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OIL COMPOSITIONS CONTAINING AMINE
SALTS OF ACID COMPOUNDS OF BORIC
ACID AND HYDROXY CARBOXYLIC ACIDSCharles E. Trautman, Cheswick, Pa., assignor to
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burgh, Pa., a corporation of DelawareNo Drawing. Application January 12, 1950,
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8 Claims. (Cl. 252-33.6)

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This invention relates to oil compositions, and in 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.

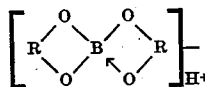
Other objects will be apparent from the following detailed description of the invention, and various advantages not specifically referred to herein will occur to those skilled in the art upon employment of the invention in practice.

In accordance with the above and related objects, I have found that the amine salts of acid compounds of boric acid and hydroxy carboxylic acids in which the hydroxyl group and the carboxylic acid group are separated by no more than two carbon atoms are excellent stabilizing agents for hydrocarbon oils, and that compositions comprising hydrocarbon oils normally subject to deterioration through oxidation or other means and 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

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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 period 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 the acid compound of boric acid and the hydroxy carboxylic acid. The latter compounds are formed by reaction between boric acid and the hydroxy acid. The nature of the reaction and the configuration of these acid compounds 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 hydroxy acid. Although the present invention is not limited to anything concerning the structure of the acid boric acid compounds, the evidence that they are chelate-type compounds is strengthened by the fact that hydroxy carboxylic acids in which the hydroxyl and carboxylic acid groups are widely separated in the molecule form the acid boric acid compounds at best only in low yields, the predominant reactions taking place being such reactions as result in the formation of unsaturated linkages and inner esters.

The formation of the acid boric acid compounds may be carried out simply by heating boric acid with a hydroxy carboxylic acid in which the hydroxyl group is separated from the

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carboxylic acid group by no more than two carbon atoms until the theoretical amount of water is evolved from the mixture. The hydroxy carboxylic acids which may be reacted with boric acid in such manner include both aliphatic and aromatic compounds; e. g., salicylic acid, glycolic acid, hydroxyisobutyric acid, α -hydroxydecanoic acid (2-hydroxy-4,6,6-trimethylheptanoic acid), lactic acid, β -hydroxybutyric acid, and mandelic acid.

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 acid boric acid compounds. This reaction may be carried out simply by heating a mixture of the acid compound 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 hydroxy acid without isolation of the intermediate acid boric acid compound 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 salts as just described. As examples of such amines, there may be mentioned aliphatic and cycloaliphatic amines, including alkylamines, 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, aminodiphenyl oxide, 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.

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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

The acid compound of boric acid and salicylic acid was prepared by introducing 276 parts (2 mols) of salicylic acid and 61.8 parts (1 mol) of boric acid into a flask fitted with a mechanical stirrer, thermometer and a reflux water trap. Approximately 350 parts of toluene were then added and the mixture was heated and stirred. Refluxing started when the pot temperature reached 94° C. Heating was continued and water was collected in the trap continuously for about 5½ hours. After cooling overnight, about 16 hours, heating was resumed for 4 more hours. During the heating the temperature of the mixture in the pot gradually rose to 113° C. and during the entire period about 51 parts of water were collected. The toluene was then distilled off and the product was dried in a vacuum oven for 5 hours at 65° C. and about 10 mm. of mercury pressure. The product was a light yellow powder melting at 265°-270° C.

The triethanolamine salt of this acid compound of boric acid and salicylic acid was prepared by reacting 28.4 parts (0.1 mol) of the acid compound and 14.9 parts (0.1 mol) of triethanolamine in about 100 parts of chloroform in a reaction flask similar to that described above. The mixture was heated to and maintained at refluxing temperature (pot temperature 61° C.) for 1 hour. The chloroform was then distilled off and the product was dried in a vacuum oven for ½ hour at 45° C. and about 10 mm. of mercury pressure. The final product was a brown solid melting at 107°-116° C. It was insoluble in ether, hexane and benzene; was soluble in hot ethyl alcohol and slightly soluble in mineral oil.

EXAMPLE II

The hexadecylamine salt of the acid compound of boric acid and salicylic acid was prepared in a manner similar to that described in Example I but using hexadecylamine in place of triethanolamine. The product obtained was a tan solid melting at 57°-85° C. It was soluble in benzene, ethyl alcohol and in hot ether and hot mineral oil and was insoluble in hexane.

EXAMPLE III

The cyclohexylamine salt of the acid compound of boric acid and glycolic acid was prepared in a manner similar to that described in Example I except that the free acid compound was not recovered as such. In preparing this salt, 217 parts of a 70 per cent water solution of glycolic acid (2 mols of the acid and 3.61 mols of water) and 61.8 parts (1 mol) of boric acid were heated in the flask. The pot temperature rose gradually

to 130° C. over a period of about 2½ hours and finally reached a temperature of 140° C. in 3 hours. 120 parts (6.66 mols) of water was collected. The product was a brown liquid which became very viscous on cooling to room temperature. The cyclohexylamine salt was prepared by adding 99 parts (1 mol) of cyclohexylamine to the flask containing the acid compound. Heating and stirring were continued for about 1½ hours. The product was a greenish brown glass-like solid with no definite melting point. At 60° to 70° C. the compound becomes fairly fluid. It is soluble in ethyl alcohol, slightly soluble in mineral oil, slightly soluble in hot benzene, slightly soluble in hot hexane and is slightly soluble in cold and soluble in hot acetone.

EXAMPLE IV

SLUDGE ACCUMULATION TESTS

Compositions were prepared comprising the amine salt prepared as described 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

Composition A was prepared by adding 0.3 per cent by weight of the amine salt of Example I 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. Composition B was prepared by adding 0.001 per cent of the amine salt of Example I to the base 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.

When testing the base oil in this way 0.1 per cent by weight of sludge was formed in 10 days and the rate of sludge formation per cent per day was 0.010. The results obtained with Composition A were 0.1 per cent by weight of sludge not formed until 43 days and the rate of sludge formation was 0.001; and with Composition B 0.1 per cent of sludge was formed in 14 days and the rate of sludge formation was 0.010.

Using another base mineral oil having the same specifications as above, a composition was prepared by adding 0.3 per cent by weight of the

amine salt of Example III, which was a somewhat larger amount than was actually soluble in the oil. The resulting composition is designated as Composition C. When testing this base oil in the manner described above, 0.1 per cent by weight of sludge was formed in 7 days and the rate of sludge formation was 0.0160. On testing Composition C it was found that 0.1 per cent of sludge was not formed until 18 days and the rate of sludge formation was 0.0075.

EXAMPLE V

LAUSON ENGINE TESTS

A composition comprising the amine salt of Example I and a mineral lubricating oil was prepared as described in Example IV. 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

The composition and the base oil 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 I

Stabilizing Agent	Varnish Rating Value	Wt. Loss of Bearing, gms.
Identity	Per cent by Weight	
None (Base Oil, alone)	8	0.264
Triethanolamine salt of boro-salicylic acid	<0.3	0.096

EXAMPLE VI

LOAD-CARRYING AND LUBRICATION TESTS

In order to determine the load-carrying and lubrication qualities of the new compositions provided by the invention, a composition containing the amine salt of Example II and the base oil was 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 II

Stabilizing Agent		Falex Load at failure, lbs.	Static Coeff. of Friction
Identity	Per Cent by Weight		
None (Base Oil Alone)		1,000	0.29
Hexadecylamine salt of boro-salicylic acid	0.2	1,000	0.21

While the preceding examples illustrate the preparation and properties of compositions consisting only of a hydrocarbon oil base and an amine salt stabilizing agent of the class disclosed herein, 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.

This application is a continuation-in-part of my application Serial No. 789,569, filed December 3, 1947, now Patent No. 2,497,521.

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 comprising a major proportion of a hydrocarbon oil and a minor proportion of an amine salt of an acid compound of boric acid and a hydroxy carboxylic acid in which the hydroxyl group and the carboxylic acid group are separated by no more than two carbon atoms, 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.

2. A composition of matter comprising 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 hydroxy carboxylic acid in which the hydroxyl group and the carboxylic acid group are separated by no more than two carbon atoms.

3. A composition of matter in accordance with claim 2 in which said hydroxy carboxylic acid is salicylic acid.

4. A composition of matter in accordance with claim 2 in which said hydroxy carboxylic acid is glycolic acid.

5. A composition of matter in accordance with claim 2 in which said amine salt is a salt of an aliphatic amine.

6. A composition of matter in accordance with claim 5 in which the aliphatic amine salt is a salt of an alkylolamine.

7. A composition of matter comprising 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 salicylic acid.

8. A composition of matter comprising 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 salicylic acid.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,312,208	Clayton et al.	Feb. 23, 1943