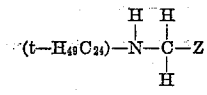
Preferably, the oil-soluble compounds of types I and II above are prepared by reacting a mixture of the amine or the N-heterocyclic compound, the aldehyde and the 8-quinolinol in mole proportions of 1:1:1 at a temperature of from about 50° C. to about 110° C. for a period of time from about 0.5 to about 18 hours. If desired, the reactions can be carried out in the presence of a solvent such as dioxane, benzene or the like.

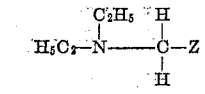
Specific compounds illustrative of the above defined class are the following:

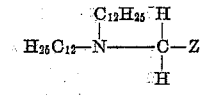


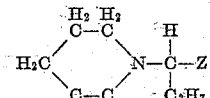


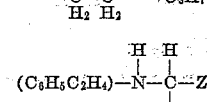


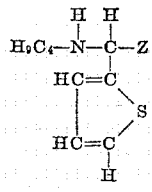




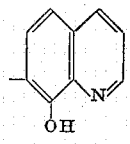








wherein Z in each of the above formulas stands for the 8-quinolinol radical



(III)

Although the above-described 8-quinolinol-azomethine reaction products all exhibit, to a definite degree, anti-corrosion and anti-oxidation properties, all are not necessarily equivalent in their effectiveness, since, depending upon the nature and severity of the service in which they are used, some variation in effectiveness may be exhibited.

The preparation of 8-quinolinol-azomethine reaction products of the type hereinabove described is illustrated by the following examples:

EXAMPLE I

A mixture of 28.2 g. (0.2 mole) t-octyl azomethine (from t-octyl primary amine and formaldehyde) and 29 g. (0.2 mole) 8-quinolinol was heated at 220° F. for 1 hour. The product, 57 g., was a viscous, light orange-brown liquid. *Analysis.*—Calculated for $C_{18}H_{25}N_2O$: N, 9.82. Found: N, 9.69.

EXAMPLE II

A mixture of 29 g. (0.2 mole) 8-quinolinol, 17 g. (0.2 mole) t-butyl azomethine (made from t-butylamine and formaldehyde), and 50 cc. benzene was refluxed 30 minutes, then evaporated on the steam bath, giving 45 g. light brown, viscous product. *Analysis.*—Calculated for $C_{14}H_{18}N_2O$: C, 73.02; H, 7.82; N, 12.17. Found: C, 73.50; H, 7.51; N, 11.78.

EXAMPLE III

A mixture of 63 g. (0.2 mole) azomethine from Primene JM–R amine (Rohm & Haas amine of neutral equivalent 303, sp. gr. 0.845, n_D 25° C. 1.460, principally t-$C_{18}H_{37}NH_2$ to t-$C_{24}H_{49}NH_2$) and formaldehyde, and 29 g. (0.2 mole) 8-quinolinol was heated at 180° F. for 30 minutes, giving 91.6 g. viscous light brown product. *Analysis.*—Calculated for $C_{28}H_{45}N_2O$: N. 6.58. Found: N, 6.29.

EXAMPLE IV

A solution of 29 g. (0.2 mole) 8-quinolinol and 20.5 ml. (0.2 mole) diethylamine in 75 ml. ethyl alcohol was treated with 16.24 ml. 37.3% aqueous formaldehyde (0.2 mole). Heat was evolved. The solution was kept at 131° F. for 1 hour, then stripped in vacuo, giving 46 g. light brown, viscous product. *Analysis.*—Calculated for $C_{14}H_{17}N_2O$: N. 11.42. Found: N, 11.13.

EXAMPLE V

To a solution of 70.6 g. (0.2 mole) Armeen 2C (principally (n-$C_{12}H_{25}$)$_2$NH) in 100 ml. isopropanol was added at 40° C. 16.24 ml. (0.2 mole) 37.3% aqueous formaldehyde. The solution was stirred 5 minutes at 40° C., 29 g. (0.2 mole) 8-quinolinol added, the mixture stirred 0.5 hour at 40° C., refluxed 1 hour, and blown with N_2 at 90° C. till all volatile material was gone. The product, 100 g., was a light brown semi-solid mass. *Analysis.*—Calculated for $C_{34}H_{58}N_2O$: C, 80.00; H, 11.37; N, 5.49; mol. wt., 510. Found: C, 79.60; H, 10.75; N, 5.26; mol. wt. 520.

EXAMPLE VI

To a stirred solution of 14.51 g. (0.1 mole) 8-quinolinol and 9.9 ml. (0.1 mole) piperidine in 20 ml. dioxane at 45° C. were added 8.83 ml. (0.1 mole) n-butyraldehyde. Heat was evolved. The solution was kept at 110° C. for 1 hour, then blown with N_2 at 110° C. till all volatile material was stripped. The red, viscous product weighed 28 g. *Analysis.*—Calculated for $C_{18}H_{24}N_2O$; N, 9.86%. Found: N, 9.52%.

EXAMPLE VII

A solution of 14.51 g. (0.1 mole) 8-quinolinol and 12.18 g. (0.1 mole) 2-phenethylamine in 20 ml. dioxane was treated with 10.13 ml. benzaldehyde. The resulting solution was refluxed 1 hour, then blown with N_2 at 224° F. to strip all volatile material. The light-brown viscous product weighed 34.2 g. *Analysis.*—Calculated for $C_{24}H_{22}N_2O$; N. 7.91%. Found: N, 7.67%.

EXAMPLE VIII

A solution of 14.51 g. (0.1 mole) 8-quinolinol, 9.9 ml. (0.1 mole) n-butylamine and 9.2 ml. (0.1 mole) α-thiophene carboxaldehyde in 20 ml. dioxane was refluxed 1 hour, then blown with N_2 at 224° F. till all volatile material was off. The dark brown viscous product weighed 28.4 g. *Analysis.*—Calculated for $C_{18}H_{20}N_2OS$; N, 8.98%; S, 10.25%. Found: N, 8.88%; S, 9.89%.

The above-described reaction products can be used in amounts of from about 0.01% to about 10% and preferably from about 0.25% to about 5% in combination with lubricant base oils, such as hydrocarbon oils, synthetic hydrocarbon oils, such as those obtained by the polymerization of hydrocarbons, such as olefin polymers; synthetic lubricating oils of the alkylene-oxide type, for example, the "Ucon oils," marketed by Carbide and Carbon Corporation, as well as other synthetic oils, such as the polycarboxylic acid ester type oils, such as the esters of adipic acid, sebacic acid, maleic acid, azelaic acid, etc.

While the above-described reaction products can be suitably employed alone in a base oil, they are usually used in combination with other lubricant addition agents which impart various desired characteristics to the base oil. Usually, these reaction products are used in conjunction with detergent-type additives, particularly those which contain sulfur or phosphorus and sulfur addition agents. This type is usually used in amounts of from about 0.002% to about 10%, and preferably from about 0.01% to about 5%. Among the phosphorus- and sulfur-containing addition agents are the neutralized reaction products of a phosphorus sulfide and a hydrocarbon, an alcohol, a ketone, an amine or an ester. Of the phosphorus sulfide reaction product additives, I prefer to employ the neutralized reaction products of a phosphorus sulfide, such as a phosphorus pentasulfide, and a hydrocarbon of the type described in U.S. 2,316,082, issued to C. M. Loane et al. April 6, 1943. As taught in this patent, the preferred hydrocarbon constituent of the reaction is a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefin hydrocarbons, such as propylene, butenes, amylenes or copolymers thereof. Such polymers may be obtained by the polymerization of mono-olefins of less than six carbon atoms in the presence of a catalyst, such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride, or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and iso-mono-olefin polymers having molecular weights ranging from about 150 to 50,000 or more, and preferably from about 500 to about 10,000. Such polymers can be obtained, for example, by the polymerization in the liquid phase of a hydrocarbon mixture containing mono- and isomono-olefins, such as butylene and isobutylene at a

temperature of from about −80° F. to about 100° F. in the presence of a metal halide catalyst of the Friedel-Crafts type, such as for example, boron fluoride, aluminum chloride, and the like. In the preparation of these polymers, a hydrocarbon mixture containing isobutylene, butylenes and butanes recovered from petroleum gases, especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline, can be used.

Another suitable polymer is that obtained by polymerizing, in the liquid phase, a hydrocarbon mixture comprising substantially C_3 hydrocarbons in the presence of an aluminum chloride-complex catalyst. The catalyst is preferably prepared by heating aluminum chloride with iso-octane. The hydrocarbon mixture is introduced into the bottom of the reactor and passed upward through the catalyst layer, while a temperature of from about 50° F. to about 110° F. is maintained in the reactor. The propane and other saturated gases pass through the catalyst, while the propylene is polymerized under these conditions. The propylene polymer can be fractionated to any desired molecular weight, preferably from about 500 to about 1,000 or higher.

Essentially paraffinic hydrocarbons, such as bright stock residuums, lubricating oil distillate, petrolatums or paraffin waxes, may be used. There can also be employed the condensation products of any of the foregoing hydrocarbons, usually through first halogenating the hydrocarbons and reacting with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride, and the like.

Examples of other high molecular weight olefinic hydrocarbons which can be employed are cetene (C_{16}), cerotene (C_{26}), melene (C_{30}), and mixed high molecular weight alkenes obtained by cracking petroleum oils.

Other preferred olefins suitable for the preparation of the phosphorus sulfide reaction products are olefins having at least 20 carbon atoms in the molecule of which from about 13 carbon atoms to about 18 carbon atoms, and preferably at least 15 carbon atoms, are in a long chain. Such olefins can be obtained by the dehydrogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

As a starting material there can be used the polymer or synthetic lubricating oil obtained by polymerizing unsaturated hydrocarbons resulting from the vapor phase cracking of paraffin waxes in the presence of aluminum chloride which is fully described in U.S. Patents 1,955,260; 1,970,402 and 2,091,398. Still another type of olefin polymer which may be employed is the polymer resulting from the treatment of vapor phase cracked gasoline and/or gasoline fractions with sulfuric acid or solid adsorbents, such as fuller's earth, whereby unsaturated polymerized hydrocarbons are removed. The reaction products of the phosphorus sulfide and the polymers resulting from the voltolization of hydrocarbons as described, for example, in U.S. Patents 2,197,768 and 2,191,787 are also suitable.

Other hydrocarbons that can be reacted with a phosphorus sulfide are aromatic hydrocarbons, such as for example, benzene, naphthalene, toluene, xylene, diphenyl, and the like, or an alkylated aromatic hydrocarbon, such as for example, benzene having an alkyl substituent having at least four carbon atoms, and preferably at least eight carbon atoms, such as a long chain paraffin wax.

The phosphorus sulfide-hydrocarbon reaction product can be readily obtained by reacting a phosphorus sulfide, for example, P_2S_5 with the hydrocarbon at a temperature of from about 200° F. to about 500° F., and preferably from about 200° F. to about 400° F., using from about 1% to about 50%, and preferably from about 5% to about 25% of the phosphorus sulfide in the reaction. It is advantageous to maintain a non-oxidizing atmosphere, such as, for example, an atmosphere of nitrogen above the reaction mixture. Usually, it is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess amount of phosphorus sulfide can be used and separated from the product by filtration or by dilution with a hydrocarbon solvent, such as hexane, filtering and subseqeuntly removing the slovent by suitable means, such as by distillation. If desired the reaction product can be further treated with steam at an elevated temperature of from about 100° F. to about 600° F.

The phosphorus sulfide-hydrocarbon reaction product, when neutralized with a basic reagent containing a metal constituent, is characterized by the presence or retention of the metal constituent of the basic reagent.

The neutralized phosphorus sulfide-hydrocarbon reaction product can be obtained by treating the acidic reaction product with a suitable basic compound, such as hydroxide, carbonate, oxide or sulfide of an alkaline earth metal or an alkali metal, such as for example, potassium hydroxide, sodium hydroxide, sodium sulfide, calcium oxide, lime, barium hydroxide, barium oxide, etc. Other basic reagents can be used, such as, for example, ammonia or an alkyl or aryl-substituted ammonia, such as amines. The neutralization of the phosphorus sulfide-hydrocarbon reaction product is carried out preferably in a non-oxidizing atmosphere by contacting the acidic reaction product either as such or dissolved in a suitable solvent, such as naphtha, with a solution of the basic reagent. As an alternative method, the reaction product can be treated with solid alkaline compounds, such as KOH, NaOH, Na_2CO_3, K_2CO_3, CaO, BaO, $Ba(OH)_2$, Na_2S, and the like, at an elevated temperature of from about 100° F. to about 600° F. Neutralized reaction products containing a heavy metal constituent, such as for example, tin, titanium, aluminum, chromium, cobalt, zinc, iron, and the like, can be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-hydrocarbon reaction product which has been treated with a basic reagent, such as above-described.

Other phosphorus sulfide reaction products which can be used are the reaction products of a phosphorus sulfide and a fatty acid ester of the type described in U.S. 2,399,243; the phosphorus sulfide-degras reaction products of U.S. 2,413,332; the reaction product of an alkylated phenol with the condensation product of P_2S_5 and turpentine of U.S. 2,409,877 and U.S. 2,409,878; the reaction product of a phosphorus sulfide and stearonitrile of U.S. 2,416,807, etc.

The effectiveness of the herein-described 8-quinolene-azomethine reaction products in inhibiting corrosion toward copper and/or lead-containing metals, such as for example, copper-lead alloys, and their oxidation inhibiting properties, are demonstrated by the data in Table I, obtained by subjecting the above samples to the following test:

A copper-lead test specimen is lightly abraded with steel wool, washed with naphtha, dried and weighed to the nearest milligram. The cleaned copper-lead test specimen is suspended in a steel beaker, cleaned with a hot trisodium phosphate solution, rinsed with water, and acetone, and dried, and 250 grams of the oil to be tested together with 0.625 gram lead oxide and 50 grams of a 30–35 mesh sand charged to the beaker. The beaker is then placed in a bath or heating block and heated to a temperature of 300° F. (±2° F.) while the contents are stirred by means of a stirrer rotating at 750 r.p.m. The contents of the beaker are maintained at this temperature for twenty-four hours, after which the copper-lead test specimen is removed, rinsed with naphtha, dried and weighed. The test specimen is then replaced in the beaker and an additional 0.375 gram of lead oxide added to the test oil. At the end of an additional twenty-four hours of test operation the test specimen is again removed, rinsed, and dried as before, and weighed. The test specimen is again placed in the beaker together with an additional 0.250 gram of lead oxide and the test continued for another twenty-four hours (seventy-two hours total). At the conclusion of this time the test specimen is removed from the beaker, rinsed in naphtha, dried and weighed.

In addition to determining the weight loss of the metal specimen, the acidity of the oil is determined at the 24, 48, and 72 hour intervals. The loss in weight of the test specimen is recorded after each weighing.

This test, known as the Sand Stirring Corrosion Test, is referred to hereinafter as "S.S.C.T."

The following samples were subjected to the above test:

Sample A (control)—A solvent extracted SAE–30 base oil containing 4.3% of a barium-containing reaction product of P_2S_5 and a polybutene of about 1000 molecular weight, containing 5.3% Ba, 2.04% P, and 1.17% S

Sample B—Sample A+0.75% quinolinol
Sample B'—Sample A+1.00% quinolinol
Sample C—Sample A+0.75% product of Example I
Sample C'—Sample A+0.20% product of Example I
Sample D—Sample A+0.75% product of Example II
Sample D'—Sample A+0.40% product of Example II
Sample E—Sample A+1.0% product of Example III
Sample E'—Sample A+0.75% product of Example III
Sample E''—Sample A+0.40% product of Example III
Sample F—Sample A+0.75% product of Example IV
Sample F'—Sample A+0.40% product of Example IV
Sample G—Sample A+0.75% product of Example V
Sample G'—Sample A+0.40% product of Example V
Sample H—Sample A+0.50% product of Example VI
Sample I—Sample A+0.75% product of Example VII
Sample J—Sample A+0.75% product of Example VIII

Table I

Sample	S.S.C.T.				
	Acidity [1]			Mg. Wt. Loss	
	24 hrs.	48 hrs.	72 hrs.	48 hrs.	72 hrs.
A	6.16	12.04	16.80	698	1,360
B	4.48	8.40	12.60	261	727
B'	1.68	5.04	9.8	249	498
C	0.84	1.4	1.68	84	117
C'	1.14	2.24	3.04	25	34
D	2.24	2.8	3.08	39	60
D'	1.4	2.52	2.8	54	77
E	0.84	1.4	1.68	57	68
E'	0.70	1.4	1.4	43	66
E''	0.98	7.0	11.0	180	468
F	2.24	3.64	3.92	20	35
F'	3.08	4.2	5.6	28	35
G	0.12	2.24	7.8	54	351
G'	1.4	4.48	10.08	201	505
H	0.84	1.4	1.8	51	71
I	1.12	1.68	1.86	51	95
J	1.12	4.76	8.4	165	392

Allowable weight losses in the above test are 200 mg. at 48 hours and 500 mg. at 72 hours.
[1] Mg. KOH per gram of oil.

The higher molecular weight reaction products of this invention also exhibit detergency properties as demonstrated by the data in Table II which were obtained by the following test, referred to as the "Indiana Stirring Oxidation Test" (ISOT). In this test, 250 cc. of the oil to be tested are heated at 330–332° F. in a 500 cc. glass beaker in the presence of 5 square millimeters of copper and 10 square millimeters of iron. Four glass rods of 6 millimeter diameter are suspended in the oil which is stirred at about 1300 r.p.m. by means of a glass stirrer having a 40° blade pitch. At intervals of 24, 48 and 72 hours, oil samples are taken and acidity and sludge (naphtha insolubles) values determined. The glass rods are inspected for evidence of varnish formation thereon. Varnish values are based on a visual rating in which glass rods free of varnish are rated 10 while badly varnish-coated rods are rated 1. Rods having appearances between these extremes are given intermediate numerical values.

The following samples were subjected to the above test:

Sample 1—A solvent extracted SAE–30 base oil (control)
Sample 2—Sample 1+1.0% product of Example III
Sample 3—Sample 1+1.0% product of Example V

Table II

Sample	ISOT								
	Acidity [1]			Varnish			Naphtha Insolubles		
	24 hrs.	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.
1	3.64	6.82	11.78	10	6	5	2.80	5.8	8.60
2	0.56	1.68	5.6	10	10	8	0	0	0.286
3	0.70	1.12	3.08	10	10	8	0.143	0.143	0.214

[1] Mg. KOH per gram of oil.

The herein described 8-quinolinol-azomethine reaction products can be employed in the form of a concentrate in a suitable oil base, the concentrate containing from about 10% to about 50% or more of the additives. Such concentrates are used for blending with a hydrocarbon oil or other oils in the proportions desired for the particular conditions of use so that upon further dilution with the oil, such as a hydrocarbon lubricating oil, a homogeneous mixture containing from about 0.001% to about 10% of said additive is obtained.

Compositions containing the herein described reaction products of 8-quinolinol and azomethines can contain other additives such as pour point depressors, antioxidants, extreme pressure agents, V.I. improvers, antiwear agents, rust inhibitors, etc. of the type well known in the art.

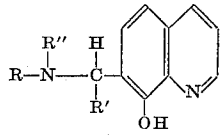
While this invention has been described in connection with the use of the herein described additives in lubricant compositions, their use is not limited thereto; but the same can be used in products other than lubricating oils, such as for example, insulating oils, greases, nondrying animal and vegetable oils, waxes, asphalts, etc.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as come within the spirit of the appended claims.

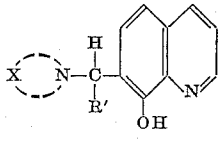
I claim:

1. A lubricant composition comprising a major proportion of an oleaginous compound and from about 0.01% to about 10% of an oil-soluble compound selected from the class consisting of a compound having the general structural formula



(I)

and a compound having the general structural formula



(II)

in which R' and R'' are selected from the class consisting of hydrogen, a hydrocarbon radical containing from 1 to about 40 carbon atoms, and a heterocyclic radical containing from 1 to about 40 carbon atoms, R is a hydrocarbon radical containing from 1 to about 40 carbon atoms, and X is the remainder of the nucleus of an N-hetero ring selected from the class consisting of a 5-membered N-hetero ring and a 6-membered N-hetero ring.

2. A lubricant composition as described in claim 1 in which R' and R'' are hydrogen and R is a butyl radical.

3. A lubricant composition as described in claim 1 in

which R' and R'' are hydrogen and R is an alkyl radical having from about 18 to about 24 atoms.

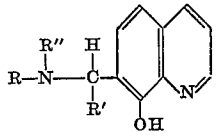
4. A lubricant composition as described in claim 1 in which R' is hydrogen, and R'' and R are ethyl radicals.

5. A lubricant composition as described in claim 1 in which R' is a phenyl radical, R'' is hydrogen, and R is a phenethyl radical.

6. A lubricant composition as described in claim 1 in which R' is C_3H_7 and X is the remainder of the nucleus of the piperidyl radical.

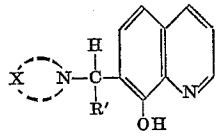
7. A lubricant composition as described in claim 1 in with the oleaginous compound is a lubricating oil.

8. A lubricant composition comprising a major proportion of a lubricating oil, from about 0.002% to about 10% of a phosphorus- and sulfur-containing neutralized phosphorus sulfide-hydrocarbon reaction product detergent lubricant additive, and from about 0.01% to about 10% of an oil-soluble compound selected from the class consisting of a compound having the general structural formula



(I)

and a compound having the general structural formula

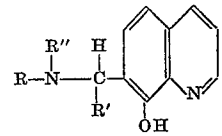


(II)

in which R' and R'' are selected from the class consisting of hydrogen, a hydrocarbon radical containing from 1 to about 40 carbon atoms, and a heterocyclic radical containing from 1 to about 40 carbon atoms, R is a hydrocarbon radical containing from 1 to about 40 carbon atoms and X is the remainder of the nucleus of an N-hetero ring selected from the class consisting of a 5-membered N-hetero ring and a 6-membered N-hetero ring.

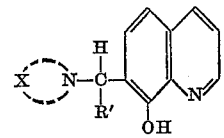
9. A lubricant composition as described in claim 8 in which the detergent additive is a barium-containing neutralized reaction product of P_2S_5 and a polybutene.

10. An addition agent for lubricant compositions consisting essentially of a concentrated solution of hydrocarbon oil containing more than 10% of an oil-soluble compound selected from the class consisting of a compound having the general structural formula



(I)

and a compound having the general structural formula



(II)

in which R' and R'' are selected from the class consisting of hydrogen, a hydrocarbon radical containing from 1 to about 40 carbon atoms, and a heterocyclic radical containing from 1 to about 40 carbon atoms, R is a hydrocarbon radical containing from 1 to about 40 carbon atoms and X is the remainder of the nucleus of an N-hetero ring selected from the class consisting of a 5-membered N-hetero ring and a 6-membered N-hetero ring.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,948,680 August 9, 1960

Ellis K. Fields

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 1, for "attaced" read -- attached --; column 6, line 4, for "subseqeuntly" read -- subsequently --; line 5, for "slovent" read -- solvent --; column 7, Table I, under the heading "24 hrs." thirteenth item, for "0.12" read -- 1.12 --.

Signed and sealed this 11th day of April 1961.

(SEAL)
Attest:
ERNEST W. SWIDER
Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents

UNITED STATES PATENT OFFICE

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