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GLYCINE AMIC ACIDS IN TURBINE OIL

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This invention relates to antirust compositions. It is more particularly concerned with mineral lubricating oils containing certain amic acids and salts thereof.

As is well known to those skilled in the art, the rusting of ferrous metal surfaces has been a common occurrence in the field of lubrication. This has been a serious problem in steam turbine lubrication, particularly during the initial operation of new installations. Rusting is most pronounced at points where the clearance between bearing surfaces is very small, as in the governor mechanism. This is usually caused by water entering the oil supply, as by condensation, and becoming entrained in the oil throughout the circulating system, thereby coming into contact with the ferrous metal surfaces. Manifestly, this constitutes a menace to the operational life of the turbine.

During the operation of marine turbines, the aforementioned rusting is more frequently encountered. This is due to the fact that in marine operation, the same lubricating oil circulates through the main drive gear system and often, through the hydraulic system, as well as through the steam turbine lubricating system. As a consequence, appreciable amounts of salt water are entrained by the oil and, accordingly, rusting is more severe and occurs more readily.

It has now been found that antirust properties in the presence of sea water can be imparted to lubricating oil by the addition of certain amic acids. It has been discovered that certain alkenyl succinamic acids and amine salts thereof are effective antirust additives for turbine oils.

Accordingly, it is a broad object of this invention to provide novel rust inhibitors. Another object is to provide lubricating oils that are inhibited against rusting of ferrous metal surfaces in the presence of sea water. A further object is to provide an antirust turbine oil containing succinamic acid rust inhibitors. A specific object is to provide a turbine oil containing certain alkenyl succinamic acids and salts thereof. Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description.

In general, the present invention provides a mineral lubricating oil containing a small amount, sufficient to prevent rusting of ferrous metal surfaces, of (1) an amic acid of alkenyl succinic acid anhydride and glycine, and (2) the salts of (1) with tertiary-alkyl primary amines having a tertiary carbon atom attached to the nitrogen atom and containing between about 6 carbon atoms and about 30 carbon atoms per tertiary-alkyl radical, and (3) monoamides of (1) with tertiary-alkyl primary amines having a tertiary-carbon atom attached to the nitrogen atom and containing between about 6 carbon atoms and about 30 carbon atoms per tertiary-alkyl radical.

The novel addition agents of this invention are amic acids obtained by condensing equimolar amounts of an alkenyl succinic acid anhydride and an amino compound reactant, without formation of water of condensation. The amino compound reactant contemplated is glycine (aminoactic acid). The condensation takes place readily upon heating the acid anhydride reactant and the amino compound reactant at temperatures ranging from ambient temperatures and upwards. The reaction is an amide formation reaction effected by the well-known addition of the anhydride group to an amino group. This addition proceeds at any temperature but temperatures of between about 90° C. and about 120° C. are preferred. The time of reaction is dependent on the size of the charge and the reaction temperature selected. Ordinarily addition of the acid anhydride is substantially complete within a few minutes. In order to ensure complete reaction, however, it is preferred to continue heating for several hours, even as much as 10 hours. In general, the reaction time varies between several minutes and about ten hours. If desired, nonpolar solvents, such as benzene, toluene, kerosines, and xylene, can be used to improve fluidity.

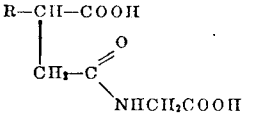
The alkenyl succinic acid anhydride reactant can have between 8 and 35 carbon atoms in the alkenyl radical, and preferably between 10 and 14 carbon atoms. Nonlimiting examples of the alkenyl succinic acid anhydride reactants are octenyl succinic acid anhydride, diisobutenyl succinic acid anhydride, 2-methylheptenyl succinic acid anhydride, 4-ethylhexenyl succinic acid anhydride, nonenyl succinic acid anhydride, decenyl succinic acid anhydride, undecenyl succinic acid anhydride, dodecenyl succinic acid anhydride, triisobutenyl succinic acid anhydride, tetrapropenyl succinic acid anhydride, tetradecenyl succinic acid anhydride, hexadecenyl succinic acid anhydride, 11-tricosenyl succinic anhydride, and 17-pentatriacontenyl succinic anhydride.

Although the anhydride is preferred, the compounds of this invention can be prepared from the corresponding alkenyl succinic acid. In this case, the condensation with amino compound reactant is accompanied by formation of one mole of water per mole of amine. The reaction, in this case, is carried out at temperatures of between about 130° C. and about 200° C., although the reaction can be effected at temperatures above and below this range. The reaction will proceed until one mole of water is evolved per mole of alkenyl succinic acid reactant, usually six to ten hours. In order to facilitate the removal of water, to effect a more complete reaction in accordance with the principle of Le Chatelier, a hydrocarbon solvent which forms an azeotropic mixture with water can be added to the reaction mixture. Heating is continued until removal of water by azeotropic distillation has substantially ceased. Examples of well-known solvents that form azeotropes are benzene, toluene, and xylene.

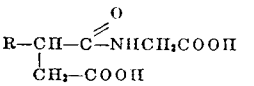
The salt of the amic acid can be made readily by warming the amic acid and a tertiary-alkyl primary amine, in equimolar proportions.

The amide of the amic acid can be prepared by any of the usual amide-forming reactions. Most readily it is prepared by reacting the amic acid and the tertiary-alkyl primary amine, in equimolar amounts, and with removal of a mole of water of condensation. The reaction conditions used are those defined hereinbefore for reacting the alkenyl succinic acid with the amine compound reactant.

Each of the amic acid types contemplated in the present invention can have two structural forms:



or



wherein R, in each case, is an alkenyl branched chain radical having between about 8 carbon atoms and about 35 carbon atoms. The product can be predominantly one or the other isomer, or even mixtures of the two.

For this reason, the amic acids of this invention are more accurately defined in the terms of the method by which they are made.

The amines utilizable in forming the salts of the amic acids are the tertiary-alkyl, primary, monoamines in which a primary amino ($-NH_2$) group is attached to a tertiary carbon atom and which contain between about 6 carbon atoms and about 30 carbon atoms in the tertiary-alkyl radical; and mixtures thereof. These amines all contain the terminal group

Non-limiting examples of the amine reactants are t-hexyl primary amine, t-octyl primary amine, t-nonyl primary amine, t-decyl primary amine, t-dodecyl primary amine, t-tetradecyl primary amine, t-octadecyl primary amine, t-eicosyl primary amine, t-docosyl primary amine, t-tetracosyl primary amine, and t-triacontyl primary amine. The amine reactants can be prepared in several ways well known to those skilled in the art. Specific methods of preparing the t-alkyl primary amines are disclosed in the Journal of Organic Chemistry, vol. 20, page 295 et seq. (1955). Mixtures of such amines can be made from a polyolefin fraction (e.g., polypropylene and polybutylene cuts) by first hydrating with sulfuric acid and water to the corresponding alcohol, converting the alcohol to alkyl chloride with dry hydrogen chloride, finally condensing the chloride with ammonia, under pressure, to produce a t-alkyl primary amine mixture.

The amic acids and salts and amides contemplated herein are effective to impart antirust properties to mineral lubricating oils, particularly highly refined mineral lubricating oils, such as, steam turbine oils. The amount of succinamic acid, salt, or amide that is added to the lubricating oil will vary between about 0.001 percent and about 10.0 percent, by weight of the oil. In preferred practice, amounts varying between about 0.05 percent and about 1.0 percent, by weight, are used. Other substances can be added to the lubricating oil to impart other properties thereto. For example, there may be added antioxidants, pour point depressants, V.I. improvers, and E.P. agents.

The following specific examples are for the purpose of illustrating the antirust lubricants of this invention and of demonstrating the effectiveness thereof. It is to be understood that this invention is not to be limited to the particular reactants employed, or to the operations and manipulations described therein. Other reactants, as described hereinbefore, can be employed, as those skilled in the art will readily understand.

AMIC ACIDS, SALTS AND AMIDES

The amine reactant used in the specific working examples, "amine A", is a mixture of primary amines having a carbon atom of a tertiary butyl group attached to the amino ($-NH_2$) group and containing 12 to 15 carbon atoms per amine molecule and averaging 12 carbon atoms per molecule. This mixture contains, by weight, about 85 percent tertiary dodecyl amine, about 10 percent tertiary pentadecyl amine, and relatively small amounts, i.e., less than about 5 percent of amines having less than 12 or more than 15 carbon atoms.

Example 1

A mixture of 75 grams (1.0 mol) glycine and 300 grams (1 mol) tetrapropenylsuccinicanhydride were slowly heated with stirring to about 110°–115° C. The reaction mixture was stirred at 110–115° C. for about 3 hours to insure complete reaction.

Example 2

A mixture of 37.5 grams (0.5 mole) glycine and 150 grams (0.5 mol) tetrapropenylsuccinicanhydride were slowly heated with stirring to about 110°–115° C. The reaction mixture was stirred at 110–115° C. for about 3 hours. The mixture was cooled to about 50° C. and 100 grams (0.5 mol) amine A was added. The mixture was stirred at 100° C. for about 3 hours to insure complete reaction.

Example 3

A mixture of 37.5 grams (0.5 mol) glycine and 150 grams (0.5 mol) tetrapropenylsuccinicanhydride were slowly heated with stirring to about 110–115° C. The reaction mixture was stirred at 110–115° C. for about 3 hours. The mixture was cooled to 50° C. and 200 grams (1.0 mol) amine A was added. The mixture was stirred at 100° C. for about 3 hours to insure complete reaction.

Example 4

A mixture of 37.5 grams (0.5 mol) glycine and 150 grams (0.5 mol) tetrapropenyl succinic acid anhydride was slowly heated, with stirring, to about 100–115° C. The reaction mixture was stirred at 100–115° C. for about 3 hours. This product, the amic acid described in Example 1, was cooled to about 50° C. and 100 grams (0.5 mol) amine A were added. The resulting mixture was then slowly heated to a final temperature of 200° C. About 9 grams (0.5 mol) water of condensation was evolved during this reaction stage, producing the amine A amide of the product of Example 1.

Example 5

Four mineral oil blends were prepared. Each blend contained a small amount of one of the additives described in Examples 1 through 4. Two base oils were used. Oil X is a highly solvent-refined mineral lubricating oil having 31° API gravity and a Saybolt Universal Viscosity of 150 seconds at 100° F. Oil Y is a highly solvent refined Mid-Continent oil having 29° API gravity and a Saybolt Universal Viscosity of 415 seconds at 100° F. Both are typical steam turbine lubricating oils. These blends were subjected to the ASTM Rust Test D665–44T using synthetic sea water. The composition of each blend and test results are set forth in Table I.

The test method used to distinguish the rusting characteristics of lubricating oil blends was the ASTM test D665–44T for determining "Rust Preventing Characteristics of Steam Turbine Oils in Presence of Water," in which synthetic sea water was used. The synthetic sea water contained 25 grams of sodium chloride, 11 grams of magnesium chloride hexahydrate, 4 grams of sodium sulfate, and 1.2 grams of calcium chloride per liter. In this test a cylindrical polished steel specimen is suspended and soaked in 300 cubic centimeters of the oil under test at 140° F. for thirty minutes. Thirty cubic centimeters of synthetic sea water are added and the mixture is stirred at 1000 r.p.m. After 48 hours, the steel specimen is removed and examined for evidence of rust on the portion of the specimen which hangs in the oil. In order to pass this test, the test specimen must be entirely free of rust.

TABLE I

Additive of Example—	Conc'n, Wt. Percent	Base Oil	ASTM Rust Test Result
	none	X	Fail.
1	0.05	X	Pass.
4	0.05	X	Pass.
	none	Y	Fail.
2	0.05	Y	Pass.
3	0.05	Y	Pass.

It will be apparent to those skilled in the art that the amic acids and amine salts thereof are effective to impart antirust properties to lubricating oils, in the presence of sea water. Thus, the mineral oil compositions are highly effective for severe service, such as, in marine turbine lubrication.

Although the present invention has been described with

preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A mineral lubricating oil containing a small amount, sufficient to prevent rusting of ferrous metal surfaces, of a material selected from the group consisting of (1) an amic acid of alkenyl succinic acid anhydride, having between about 8 and about 35 carbon atoms in the alkenyl radical, and an equimolar amount of glycine, (2) amine mono- and di-salts of (1) wherein the salt-forming amine is a tertiary-alkyl primary amine having a tertiary carbon atom attached to the nitrogen atom and containing between about 6 carbon atoms and about 30 carbon atoms per tertiary-alkyl radical, and (3) monoamides of (1) wherein the amide-forming amine is a tertiary-alkyl primary amine having a tertiary-carbon atom attached to the nitrogen atom and containing between about 6 carbon atoms and about 30 carbon atoms per tertiary-alkyl radical.

2. The lubricating oil composition defined in claim 1, wherein said mineral lubricating oil is a steam turbine lubricating oil and said material is present in an amount varying between about 0.001 percent and about 10 percent, by weight of the oil.

3. A steam turbine lubricating oil containing between about 0.05 percent and about one percent, by weight of the oil, of an amic acid of tetrapropenyl succinic acid anhydride and an equimolar amount of glycine.

4. A steam turbine lubricating oil containing between about 0.05 percent and about one percent, by weight of the oil, of an amine mono-salt of an amic acid of tetrapropenyl succinic acid anhydride and an equimolar amount of glycine, wherein the salt-forming amine is a mixture of primary tertiary-alkyl amines having a tertiary carbon atom attached to the nitrogen atom and containing between 12 and 15 carbon atoms per tertiary-alkyl radical and having an average of about 12 carbon atoms per molecule.

5. A steam turbine lubricating oil containing between about 0.05 percent and about one percent, by weight of the oil, of an amine di-salt of an amic acid of tetrapropenyl succinic acid anhydride and an equimolar amount of glycine, wherein the salt-forming amine is a mixture of primary tertiary-alkyl amines having a tertiary carbon atom attached to the nitrogen atom and containing between 12 and 15 carbon atoms per tertiary-alkyl radical and having an average of about 12 carbon atoms per molecule.

6. A steam turbine lubricating oil containing between about 0.05 percent and about one percent, by weight of the oil, of the monoamide of an amic acid of tetrapropenyl succinic acid anhydride and an equimolar amount of glycine, wherein the amide-forming amine is a mixture of primary tertiary-alkyl amines having a tertiary carbon atom attached to the nitrogen atom and containing between 12 and 15 carbon atoms per tertiary-alkyl radical and having an average of about 12 carbon atoms per molecule.

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