MINERAL OIL COMPOSITIONS

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This invention relates to mineral oil compositions, and in particular concerns mineral oil compositions adapted to protect ferrous and other metal surfaces with which they come in contact from rusting and other types of corrosion.

As is well known, simple mineral oil films afford only limited protection to metal surfaces against rusting and other types of corrosion, and in general cannot be relied upon to provide sufficient protection in the presence of moisture or even under conditions of high humidity. Consequently, it has become common practice to employ corrosion inhibitors or anticorrosion agents as additives in mineral oil compositions for the purpose of providing additional protection against rusting and corrosion. Such additives have been used in various types of lubricating compositions, such as machine oils, turbine oils, internal combustion engine and diesel lubricating oils, greases, etc., as well as in slushing oils and the like. The anticorrosion agents heretofore used in this manner, however, have not proved entirely satisfactory under present-day service conditions. Certain of such agents do not provide protection against corrosion under extreme conditions of moisture, humidity, and temperature. Others, while being satisfactory for use in mineral oil compositions which are employed in the presence of only relatively pure water or water vapor, do not provide protection against corrosion by salt-water or other aqueous solutions. Others deleteriously affect certain desirable properties of the compositions in which they are used, e.g., lubricating value, demulsibility, etc.

Accordingly, it is an object of the present invention to provide mineral oil compositions which protect metal surfaces with which they come in contact against rusting and corrosion under extreme conditions of service.

Another object is to provide mineral oil compositions capable of protecting metal surfaces against corrosion even by salt water.

A further object is to provide improved mineral oil compositions containing an effective anticorrosion additive which does not adversely affect the desirable properties of the oil itself.

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.

I have now found that the above objects and attendant advantages may be realized by incorporating into mineral oil compositions as an anticorrosion additive a minor amount of a water-insoluble, oil-soluble reaction product between an aliphatic dicarboxylic acid anhydride containing as a substituent a hydrocarbon radical such as an alkyI, aryl, alkenyl, aralkyl, or cycloalkyl radical and a tertiary amine. I have found that reaction products of this class are particularly well adapted for use as anticorrosion additives for mineral oils, since they effectively inhibit rusting and corrosion of metals, and at the same time do not adversely affect the lubricating properties of the oil.

The reaction products between the substituted aliphatic dicarboxylic acid anhydrides and the tertiary amines can be prepared in a simple manner. I have found that they can be prepared efficiently by mixing equi-molecular quantities of the anhydride and the amine. In most cases the reaction begins upon admixture, but if evidence of reaction is not immediately apparent, heating is desirable in order to start the reaction. To insure adequacy of reaction the mixture should attain an elevated temperature, preferably a temperature of at least 250° F. Where the heat of reaction is sufficient to raise the temperature of the mixture at least to this point, no additional heat is required, but where necessary it is advisable to heat the mixture to the temperature in question which should be maintained for at least five minutes. The products obtained are insoluble in water and are soluble in oil at least to an extent sufficient to permit their solution in oil in an amount equal to at least 0.005 per cent and preferably at least 1.0 per cent. The preferred reaction products are obtained from substituted aliphatic dicarboxylic acid anhydrides in which the substituent contains at least six carbon atoms.

The reaction products prepared as described above and adapted for use in the compositions of the invention are relatively high boiling, light-colored, viscous liquids to darker-colored, semiliquid or soft resinsous solids. In addition, to being sufficiently soluble in mineral oils to act as very effective corrosion inhibitors, they are also soluble in such organic solvents as hexane, chloroform, and benzene.

The specific chemical nature of the reaction products employed in accordance with the invention is not understood. Since they are prepared under anhydrous conditions employing the acid anhydride, they are not simple salts of the corresponding acid and the amine. Moreover, salts between the acids and the amines are soluble in water, whereas the reaction products with which this invention is concerned are substan-
tially water-insoluble. On the other hand, all evidence indicates that the reaction products are not amides or imides which are produced from substituted aliphatic dicarboxylic acid anhydrides in which the substituted group is a hydrocarbon radical containing at least six carbon atoms. Reaction products of acid anhydrides having as a substituent an alkyl group containing at least six carbon atoms are particularly advantageous.

As indicated above, the preferred reaction products are those which are prepared from substituted aliphatic dicarboxylic acid anhydrides in which the substituent group is a hydrocarbon radical containing at least six carbon atoms. Reaction products of acid anhydrides having as a substituent an alkyl group containing at least six carbon atoms are particularly advantageous. The especially preferred products are those obtained with the use of substituted aliphatic dicarboxylic acid anhydrides in which the substituent contains a relatively large number of carbon atoms, for example, 8 to 12 carbon atoms.

The substituted dicarboxylic acids employed in preparing the new anti-corrosion agents are all derivatives of the homologous series of which malonic acid is the first member. Higher acids of this series include succinic, maleic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acids, decane dicarboxylicacid, undecane dicarboxylic acid, etc. The substituent may be any hydrocarbon radical and preferably contains at least 6 carbon atoms. Examples of such substituents include alky! and alkyl groups of any chain length: aryl groups, such as phenyl, tolyl, xylol, butylbenzyl, naphtyl, xenyl, etc.; aralkyl groups, such as benzyl, phenyl-ethyl, methylbenzyl; etc., and cyclalkyl, such as cyclohexyl, methylcyclohexyl, ethylcyclohexyl, cyclohexyl, etc. Mixtures of dicarboxylic acids containing different substituents may also be employed.

Examples of tertiary amines which may be reacted with the substituted aliphatic dicarboxylic acid anhydrides in preparing the new anti-corrosion agents are the following: trimethylamine, triethylamine, triisopropylamine, triethanolamine, triisopropanolamine, triethanolamine ethylphosphatic acid, and pyridine.

Any of the above, or mixtures thereof, or various oxygen, halogen, sulfur, nitrogen, or phosphorus derivatives of these compounds may be reacted with the above homologous series of dicarboxylic acids to form the anti-corrosion agents employed in mineral oil compositions in accordance with the invention.

The mineral oil compositions of the present invention may be of various types having special properties adapting them for certain particular applications. Thus, they may be lubricating oil compositions ranging from light machine and household oils to heavy lubricants for large internal combustion engines, including diesel engines. Alternatively, they may be of the nature of protective oils or greases, such as slushing oils or gun greases, or they may be adapted for use as metal working oils or the like. They are particularly well suited for use as steam turbine oils since they provide adequate protection against rusting and corrosion in the presence of water and water vapor, and do not readily emulsify with water. They may also be fuel oil compositions, including diesel engine fuels and domestic burner oils, whereby the anti-corrosion agent protects the tanks in which such oil is stored against corrosion brought about by the water with which such oils are often contaminated, as for example in the case of marine fuel oils which usually are contaminated with salt water, giving rise to very serious corrosion in the storage bunkers.

Regardless of the particular type of composition or the specific use to which it is adapted, the new compositions of the invention are prepared simply by mixing the herein-defined anti-corrosion agents with the desired mineral oil base to form the desired composition. These agents function independently of other common oil additives, e.g., anti-oxidants, detergents, viscosity index improvers, anti-foam agents, demulsifying agents, pour point depressants, etc., and accordingly may be used in conjunction with such additives. They may be employed in varying amounts depending upon the severity of the corrosion conditions under which the composition will be used. Ordinarily, however, lubricating compositions contain less than about 1 per cent, usually between about 0.1 per cent and about 0.5 per cent, of the anti-corrosion agent, based on the weight of the base oil, whereas slushing oil types of compositions may contain up to 10 or more per cent by weight of the corrosion inhibitor to provide adequate protection against corrosion during storage for long periods of time under very drastic climatic conditions.

In testing and demonstrating the efficiency of the new compositions in providing protection against corrosion, use may be made of the so-called "ASTM Corrosion Test" which is a modification of a test specifically included in the "ASTM Standards on Petroleum Products and Lubricants," September, 1943, designated as ASTM D-665-44T. In brief, this test consists in placing a 300 ml. sample of the oil or oil composition to be tested in a 400 ml. beaker which is immersed in a constant temperature bath maintained at 140° F. The beaker is fitted with a cover provided with openings for a stainless steel motor-driven stirrer and for insertion of a standard steel test bar, 1/4 inch in diameter and 5 inches long, which has been very carefully cleaned and polished just prior to the test. The beaker is heated in a water bath to 140° F for 48 hours, after which time the test bar is removed and examined for rust spots. If there are no rust spots on the steel bar, the sample is said to pass this test. Any rusting of the bar indicates failure.

In a modification of the above-described test, artificial sea water having the following composition:

| Parts by weight |
|-----------------|-----------------|
| NaCl           | 25.0            |
| MgCl₂·6H₂O     | 11.0            |
| Na₂SO₄         | 6.0             |
| CaCl₂          | 1.2             |
| Distilled water| 1000.0          |

is used instead of the distilled water. This test is referred to as the "Salt Water Corrosion Test" and provides an evaluation of the composition under very drastic corrosion conditions.

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 scope thereof. Unless otherwise stated, the oil compositions prepared and tested as described in these examples consisted only of the anti-
corrosion agent and a refined lubricating oil having the following specifications:

Gravity, °API 31.5-33.5
Viscosity at 100° F., SVP 145-155
Viscosity at 210° F., SVP 43 minimum
Viscosity index 107
Color 1.0-1.5
Flash point °F 400
Fire point °F 450
Neutralization number Neutral

Example I

Approximately 227 parts by weight (1 mol) of a technical grade of triamylamine were added in small increments to approximately 266 parts by weight (1 mol) of mixed alkenyl succinic acid anhydrides. The latter material was a light-yellow, oily liquid, commercial product consisting of a mixture of alkenyl succinic acid anhydrides in which the alkenyl substituent contained an average of from 10 to 12 carbon atoms. During the addition of the amine, heat was evolved and the mixture was maintained at about 250° F. for about 5 minutes. The resulting reaction product was a dark viscous liquid. A composition consisting of 0.10 per cent by weight of this product and 99.9 per cent by weight of the above-described base oil successfully passed both of the heretofore-described corrosion tests. The base oil itself failed to pass either of these tests, as did a composition consisting of 0.10 per cent by weight of the alkenyl succinic acid anhydride dissolved in the base oil.

Example II

Approximately 16 parts by weight of pyridine were reacted with approximately 54 parts by weight of the mixed alkenyl succinic acid anhydrides employed in Example I, substantially as described in that example. The reaction product obtained was a very viscous yellow liquid. A composition consisting of 0.08 per cent by weight of this product dispersed in the base oil successfully passed both of the heretofore-described corrosion tests.

Example III

Approximately 130 parts by weight of diethanolamine-ethyl-phosphoric acid were reacted with approximately 26 parts by weight of the mixed alkenyl succinic acid anhydrides employed in Example I, substantially as described in that example. The reaction product obtained was a brown viscous liquid. A composition consisting of 0.10 per cent by weight of this product dispersed in the base oil successfully passed both of the heretofore-described corrosion tests.

Example IV

Approximately 88 parts by weight of triestearyl-trithanolamine were reacted with approximately 26 parts by weight of the mixed alkenyl succinic acid anhydrides employed in Example I, substantially as described in that example. The reaction product obtained was a very viscous dark liquid. A composition consisting of 0.01 per cent by weight of this product dispersed in the base oil successfully passed both of the heretofore-described corrosion tests.

Example V

A composition similar to that described in the foregoing examples, valuable anti-corrosion agents can be prepared by combining others of the class of substituted aliphatic dicarboxylic acid anhydrides and tertiary amines. For example, by maintaining a mixture of triethanolamine and the mixed alkenyl succinic acid anhydrides described in Example I at a temperature of about 250° F. for a few minutes, a clear amber plastic solid is obtained which is an excellent rust preventive. The reaction product between the mixed alkenyl succinic acid anhydrides and tri-ethyamine, prepared as described in the examples, is a very viscous sticky liquid which when added to the base oil so as to be present in the amount of 0.10 per cent by weight produces a composition that passes both of the heretofore described corrosion tests. Similar products are obtained by combining, under the conditions described in the examples, alpha-cyclohexylmalonic acid anhydride and triamylamine; alpha-hexyl-decyl-malic acid anhydride and triethanolamine; alpha-n-octyl-nonyl dicarboxylic acid anhydride and pyridine; and alpha-benzyl-succinic acid anhydride and triamylamine.

This application is a continuation-in-part of my co-pending applications Serial No. 708,163 and Serial No. 708,166, filed on November 6, 1946, now abandoned.

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

I claim:
1. An improved mineral oil composition comprising a major amount of a mineral oil and dissolved in said oil a minor amount of a water-insoluble reaction product obtained by a process comprising maintaining a mixture of about equimolecular quantities of mixed alkenyl-substituted succinic acid anhydrides in which the alkenyl substituents contain an average of about 10 to 12 carbon atoms and an amine selected from the group consisting of trimethylamine, triethanolamine, triamylamine, triethanolamine, tribenzylamine, tristearyl-trithanolamine, trimethoxyphosphoric acid and pyridine, at an elevated reaction temperature of about 250° F. for about 5 minutes, the amount of said reaction product being sufficient to impart corrosion-inhibiting properties to said composition.
2. The composition of claim 1 in which the amine is triamylamine.
3. The composition of claim 1 in which the amine is pyridine.
4. The composition of claim 1 in which the amine is triethanolamine-ethylyphosphaticid acid.
5. The composition of claim 1 in which the amine is tristearyl-trithanolamine.

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