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2,198,961

LUBRICANT

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24 Claims. (Cl. 87—9)

This invention relates to lubricants and particularly to viscous hydrocarbon oils having incorporated therein materials for improving their properties.

It is well known that viscous hydrocarbon oils, particularly when employed as lubricants in internal combustion engines and in transformers, deteriorate during service, such deterioration being the result of the action of oxygen, heat, moisture and the catalytic effect of bearing metals. Such deterioration generally results in the formation of sludge of indefinite composition and of acidic products which are frequently highly corrosive to the metals and alloys with which they come in contact during lubrication. The formation of corrosive products is particularly noticeable in highly refined oils which, however, possess very desirable characteristics in other respects, notably in their viscosity-temperature relationships, and in reduced tendency to carbon formation. Therefore, it has long been desired to eliminate the formation of sludge and corrosive products in the oils, and many proposals have been made by those skilled in the art for the solution of such problem.

It is an object of the present invention to produce viscous hydrocarbon oils having improved stability against deterioration and reduced tendency to form corrosive products, particularly when subjected to the conditions of service present in internal combustion engines. Another object is to produce viscous hydrocarbon oils having a greatly reduced tendency to corrode metals and alloys with which they come into contact during service. A further object is to provide a method for producing such improved viscous hydrocarbon oils. A still further object is to provide a method of lubricating certain alloy bearings without corroding such bearings to an objectionable extent. Still other objects are to provide new compositions of matter and to advance the art. Other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with my invention which comprises incorporating in viscous hydrocarbon oils a small proportion of at least one compound consisting of carbon, hydrogen, nitrogen and ethereal oxygen having the formula $R(X)_y$, wherein R represents a pyridine or quinoline nucleus, Y is an integer from 1 to 3, preferably 1, and X is a radical containing a tertiary nitrogen connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms, and which radical X is selected from tertiary alkylamines, N-alkyl pyrroles, N-alkyl piperidines and pyridines. It will be found that the resulting product will have a greatly decreased tendency to deteriorate and form sludge or corrosive products in use, particularly under the conditions occurring in internal combustion engines.

By the term "viscous hydrocarbon oil", I mean a hydrocarbon oil having viscosities within the range employed for lubricating metallic bearing surfaces moving relatively to each other and mutually carrying a load. The preferred oils will be the lubricating oils obtained from petroleum.

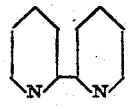
By the term "ethereal oxygen", it will be understood that I mean the oxygen which is essential to every ether and has both valences satisfied by carbon atoms of organic radicals which form with the oxygen an ether.

The term "consisting of carbon, hydrogen, nitrogen and ethereal oxygen" shall be understood to be generic and to include compounds which do not contain ethereal oxygen as well as those which do contain ethereal oxygen.

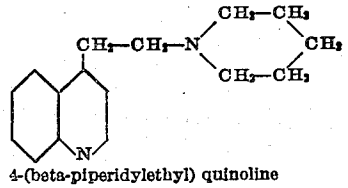
By the term "tertiary alkylamines", I mean amines which are aliphatic in nature and intend to exclude amines containing a benzene ring.

While compounds falling within the formula $R(X)_y$, as heretofore defined, will be effective for my purpose, I have found that those compounds in which X represents a pyridine ring and an N-alkyl piperidine group are the most effective and represent the preferred embodiments of my invention. Also, while the nuclei of R and X may contain substituents such as alkyl, aryl, aryloxy and amino radicals, and particularly methyl, ethyl, isopropyl, methoxy and butoxy groups, preferably, such nuclei are unsubstituted. Amongst the compounds of my invention, I have found that alpha, alpha'-dipyridyl, a mixture of dipyridyls, a mixture of 4-(di- and tri-piperidylmethyl)-methylquinoline, 4-(beta-piperidylethyl)-quinoline and 4-(beta-piperidylethyl)-6-methoxyquinoline are particularly effective for my purpose. Mixtures of compounds, such as those generally obtained in the synthesis thereof, appear

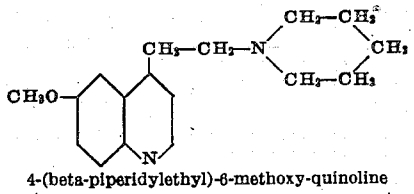
to be particularly effective. The structure of my compounds will be apparent from the following formulae:



Alpha-alpha'-dipyridyl



4-(beta-piperidylethyl) quinoline



4-(beta-piperidylethyl)-6-methoxy-quinoline

The compounds of my invention may be employed in purified form or as the crude product. They may be employed with other lubricant addition agents such as compounds for depressing pour points, increasing film strength or improving the viscosity index of the oils. The amount of compound to be employed with the lubricating oil may vary from about 0.02 to about 10% based on the oil. Larger amounts may be employed, but without advantage. Preferably, my compounds are employed in the proportion of about 0.10 to 2.0% based on the oil. The use of my compounds is not restricted to liquid oils, but they may be employed in greases or other lubricating media of petroleum origin.

In order to more clearly illustrate my invention, the general methods of preparing my compounds, the preferred mode of carrying my invention into effect and the advantageous results to be obtained thereby, the following examples are given:

Example 1

Two thousand grams of pyridine and 1633 grams anhydrous ferric chloride were mixed and placed in a glass-lined autoclave which was then heated at 320° to 350° C. for seven hours. On cooling, the mixture was crushed, made strongly alkaline with potassium hydroxide, and steam distilled. The distillate, after acidification with sulfuric acid, was concentrated to one-tenth its original volume and made alkaline with potassium hydroxide. A considerable quantity of solid which separated was removed by filtration and the filtrate extracted several times with ether. The ether layers were dried and distilled, the unreacted pyridine distilling with the lower boiling fractions. The high boiling fraction solidified and, together with the solid which had previously been separated, was crystallized from petroleum naphtha. One hundred and eighty-six grams of product melting at 70° to 72° C. was obtained which was alpha, alpha'-dipyridyl.

Example 2

Fifty grams of pyridine and 20 grams sodamide were heated eight hours at 145° C. The reaction mixture was decomposed with 100 cc. water and the oily layer distilled. The fraction boiling below 150° C. was discarded while a fraction boiling between 150° and 200° C. was washed with water, dried over sodium sulfate, and added to the residue remaining from the distillation. From these combined materials a total of 35 grams of material boiling between 200° and 350° C. was obtained. This consisted essentially of a mixture of isomeric dipyridyls.

Example 3

Twenty and three-tenths grams of 37 per cent formaldehyde were neutralized with aqueous sodium hydroxide and added with cooling to 21.3 grams piperidine. Thirty-eight and five-tenths grams lepidine were then added and the mixture heated in a sealed tube to 120° C. for sixteen hours. After cooling, the reaction product was extracted with several portions of ether, the ether solutions dried over anhydrous potassium carbonate, concentrated, and distilled under reduced pressure. Twenty-two grams of material boiling at 175° to 178° C. at 3.5 mm. was obtained, which appears to be 4-(beta-piperidylethyl)-quinoline. An additional 9.5 grams of material boiling at 200° to 210° C. at 3.5 mm. was obtained which appears to be a mixture of the 4-(di- and tripiperidylmethyl)-methylquinoline.

The effectiveness of the compounds of the type given above was determined by a procedure similar to that described in the Analytical Edition of Industrial and Engineering Chemistry, volume 6, page 419 (1934), modified by suspending in the oil strips which had been cut from cadmium-silver bearings and placed in such a fashion that the strips were completely immersed while the air which was bubbled through the oil washed over the exposed surfaces. In this test, a volume of 300 cc. of oil was used through which washed air was bubbling at a rate of ten liters per hour, the oil temperature being maintained at 171° to 172° C. The cadmium-silver strip was removed at various intervals and weighed. From the curve showing loss in weight against time, there was determined the time required for a loss of ten milligrams per square inch of exposed surface to occur. Viscosity determinations were made on the oil after oxidation to determine the degree of thickening caused by dissolved decomposition products. A further estimate of the amount of oxidized products formed was secured by diluting ten grams of oil to 100 cc. volume with a special petroleum naphtha and weighing the amount of insoluble material which precipitated out on standing.

Example 4

The effectiveness of alpha, alpha'-dipyridyl in eliminating the formation of corrosive products was determined in the above test using a solvent extracted paraffin base oil with a viscosity at 210° F. of 46.8 seconds Saybolt Universal.

Concentration of alpha, alpha'- di-pyridyl, percent by weight	Hours to 10 mg./sq. in. corrosion of cadmium-silver	Sludge after 41 hrs. of test mg./10 gm.	Viscosity at 210° F. after 157 hrs., seconds
None	30	126.0	67
0.10	180	18.8	50.2
0.25	260	14.1	49.8
0.50	140	15.0	51.2

Example 5

The mixed dipyridyls and the mixture of (di- and tripiperidylmethyl)-methylquinoline were

tested in 0.25% concentration in a solvent extracted Mid-Continent base oil of S. A. E.-30 grade with the following results.

Compound added to oil	Hours to 10 mg./sq. in. corrosion of cadmium-silver	Viscosity at 210° F. after 100 hrs. of test
None	8	99
Mixed dipyridyls	236	72.6
(Di- and tripiperidyl-methyl)-methyl-quinoline	212	73.3

Example 6

The effect of 0.25% concentration of 4-(beta-piperidylethyl)-quinoline was determined in another sample of solvent extracted Mid-Continent base S. A. E.-30 oil.

Compound added to oil	Hours to 10 mg./sq. in. corrosion of cadmium-silver	Viscosity at 210° F. after 113 hrs. of test
None	22	130.7
4-(beta-piperidyl-ethyl)-quinoline	187	72.7

Heretofore, others skilled in the art have proposed adding to viscous hydrocarbon oils primary and secondary amines, that is, compounds containing nitrogen atoms to which one or two hydrogen atoms are attached, for stabilizing such hydrocarbon oils. However, such primary and secondary amines have not proved to be satisfactory, particularly for lubricants subjected to the high temperatures occurring in internal combustion engines and the like. On the other hand, my compounds are effective stabilizing agents under such conditions. This is shown in the following Example 7:

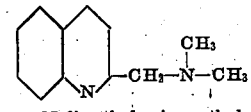
Example 7

Fifty grams of a commercial paraffin base oil of an S. A. E.-20 W grade, to which had been added 0.5% of the compound under test, was placed in a 125 cc. Erlenmeyer flask. The flask was fitted with a cork stopper containing a 1 mm. capillary tube which extended within ⅛ inch of the bottom of the flask. Weighed strips, approximately 1⅜ inches by ½ inch, cut from cadmium-silver and copper-lead bearings of the type used in present day internal combustion engines, together with similar strips cut from sheets of autobody steel, were suspended in the flask in such a fashion as to be immersed to approximately half their lengths in oil. The unit was placed in an oil bath maintained at substantially 175° C., and air, which had been passed through two wash bottles of distilled water, was bubbled through the capillary tube at a rate of 2.5 to 3.0 liters per hour. The strips of cadmium-silver and copper-lead bearing metals were removed at intervals and weighed after washing with chloroform and acetone. From the curve of loss of weight against time of exposure, it was possible to determine the time at which a 10 mg. loss per 10 grams of bearing metal had accurred. The amount of oxidized material in the oil was determined by diluting 10 grams to 100 cc. volume with a special petroleum naphtha, allowing the solution to stand for three hours at 0° C., followed by filtering and weighing the insoluble oxidation product. The weight of this insoluble material is a measure of the amount of oxidation which the oil has undergone. Low values indicate a high degree of lubricant stability.

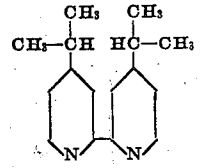
Compound added to oil (0.5%)	Hours to 10 mg./gm. loss		Sludge values	
	Cadmium-silver	Copper lead	Hours of test	Mg./10 gm.
None—control	26	24	100	394.6
Diethyl-o-phenylene-diamine	22	25	100	*Excessive
None—control	23	22	48	112.8
Sym.-diphenylethyl-enediamine	23	24	48	144.1
Alpha, alpha'-dipy-ridyl	47	Above 45	48	49.6
None—control	23	24	70	103.0
Tetramethyl pipera-zine	Below 20	21	70	*Excessive
4-(beta-piperidyl-ethyl)-6-methoxy-quinoline	Above 70	Above 70	70	50.4

*These samples contained much more sludge than the controls, so much that it could not be filtered out for measurement.

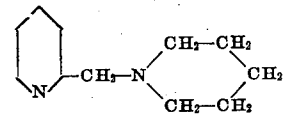
While I have disclosed the preferred embodiments of my invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in the art that many variations and modifications may be made therein, particularly in the compounds employed, without departing from the spirit of my invention. For example, other compounds which will be suitable for my purpose are as follows:



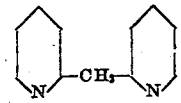
2-N-dimethylaminomethyl quinoline



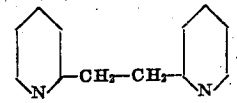
Gamma, gamma'-diisopropyl-alpha, alpha'-dipyridyl



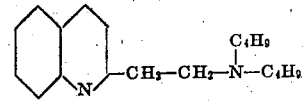
Alpha-piperidylmethyl pyridine



Alpha, alpha'-dipyridyl methane



Alpha, alpha'-dipyridyl ethane



2-beta-N-dibutylaminoethyl quinoline

I claim:

1. A viscous hydrocarbon oil having incorporated therein a small proportion of at least one compound consisting of carbon, hydrogen, nitrogen and ethereal oxygen having the formula $R(X)_y$ wherein R is a nucleus of the group consisting of pyridine and quinoline nucelei, Y is an integer from 1 to 3 and X is a radical containing

a tertiary nitrogen connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms and which radical is a member of the group consisting of tertiary alkyl amines, N-alkyl pyrroles, N-alkyl piperidines and pyridines.

2. A viscous hydrocarbon oil having incorporated therein a small portion of at least one compound consisting of carbon, hydrogen, nitrogen and ethereal oxygen having the formula $R(X)_y$ wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei, Y is an integer from 1 to 3 and X is an N-alkyl piperidine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

3. A viscous hydrocarbon oil having incorporated therein a small proportion of at least one compound consisting of carbon, hydrogen, nitrogen and ethereal oxygen having the formula RX wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei and X is a radical containing a tertiary nitrogen connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms and which radical is a member of the group consisting of tertiary alkyl amines, N-alkyl pyrroles, N-alkyl piperidines and pyridines.

4. A viscous hydrocarbon oil having incorporated therein a small proportion of at least one compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei, and X is an N-alkyl piperidine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

5. A viscous hydrocarbon oil having incorporated therein a small proportion of at least one compound consisting of carbon, hydrogen and nitrogen having the formula $R(X)_y$ wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei, Y is an integer from 1 to 3 and X is a pyridine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

6. A viscous hydrocarbon oil having incorporated therein a small proportion of at least one compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei and X is a pyridine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

7. A viscous hydrocarbon oil having incorporated therein a small proportion of at least one dipyridyl.

8. A viscous hydrocarbon oil having incorporated therein a small proportion of a mixture of dipyridyls.

9. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, at least one compound consisting of carbon, hydrogen, nitrogen and ethereal oxygen having the formula $R(X)_y$ wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei, Y is an integer from 1 to 3 and X is a radical containing a tertiary nitrogen connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms and which radical is a member of the group consisting of tertiary alkyl amines, N-alkyl pyrroles, N-alkyl piperidines and pyridines.

10. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, at least one compound consisting of carbon, hydrogen, nitrogen and ethereal oxygen having the formula $R(X)_y$ wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei, Y is an integer from 1 to 3 and X is an N-alkyl piperidine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

11. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, at least one compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei and X is a radical containing a tertiary nitrogen connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms and which radical is a member of the group consisting of tertiary alkyl amines, N—alkyl pyrroles, N—alkyl piperidines and pyridines.

12. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, at least one compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei, and X is an N—alkyl piperidine radical in which the teritary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

13. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but

which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, at least one compound consisting of carbon, hydrogen and nitrogen having the formula $R(X)_y$ wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei, Y is an integer from 1 to 3 and X is a pyridine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

14. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, at least one compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a nucleus of the group consisting of pyridine and quinoline nuclei and X is a pyridine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of R through from 1 to 3 carbon atoms.

15. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, at least one dipyridyl.

16. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, a mixture of dipyridyls.

17. A viscous hydrocarbon oil having incorporated therein a small proportion of a compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a quinoline nucleus and X is an N-alkyl piperidine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of the quinoline nucleus through from 1 to 3 carbon atoms.

18. A viscous hydrocarbon oil having incorporated therein a small proportion of 4-(beta-piperidylethyl)-quinoline.

19. A viscous hydrocarbon oil having incorporated therein a small proportion of a compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a quinoline nucleus and X is an N-dialkylaminoalkyl radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of the quinoline nucleus through from 1 to 3 carbon atoms.

20. A viscous hydrocarbon oil having incorporated therein a small proportion of 2-beta-N-dibutylaminoethyl quinoline.

21. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, a compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a quinoline nucleus and X is an N-alkyl piperidine radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of the quinoline nucleus through from 1 to 3 carbon atoms.

22. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, 4-(beta-piperidylethyl)-quinoline.

23. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, a compound consisting of carbon, hydrogen and nitrogen having the formula RX wherein R is a quinoline nucleus and X is an N-dialkylaminoalkyl radical in which the tertiary nitrogen is connected to a carbon of the pyridine ring of the quinoline nucleus through from 1 to 3 carbon atoms.

24. A method of lubricating metallic bearing surfaces which comprises maintaining between the bearing surfaces, one of which contains a characterizing proportion of a metal of the group consisting of cadmium, silver, copper and lead, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid surface and maintaining the effectiveness of the lubricating oil by incorporating therein, in a small but sufficient proportion to substantially retard the corrosion, 2-beta-N-dibutylaminoethyl quinoline.

MELVIN A. DIETRICH.