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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 anti-corrosion 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 anti-corrosion agents heretofore employed in this manner, however, have not proved entirely satisfactory under present-day service conditions. Certain of such agents do not provide adequate 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 anti-corrosion lubricating oil compositions suitable for use under extreme conditions of moisture and moisture vapor, e. g., steam turbine oil compositions.

A still further object is to provide improved mineral oil compositions containing an effective anti-corrosion 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.

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I have now found that the above objects and attendant advantages may be realized by incorporating into mineral oil compositions as an anti-corrosion additive a minor amount of a water-insoluble amide or imide of a substituted aliphatic dicarboxylic acid containing as a substituent a hydrocarbon radical such as an alkyl, aryl, alkenyl, aralkyl, or cycloalkyl radical. I have found that amides and imides of this class are particularly well adapted for use as anti-corrosion additives for mineral oils, since they effectively inhibit rusting and corrosion of metals under very drastic corrosion conditions, and at the same time do not adversely affect the lubricating properties of the oil. Mineral oil compositions containing such products as corrosion inhibitors are especially well suited for use as lubricants in the presence of water and water vapor, e. g., as steam turbine oils and the like, since they provide adequate protection against corrosion and do not tend to emulsify with the water.

The amides and imides may be made by any suitable method. They can be made efficiently by reacting ammonia or a primary or secondary amine with an anhydride of one of the substituted aliphatic dicarboxylic acids. The reaction usually takes place readily with the evolution of heat, but in some cases mild heating is desirable to start the reaction. Because of the exothermic nature of the reaction, it is usually preferable to add the ammonia or amine to the substituted aliphatic dicarboxylic acid in small increments so that the temperature does not rise uncontrollably. To insure adequacy of reaction the mixture should attain a temperature of about 250° F. or higher. If the exothermic heat of reaction is not sufficient under the conditions of operation to raise the temperature to this point, the mixture should be heated. It appears that an amide is the product initially formed, particularly at the lower reaction temperatures, and when ammonia or a primary amine is employed the resulting amide may be converted at least in part to the imide at more elevated temperatures. The reaction products may be referred to as amido reaction products as they may be composed of the amide or the imide or mixtures of the two. I prefer to employ about equimolecular quantities of the anhydride and the ammonia or amine since entirely satisfactory products are obtained under these conditions. However, the ammonia or amine may be used in excess so as to produce at the lower reaction temperatures a product containing a substantial proportion of the di-amide.

The amides and imides employed in accordance with the present invention may also be prepared from the substituted aliphatic dicarboxylic acids directly. Since at low temperature conditions the reaction product between ammonia or a primary or secondary amine and a substituted aliphatic dicarboxylic acid is a salt, it is necessary in order to produce the amide or imide to mix the acid and the nitrogen compound at an elevated temperature, which should be at least 250° F., or to heat the mixture prepared at a low temperature to such an elevated temperature. The elevated temperature should be maintained for a time sufficient to cause the decomposition of a salt between the substituted aliphatic dicarboxylic acid and the ammonia or amine and the production of the corresponding amide or imide. It is important to insure that any salt formed is converted to the amide or imide as the salts are generally highly water-soluble and therefore unsuitable for use in the compositions of the present invention.

The amides and imides that are adapted for use in the compositions of the invention, and prepared for example as described above, are relatively high boiling, light-colored liquids of medium viscosity to darker-colored semi-liquids or soft resinous solids. They are sufficiently soluble in mineral oils to act as very effective corrosion inhibitors in mineral oil compositions. They are also soluble in such organic solvents as hexane, chloroform, and benzene.

It will be obvious to those skilled in the art that within the general description of the amides and imides given above compounds of varying degrees of solubility in mineral oil are included. The amides or imides that are especially suitable for use in the present compositions are those which are soluble in the mineral oil that forms the base for the compositions in an amount equal to at least 0.005 per cent by weight of the oil at atmospheric temperatures. The preferred amides or imides are those which are derivatives of substituted aliphatic dicarboxylic acids in which the substituent group is a hydrocarbon radical containing at least 6 carbon atoms and preferably an alkyl group containing at least 6 carbon atoms. Moreover, in cases where ammonia or an amine containing a relatively small number of carbon atoms is employed for the production of the amide or imide, the substituent of the dicarboxylic acid should contain 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-dicarboxylic acid, undecane-dicarboxylic acid, etc. The substituent may be any hydrocarbon radical and preferably contains at least 6 carbon atoms. Examples of such substituents include alkyl and alkenyl groups of any chain length; aryl groups, such as phenyl, tolyl, xylyl, butylphenyl, naphthyl, xenyl, etc.; aralkyl groups, such as benzyl, phenyl-ethyl, methylbenzyl, etc.; and cycloalkyl, such as cyclohexyl, methylcyclohexyl, ethylcyclohexyl, cycloheptyl, etc. Mixtures of dicarboxylic acids containing different substituents may likewise be employed.

The organic nitrogen compounds which may be reacted with the above-defined dicarboxylic

acids in preparing the new anti-corrosion agents may be grouped as follows:

I. Aliphatic and cycloaliphatic amines, such as:

1. Methylamine
2. Ethylamine
3. Diethylamine
4. Amylamine
5. Ethanolamine
6. Diethanolamine
7. Isopropanolamine
8. Laurylamine
9. Ethylenediamine
10. Diethylenetriamine
11. Triethylenetetramine
12. Cyclohexylamine
13. Dicyclohexylamine

II. Aromatic amines, such as:

1. Aniline
2. Naphthylamine
3. Methylaniline
4. Diethylaniline
5. Toluidine
6. Phenetidine
7. Diphenylamine
8. Diamino-diphenylmethane
9. Amino-phenol
10. Amino-cresol
11. Phenylenediamine
12. Benzidine
13. Amino-diphenyl
14. Amino-diphenyloxide
15. Acetanilide
16. Chloraniline

III. Heterocyclic amines and nitrogen bases, such as:

1. Morpholine
2. Piperidine
3. Amino-benzothiazole
4. Phenothiazine
5. Pyramide
6. Oxazoline

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-defined class of dicarboxylic acids to form the anti-corrosion agents employed in mineral oil compositions in accordance with the invention.

The nitrogen compounds of the above groups that can be employed in preparing the amides or imides may be termed primary or secondary amines as they contain at least one hydrogen atom attached to an amino nitrogen atom.

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 contami-

nated, 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 a homogeneous 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 0.01 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 that specified in the "ASTM Standards on Petroleum Products and Lubricants," September, 1945, 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, ½ inch in diameter and 5½ inches long, which has been very carefully cleaned and polished just prior to the test. The stirrer is started and when the oil sample in the beaker reaches a steady temperature of 140° F. the test bar is inserted in the proper opening and hangs suspended from the beaker cover. After 30 minutes of stirring, 30 ml. of distilled water are added to the beaker, and stirring is then continued 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
MgCl ₂ ·6H ₂ O	11.0
Na ₂ SO ₄	4.0
CaCl ₂	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 same. 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., SUV	145-155
Viscosity at 210° F., SUV	43 minimum
Viscosity index	107
Color	1.0-1.5
Flash point, °F	400
Fire point, °F	450
Neutralization number	Neutral

Example I

Approximately 18.5 parts by weight (1 mol) of a technical grade of dodecylamine were added in small increments to approximately 18.6 parts by weight (1 mol) of alpha-cyclohexyl-malonic acid. During the addition of the amine, heat was evolved. The mixture was then heated to about 250° F. and maintained at this temperature for about 5 minutes. Upon completion of the reaction the amido reaction product was obtained as a yellowish wax-like solid. A composition consisting of 0.05 part by weight of this product and 100 parts by weight of the above-described base oil successfully passed both of the herein-before-described corrosion tests. The base oil itself failed to pass either of these tests as did a composition consisting of 0.05 per cent by weight of free cyclohexyl-malonic acid dispersed in the base oil. Heavy rusting of the steel specimen occurred in both cases.

Example II

Approximately 18.5 parts by weight (1 mol) of technical dodecylamine were reacted with approximately 35.6 parts by weight (1 mol) of alpha-hexadecylmalonic acid as described in Example I. The amido reaction product obtained was a yellow waxy solid. A composition consisting of 0.05 per cent by weight of this product dispersed in the base oil successfully passed both the ASTM and Salt Water Corrosion tests. A similar composition containing the free hexadecylmalonic acid failed the Salt Water Corrosion test.

Example III

Approximately 87.6 parts by weight of mixed alkenyl-succinic acids in which the alkenyl substituents contained an average of 10-12 carbon atoms were reacted with approximately 510 parts by weight of diphenyloxide in the presence of aluminum chloride to obtain a thick viscous liquid product consisting of mixed (phenoxy-phenyl-alkyl)-succinic acids in which the alkyl groups contained an average of 10-12 carbon atoms. Approximately 45 parts by weight of this product were treated with 0.7 part by weight of butylamine as described in Example I. The amido reaction product obtained was a dark-brown viscous liquid. This product was incorporated in the base oil in an amount of 0.10 per cent by weight. The resulting composition passed the ASTM and Salt Water Corrosion tests, whereas a composition containing the same amount of mixed (phenoxy-phenyl-alkyl)-succinic acids failed both of these tests.

Example IV

Approximately 27.0 parts by weight of mixed alkenyl-succinic acids in which the alkenyl substituents contained an average of 10-12 carbon atoms were mixed with approximately 18.1 parts by weight of dicyclohexylamine, and the mixture was warmed slightly to promote reaction. The

mixture was heated to about 250° F. and was maintained at this temperature for about 5 minutes. Upon completion of the reaction the amido reaction product obtained was a light-yellow sticky solid reaction product. This product was incorporated in the base oil in amount of 0.05 per cent by weight. The resulting composition successfully passed the Salt Water Corrosion test, whereas a composition consisting of the same amount of the free alkenyl-succinic acid dispersed in the base oil failed this test.

Example V

Approximately equi-molecular proportions of alpha-n-octyl-nonane dicarboxylic acid and technical hexadecylamine were reacted as described in Example I. The reaction product obtained was a light yellow waxy solid. This product was incorporated in the base oil in amount of 0.05 per cent by weight to obtain an oil composition which successfully passed the ASTM Corrosion test.

Example VI

Approximately 19.8 parts by weight of cyclohexylamine (2 mols) were added in small increments to approximately 27.0 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 substituents contained an average of from about 10 to 12 carbon atoms. The mixture was heated to about 250° F. for about 5 minutes whereby reaction to form the corresponding amido product took place readily. The amido reaction product was a very viscous, clear, amber liquid. A composition consisting of 0.10 per cent by weight of this product dissolved in the base oil was subjected to the ASTM and Salt Water Corrosion tests. This composition passed both tests, whereas a composition consisting of 0.10 per cent of the alkenyl-succinic acid anhydride itself dissolved in the base oil, failed both tests.

This application is a continuation-in-part of my co-pending applications, Serial No. 708,183 and Serial No. 708,186, filed on November 6, 1946 and 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 com-

prising a major amount of a mineral oil and a minor amount of an amide of dodecylamine and an acid selected from the group consisting of alpha-cyclohexyl malonic acid and alpha-hexadecyl malonic acid, the amount of said amide being sufficient to impart corrosion inhibiting properties to said composition.

2. An improved mineral oil composition comprising a major amount of a mineral oil and a minor amount of an amide of dodecylamine and alpha-cyclohexyl malonic acid, the amount of said amide being sufficient to impart corrosion inhibiting properties to said composition.

3. An improved mineral oil composition comprising a major amount of a mineral oil and a minor amount of an amide of dodecylamine and alpha-hexadecyl malonic acid, the amount of said amide being sufficient to impart corrosion inhibiting properties to said composition.

4. An improved mineral oil composition comprising a major amount of a mineral oil and a minor amount of the amide which is formed by reacting about equimolecular amounts of a basic organic amine having at least one hydrogen atom attached to the amino nitrogen atom and a malonic acid having a hydrocarbon substituent of at least six carbon atoms, the amount of said amide being sufficient to impart corrosion inhibiting properties to said composition.

5. An improved mineral oil composition comprising a major amount of a mineral oil and a minor amount of the amide which is formed by reacting about equimolecular amounts of a basic organic amine having at least one hydrogen atom attached to the amino nitrogen atom and a malonic acid having an alkyl substituent of at least six carbon atoms, the amount of said amide being sufficient to impart corrosion inhibiting properties to said composition.

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