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OIL COMPOSITIONS CONTAINING AMINE SALTS OF BORO-DIOL COMPLEXES

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This invention relates to oil compositions, and n particular concerns new hydrocarbon oil compositions having improved stability characteristics, including improved resistance to sludge-formation and improved anti-corrosion properties.

It is well known that hydrocarbon oils, particularly those of mineral origin, have a tendency to deteriorate and form sludge-like deposits when allowed to stand over long periods of time at moderately elevated temperatures, or in a relatively short time under service conditions such as those encountered in modern internal combustion engines. This type of deterioration is attributed to the oxidation of certain of the hydrocarbons present in such oils. It is also known that such oils tend to promote corrosion of metal surfaces, particularly alloy bearing surfaces, with which they come in contact during service. This type of corrosion is in many cases believed to be due to the presence of oxidation products formed by deterioration of the oil rather than to components of the oil itself.

It is an object of the present invention to provide oil compositions having improved resistance to deterioration and sludge-formation.

Another object is to provide oil compositions having improved anti-corrosive properties, particularly with respect to alloy bearings.

A further object is to provide oil compositions having improved service characteristics.

A still further object is to provide means for improving the general stability characteristics of hydrocarbon oils without detracting from their load-carrying and lubrication qualities.

Other objects will be apparent from the following detailed description of the invention, and various advantages not specifically referred to herein will occur to those skilled in the art upon employment of the invention in practice.

In accordance with the above and related objects, I have found that the amine salts of boro-diol complexes are excellent stabilizing agents for hydrocarbon oils, and that compositions comprising hydrocarbon oils normally subject to deterioration through oxidation or other means and

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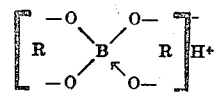
relatively small amounts of such amine salts have greatly improved resistance to sludge-formation and other manifestations of deterioration, including a tendency to promote corrosion of bearing alloys and the like. This improvement is secured with no loss of load-carrying qualities, and in fact in certain instances the general lubrication characteristics are improved. The various amine salts differ among themselves as to their degree of effectiveness in imparting one or more desirable properties to the compositions. For example, certain of such salts may be particularly effective in reducing sludge-formation, whereas others may be more effective in inhibiting bearing-corrosion. Others may secure one or both of these benefits and in addition improve lubrication properties. In general, however, all of such salts act as stabilizing agents to improve the resistance of hydrocarbon oils to deterioration during storage or service. Accordingly, the oil compositions provided by the invention are particularly suited to use as lubricants in internal combustion engines where they are subjected to very drastic deterioration conditions. They are also useful as heat-transfer media and the like, e. g., transformer oils, where it is desired to maintain a high degree of resistance to sludging over long periods of time.

The amine salts which are employed as stabilizing agents in the oil composition provided by the invention are obtained by the direct addition of an organic amine to a boro-diol complex. The latter complexes are formed by reaction between boric acid and an organic compound containing at least two hydroxyl groups, e. g., ethylene glycol. The nature of the reaction and the configuration of these complexes are not known with certainty, although in some instances structural formulae have been proposed. In general they are believed to be chelate-type compounds containing the nucleus:



wherein R represents the residue of the dihy-

droxy compound. The present invention, however, is in no way limited by any theory concerning the structure of the boro-diol complexes whose amine salts are employed as stabilizing agents in the new compositions.

The formation of the boro-diol complexes may be carried out simply by heating boric acid with an organic compound containing at least two hydroxyl groups until the theoretical amount of water is evolved from the mixture. The polyhydroxy compounds which may be reacted with boric acid in such manner include both aliphatic and aromatic compounds, i. e., polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, trimethylene glycol, erythritol, glycerol, triethylene glycol, tetramethylene glycol, etc., and polyhydric phenols such as catechol, resorcinol, orcinol, beta - naphthohydroquinone, dihydroxytoluene, phenylcatechol, ethylcatechol, etc. They may also be compounds in which one of the hydroxyl groups is part of a carboxyl group, e. g., salicylic acid, glycollic acid, melilotic acid, coumaric acid, and similar hydroxycarboxylic acids, or cyclic compounds such as dihydroxycyclohexane, dihydroxyfuran, etc.

As previously mentioned, the amine salts which are employed as stabilizing agents in the oil compositions provided by the invention are formed by the direct addition of organic amines to the above-described boro-diol complexes. This reaction may be carried out simply by heating a mixture of the complex and the amine to a suitable reaction temperature until reaction is complete. Usually the optimum reaction temperature will be between about 50° C. and about 200° C., although this range is not critical and temperatures outside this range may be employed. If desired, the reaction may be carried out in the presence of an inert solvent such as water, benzene, toluene, naphtha, etc. Also, if desired, the amine salts may be prepared directly from boric acid and the desired organic amine and polyhydroxy compound without isolation of the intermediate boro-diol complex by heating a mixture of the three reactants, either under anhydrous conditions as proposed in U. S. Patent 1,975,890 or in the presence of water as disclosed by Boesken et al., Rec. Trav. Chim., 37, 184 (1918).

Any organic amine may be employed in preparing the boro-diol complex salts as just described. As examples of such amines, there may be mentioned aliphatic and cycloaliphatic amines, including alkylolamines, such as methylamine, ethylamine, diethylamine, amylamine, tributylamine, ethanolamine, diethanolamine, triethanolamine, isopropanolamine, trimethylamine, laurylamine, hexadecylamine, ethylenediamine, diethylenetriamine, triethylenetetramine, cyclohexylamine, dicyclohexylamine, tristearylamine, guanidine, etc.; aromatic amines, such as aniline, naphthylamine, methylaniline, diethylaniline, toluidine, phenetidine, diphenylamine, triphenylamine, diaminodiphenylmethane, aminocresol, aminophenol, phenylenediamine, benzidine, amino-diphenyl, aminodiphenyloxide, diphenylguanidine, benzylamine, diphenylethylamine, etc.; and heterocyclic amines, such as pyridine, piperidine, aminobenzothiazole, morpholine, etc.

The amine salts of the present class are effective as stabilizing agents for hydrocarbon oils in relatively small amounts, e. g. from as little as 0.001 per cent by weight up to the limit of their solubility in the oil, which is usually somewhat less than about 0.5 per cent by weight. Since it is usually desirable to provide compositions of maximum stability, i. e., compositions containing a maximum effective amount of the stabilizing agent, the new compositions are usually prepared by adding the stabilizing agent to the oil in an amount in excess of that soluble in the quantity of oil taken. After promoting as complete solution as possible through the use of agitation and/or heat, the composition is filtered to recover the undissolved stabilizing agent and to insure a homogeneous product. If desired, however, the stabilizing agent may be added to the oil in predetermined amounts just sufficient to effect the desired degree of improvement in stability.

In testing and demonstrating the improved stability of the new oil compositions provided by the invention, use may be made of several standard testing procedures. A convenient test of stability in general is the so-called "sludge accumulation test," designated as ASTM D670–42T, Method A. Bearing-corrosion tendencies may be determined by the Lauson engine test, and load-carrying and general lubrication qualities may be determined by the Falex and static coefficient of friction tests, respectively. These various tests are described more fully hereinafter.

The following examples will illustrate several ways in which the principle of the invention has been applied, but are not to be construed as limiting the same. All proportions are specified as parts by weight.

EXAMPLE I

Preparation of amine salts of boro-diol complexes

The complex of boric acid and ethylene glycol was prepared by heating a mixture of 248 parts (4 mols) of ethylene glycol and 123.6 parts (2 mols) of boric acid in a flask fitted with a mechanical stirrer, thermometer, and reflux water trap. The flask and contents were initially heated at a temperature of about 100° C. for 1 hour, after which time 100 parts of toluene were added and the heating was continued at reflux temperature while collecting water in the trap. Approximately 114 parts of water were collected in this manner. When the temperature of the contents of the flask reached about 121° C., the water trap was disconnected and the toluene was distilled off until the temperature reached about 200° C. Upon cooling and standing overnight, the boro-ethylene glycol complex was obtained as a white powdery solid having a melting point of about 135°–143° C.

A mixture of 17.1 parts (0.1 mol+30% excess) of the boro-ethylene glycol complex so prepared and 24.1 parts (0.1 mol) of hexadecylamine was placed in a flask and heated at a temperature of about 150° C. for 20 minutes. It was then allowed to cool to about 50° C., and approximately 200 parts of benzene were added. The mixture was then heated at reflux temperature for 1 hour, after which it was cooled and filtered to remove a small quantity of unreacted complex. The benzene was then distilled off, and the product was dried in a vacuum oven. The hexadecylamine salt of the boro-ethylene glycol complex so obtained was a yellow waxy solid having a melting point of about 60°–69° C.

A number of amine salts of different boro-diol complexes were prepared by the procedure just

described. The properties of these products are tabulated below:

TABLE I

Product	Appearance	M. P., °C.	Solubility [1]				
			Ether	Hexane	Benzene	Alcohol	Mineral Oil
Hexadecylamine salt of boro-ethylene glycol.	Yellow waxy solid	60–69	S	S	S	V. S.	Sl. S.
Cyclohexylamine salt of boro-ethylene glycol.	Brown waxy solid			I			Sl. S.
Triethanolamine salt of boro-ethylene glycol.	Brown semi-liquid		I	I	I	V. S.	Sl. S.
Hexadecylamine salt of boro-catechol	Tan powder	146–152	I	I	S. H.	V. S.	Sl. S.
Triethanolamine salt of boro-catechol	Brown viscous liquid						Sl. S.
Hexadecylamine salt of boro-salicylic acid.	Tan solid	57–85	S. H.	I	S	S	S. H.
Triethanolamine salt of boro-salicylic acid.	Brown solid	107–116	I	I	I	S. H.	Sl. S.
Hexadecylamine salt of boro-propylene glycol.	Brown waxy solid		Sl. S. H.	S. H.	S	S	Sl. S.
Hexadecylamine salt of boro-trimethylene glycol.	Yellow waxy solid	60–69	S	S	S	V. S.	Sl. S.
Triethanolamine salt of boro-trimethylene glycol.	Brown semi-liquid		I	I	Sl. S.	S	Sl. S.

[1] Solubility: I=Insoluble; S=Soluble; Sl. S.=Slightly Soluble; V. S.=Very Soluble; S. H.=Soluble Hot.

EXAMPLE II

Sludge accumulation tests

Compositions were prepared comprising certain of the boro-diol complex amine salts set forth in Example I and a mineral oil base having the following specifications:

Gravity, ° API	28.0
Viscosity @ 100° F., SUV	54.4
Viscosity @ 210° F., SUV	33.6
Flash point, ° F	275
Fire point, ° F	310
Neut. No	0.01

Each of the compositions was prepared by adding 0.3 per cent by weight of the amine salt to the base oil, after which the mixture was warmed and stirred to promote solution. The composition was then filtered to remove any of the amine salt which had not dissolved in the oil. Each of the compositions so prepared was then subjected to the sludge accumulation test, ASTM D670–42T, Method A, as described in "ASTM Standards on Petroleum Products and Lubricants," December 1946, modified as follows: Instead of subjecting three samples to the test and determining the amount of sludge formed at the end of the three given periods of time, five samples of each composition tested were placed in the apparatus. After starting the test, the samples were examined from time to time and at the first evidence of sludge formation one sample was removed and the sludge content determined in the usual manner. The test was continued with samples being withdrawn and sludge determinations made at intervals of time depending upon the apparent rate of sludge formation. When all five samples had been used up in this manner, a curve was plotted of the amount of sludge formed versus time. The time required for formation of 0.1 per cent by weight of sludge was read from this curve and taken as a convenient value for comparison purposes. The rate of sludge formation was determined from the slope of the curve. The results of the tests carried out in this manner are tabulated below:

TABLE II

Stabilizing Agent		Rate of Sludge Formation, %/Day	Time to Form 0.1% by Wt. of Sludge, Days
Identity	Per Cent by Wt.		
None (Base oil alone)	0.0	0.010	10
Triethanolamine salt of boro-ethylene glycol	<0.3	0.003	34
Hexadecylamine salt of boro-catechol	<0.3	0.0035	34
Triethanolamine salt of boro-catechol	<0.3	0.0015	>60 (est.)
Triethanolamine salt of boro-trimethylene glycol	<0.3	0.0035	38
Triethanolamine salt of boro-trimethylene glycol	[1] 0.001	0.0095	12
Triethanolamine salt of boro-salicylic acid	<0.3	0.001	43
Triethanolamine salt of boro-salicylic acid	[1] 0.001	0.010	14
Triethanolamine salt of boro-propylene glycol	<0.3	0.003	38

[1] Composition was prepared by dissolving the given amount of stabilizing agent in the base oil.

EXAMPLE III

Lauson engine tests

Compositions comprising three of the amine salts set forth in Example I and a mineral lubricating oil were prepared as described in Example II. The base oil employed was a highly paraffinic lubricating base having the following specifications:

Gravity, °API	29.2
Viscosity @ 100° F., SUV	506
Viscosity @ 210° F., SUV	66
Flash point, °F	440
Fire point, °F	505
Color	2
Neut. No	0.01

These compositions were tested for bearing-corrosion tendencies in the crankcase of a standard single-cylinder Lauson engine equipped with a

copper-lead bearing and operated under the following conditions (L-4 prototype procedure):

Water-jacket temperature, °F	210°±2°
Oil temperature, °F	280°±2°
Load, H. P	1
Oil charge, ml	183
Air/fuel ratio	14.5:1±0.2
Speed, R. P. M	1820±10

After 4 hours of operation and at the end of each alternate 8-hour period thereafter, 23 ml. of fresh oil were added to the crankcase. At the end of the first 8-hour running period and after each accumulative 8-hour period thereafter, 10 ml. of the oil were withdrawn from the crankcase, the crankcase volume was corrected to 160 ml. and 23 ml. of fresh oil were added. The copper-lead bearing was examined after each 8-hour period, and at the end of 40 hours was weighed to determine the loss of weight. The piston was also examined at the end of 40 hours for evidence of varnish formation and was compared with a set of prepared standards and given an arbitrary varnish rating value ranging from 10 (no varnish formed) to 0 (very heavy varnish formation). The results of these tests are tabulated below:

TABLE III

Stabilizing Agent		Varnish Rating Value	Wt. Loss of Bearing, gms.
Identity	Percent by Wt.		
None (Base Oil, alone)	----------	8	0.264
Hexadecylamine salt of boro-ethylene glycol	<0.3	9+	0.119
Triethanolamine salt of boro-salicylic acid	<0.3	8	0.096
Triethanolamine salt of boro-trimethylene glycol	<0.3	7+	0.097

EXAMPLE IV

Load-carrying and lubrication tests

In order to determine the load-carrying and lubrication qualities of the new compositions provided by the invention, a number of the compositions were subjected to suitable tests. Load-carrying properties were tested by the standard Falex seizure test employing steel V-blocks and steel pins. After a 3-minute break-in period at 300 lbs. jaw load, followed by a 1-minute period at 500 lbs. load, the load was increased in increments of 250 lbs. with one minute running time until failure occurred. The load at failure is a measure of the load-carrying properties of the composition under test. A measure of the lubrication properties of the new compositions was obtained by a determination of the static coefficient of friction at room temperature on a modified Herschel-type machine employing steel balls on a steel race. The results of these tests are tabulated below:

TABLE IV

Stabilizing Agent		Falex Load at failure, lbs.	Static Coeff. of Friction
Identity	Per cent by Wt.		
None (Base Oil alone)	----------	1,000	0.29
Triethanolamine salt of boro-catechol	<0.2	1,500	0.22
Hexadecylamine salt of boro-ethylene glycol	0.1	1,000	----------
Hexadecylamine salt of boro-trimethylene glycol	0.2	1,250	0.20
Triethanolamine salt of boro-trimethylene glycol	<0.2	1,250	----------
Hexadecylamine salt of boro-salicylic acid	0.2	1,000	0.21
Hexadecylamine salt of boro-propylene glycol	0.2	1,250	----------

While the preceding examples illustrate the preparation and properties of compositions consisting only of a hydrocarbon oil base and a boro-diol complex amine salt stabilizing agent, it is to be understood that the compositions provided by the invention may contain other additive agents, e. g., pour point depressants, anti-foam agents, viscosity index improvers, detergents, extreme pressure agents, etc. They may also contain corrosion inhibitors of the type which is effective against corrosion in the presence of water or water vapor. Similarly, the base oil employed may be derived from various types of stocks, e. g., paraffinic, naphthenic, or asphaltic stocks, or blends thereof, as well as from synthetic hydrocarbon oils, and may be of various degrees of refinement. They may vary widely in physical characteristics depending upon the use to which they are to be put.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the methods or ingredients employed, provided the products defined by the following claims be obtained.

I claim:

1. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of an amine salt of an acid compound of boric acid and a member selected from the group consisting of glycols and polyhydroxy benzenes.

2. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and a minor proportion of an amine salt of an acid compound of boric acid and a member selected from the group consisting of glycols and polyhydroxy benzenes, said amine salt being present in an amount ranging from about 0.001 per cent by weight to the limit of its solubility in said oil.

3. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of an amine salt of an acid compound of boric acid and a glycol.

4. A composition of matter in accordance with claim 3 in which said glycol is ethylene glycol.

5. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of an amine salt of an acid compound of boric acid and a polyhydroxy benzene.

6. A composition of matter in accordance with claim 5 in which said polyhydroxy benzene is catechol.

7. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of an aliphatic amine salt of an acid compound of boric acid and a member selected from the group consisting of glycols and polyhydroxy benzenes.

8. A composition of matter consisting of essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of an alkylolamine salt of an acid compound of boric acid and a member selected from the group consisting of glycols and polyhydroxy benzenes.

9. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of an aliphatic

amine salt of an acid compound of boric acid and a glycol.

10. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of an aliphatic amine salt of an acid compound of boric acid and a dihydroxy benzene.

11. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of the hexadecylamine salt of an acid compound of boric acid and ethylene glycol.

12. A composition of matter consisting essentially of a major proportion of a hydrocarbon oil and between about 0.001 and about 0.5 per cent by weight of the composition of the triethanolamine salt of an acid compound of boric acid and catechol.

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