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ANTICORROSION COMPOSITION

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This invention relates principally to mineral oil fractions modified by the addition of various materials for various uses wherein an addition agent is employed to impart the characteristic of resisting corrosion of metal surfaces where said surfaces are contacted with the oils in the presence of water. The invention is particularly applicable to turbine lubricating oils wherein the anti-corrosion addition agent protects the metal parts from the effects of water which is characteristically present. Such an oil must possess not only good lubricating properties but also good anticorrosion properties and good nonemulsifying and de-emulsifying characteristics. All of these characteristics are imparted by the additive material of the present invention which is at least primarily an oil-soluble fatty acid amide containing an alkyl substituent. The invention, however, is not necessarily limited to application to turbine oils but may be used in connection with other lubricants which might contain water or come in contact with water or become contaminated with water, such as various lubricating oils, greases, cutting oils, soluble oils, marine lubricants, rust inhibitors of liquid or paste type, and the like. Also, rust-removing compositions may contain indicated proportions of the mentioned amide-type material.

The principal object of the invention is to provide turbine oils and similar petroleum products of the mentioned type which will possess the necessary anti-corrosion characteristics and will at the same time meet current specifications for such oils, such as the United States Navy specifications for nonemulsifying and de-emulsifying characteristics in turbine oils. Another important object is to provide products possessing good rust-inhibiting and rust-removing characteristics.

Briefly stated, the invention resides principally in an appropriate petroleum fraction containing the indicated amide-type material in very minor proportion but sufficient to impart the desired anticorrosion properties. Such a material shall be normally liquid and readily oil-soluble. For turbine oils the preferred proportions of the agent are about 0.1% to 0.2%. Other usable proportions are stated hereinafter. Where used for turbine oils and the like, the above mentioned nonemulsifying and de-emulsifying characteristics must be present; although in cases of some soluble oils, cutting oils, and the like, emulsifying characteristics in the product are not particularly objectionable. Broadly stated, the mentioned amide type material is produced by

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reacting oleic acid or kindred unsaturated fatty material (as hereinafter described) with an aliphatic alcohol amine (alkanolamine) which contains alkyl groups of a sufficient number of carbons to yield an oil-soluble product, and having at least one free hydrogen on the nitrogen whereby the corresponding amide forms. The product possibly contains also an appreciable proportion of esterified amide as hereinafter described.

Amines of the monoethanol amine type do not yield sufficiently oil-soluble products. The amine apparently must contain an alkyl group or groups totaling at least four carbons per molecule to impart sufficient oil-solubility. The best material so far produced has been obtained with diethanol amine. In general, oleic acid, or similar high molecular weight oil-soluble unsaturated fatty acid is preferred, but fats containing very large proportions of the glyceride of oleic acid have been successfully used.

Therefore, the invention in a preferred form resides in petroleum fractions containing minor proportions of the amide produced from diethanol amine reacted with oleic acid or fatty oils of the mentioned type to yield the indicated amides. Mono- and di-butanol amines also may be employed and also di-propanol amines, including the normal and isoamines, the higher molecular weight imparted by these alkyl constituents imparting good oil-solubility. Monopropanol amine apparently does not yield a product possessing sufficient solubility for practical use. Presumably, higher alkanolamines not now available could be expected to behave similarly to diethanolamine, dipropanolamine and butanolamine products mentioned, so long as corrosion-inhibiting properties are not materially reduced, as on account of excessive chain length or other reason.

Since preparation of the present product requires heating for a much longer time than to produce amine soaps of the fatty materials, whereby to pass from the soap stage into the amide stage, the invention also resides in the method of preparation and also in products produced by such method.

According to the present invention, the proportions of amide which are normally employed are in the order of about 0.1% or 0.2% for turbine oils and the like, although for such uses the proportions may vary, as between the limits of about 0.001% or 0.01% and about 0.5%. For these purposes greater proportions than about 0.2% seem normally to impart no added benefit. However, in other instances such as for rust-removers, penetrating oils, cutting oils and the like, greater proportions such as in the order of 1% to 2% may be satisfactorily employed. The invention therefore also extends to these greater proportional ranges for the indicated types of products.

In general, the following specifications will relate to products containing the preferred amide, that is, the amide produced by reacting diethanol amine with oleic acid, whereby a diethanol oleyl amide is produced. Apparently the product contains also an appreciable proportion of such amide where the alcoholic OH group of part of the material is esterified by oleic acid to yield the earlier-mentioned esterified amide. The invention, as has been indicated, is not limited to oleic acid product inasmuch as fatty materials may be employed containing large proportions of the glyceride of oleic acid, especially where they contain only small proportions of materials yielding oil-insoluble products. Thus, lard oil may be employed instead of oleic acid, and any resultant otherwise oil-insoluble products which are not solubilized by the soluble amides may be removed. Also, the same types of reaction products obtained from the mono-butanol and dibutanol amines and from dipropanol amines may be employed.

The reaction between oleic acid and diethanol amine to produce soap is presumed to be as follows, where RC represents the oleic radical in general:

$$RCOOH+H.N(C_2H_4OH)_2 = RCOOH.H.N(C_2H_4OH)_2$$

Following the soap-forming operation it appears that additional heating causes water to be split out to form the amide according to the following:

$$RCOOH.H.N(C_2H_4OH)_2 + \text{heat} = R\underset{\underset{O}{\|}}{C}.N(C_2H_4OH)_2 + H_2O$$

It now seems probable that an appreciable proportion of an esterified amide, perhaps sometimes as much as 25% (but usually less), is formed along with the above indicated amide, inasmuch as to obtain the desired complete reaction more oleic acid is employed than would be accounted for if the amide alone is formed. Such a reaction is speculated to be approximately as follows:

$$R\underset{\underset{O}{\|}}{C}N(C_2H_4OH)_2 + RCOOH = R\underset{\underset{O}{\|}}{C}.N(C_2H_4OH)\left(C_2H_4O\underset{\underset{O}{\|}}{C}R\right) + H_2O$$

Corresponding reactions occur of course with the other indicated amines. It is possible that small proportions of other reaction products are formed such as furane ring compounds which may or may not be objectionable and may in fact have some value.

Example 1

A preferred method for producing oil-soluble diethanol oleic amides of the present invention is the following:

300 grams of oleic acid and 105 grams of commercial diethanol amine are mixed together in a liter glass vessel equipped with a stirrer and heated sufficiently above 212° F. to produce dehydration, for example within a range of about 250° F. to 350° F., or in a specific instance, to about 300° F. on a hot plate. No solvent or refluxing material is required and operation is carried on at atmospheric pressure or at somewhat reduced pressure to facilitate the operation. The stirring may be only slight, and the heating is continued

for about ten hours to insure rather complete reaction. The time of treatment may vary according to conditions, e. g. pressure, as will be apparent to one skilled in the art. Ordinarily, the product of this reaction is the final product, inasmuch as filtering ordinarily is not required. This material has excellent corrosion resistance in compositions herein described.

Example 2

However, it is sometimes desirable to operate in the presence of a refluxing medium, and this also may be done at atmospheric pressures. Thus, 300 grams of oleic acid were mixed with 105 grams of diethanol amine in a liter round-bottom glass flask, together with 250 ml. of xylene as a high temperature refluxing medium, the flask being connected with an ordinary refluxing tube. Here again the operation was carried on at about 300° F. and for a total period of about twelve hours. The product was substantially the same as that of Example 1 and likewise possessed excellent corrosion resistance.

Where the products of the present invention are intended for use in turbine oils, it is apparently important that a substantially pure oil-soluble diethanol oleic amide be obtained and that it be as near neutral as possible. Preferably such an amide is obtained by employing oleic acid. However, for some of the uses above indicated, it is permissible to employ fatty oils, i. e. normally liquid fats, which contain relatively large proportions of glycerides of oleic acid. In many instances of such other uses, it is possible to employ other oil-soluble unsaturated fatty acids than oleic acid, and corresponding glycerides, although ordinarily oleic acid (which has only one double bond and is non-hydroxy) or fatty oils containing large proportions of glycerides of oleic acid are to be preferred. Also, doubtless palmitoleic acid, which is found in some oils as glyceride, and other similar acids which have only one double bond and are non-hydroxy, may be used.

Thus, olive oil is a desirable starting material inasmuch as it represents about 80% to 85% of oleic acid with only about 10% of saturated fatty acids. Peanut oil also may be employed, which represents about 60% of oleic acid and about 20% of linoleic acid. Cottonseed oil representing between 30% and 35% of oleic acid and around 40% to 45% of linoleic acid also is an acceptable material. Corn oil is another desirable fatty oil inasmuch as it represents about 45% oleic acid and about 40% linoleic acid, with only about 10% of saturated fatty acids. Two other possible oils representing only about 10% of saturated fatty acids are soya bean oil and linseed oil. While these oils will yield good products from the anti-corrosion standpoint they have the practical objection of containing more than 50% of the two and three double-bonded linoleic and linolenic drying oils. Linseed oil probably would be the more objectionable because it represents only 5% oleic acid and an objectionably large proportion of drying oils, i. e. about 60% of linoleic acid and approximately 25% of linolenic acid, whereas the soya bean oil represents nearly 35% of oleic acid, about 50% of linoleic acid, and only 2% or 3% of linolenic acid. The objection to these materials containing two and three double bonds is that in many uses their products may oxidize and form sludges too readily.

Another oil which will be more desirable than linseed oil is lard oil which contains 50% to 60% of oleic acid and not substantially over 10% of linoleic acid with little or no linolenic acid, although there is an objectionably large content of the saturated palmitic and stearic acids totaling about 35% to 40%. Other oils which it is possible to use are rapeseed oil, sesame seed oil and rice oil.

It appears that a portion of the otherwise oil-insoluble amides from the saturated fatty acids is solubilized by the presence of the oil-soluble amides of the unsaturated fatty acids. For most uses, the solubilized portions of the saturated fatty acid amides are not objectionable. Where there are excess proportions of the saturated fatty acid amides which are not solubilized, these may nevertheless be retained where they are not objectionable, as in the case of solid greases. However, where these oil-insoluble amides tend to cloud out of liquid products in an objectionable manner, they may be removed from the liquid amide product itself, or from oil-solutions or the like by settling, filtering, or otherwise. Also, the oil-insoluble unsaturated hydroxy fatty acids are as objectionable as the oil-insoluble saturated fatty acids. Therefore, the non-hydroxy unsaturated fatty acids are those which are used for the present invention because their amide products are oil-soluble.

From the foregoing, it will be apparent that the single double-bonded non-hydroxy oleic acid itself is ordinarily preferred, and that fatty oils containing relatively large proportions of oleic glycerides with only small proportions of saturated fatty acid glycerides and only small proportions of plural double-bonded, unsaturated, drying type glycerides are next preferred. It is also apparent that the smaller the proportion of the saturated fatty acid content of the oil the more desirable, and at the same time the smaller the proportion of the drying oil type the more desirable the oil will be for the present uses. Thus, in general, olive oil and peanut oil represent preferred oils because they have relatively small contents of both saturated fatty acid glycerides and drying type glycerides. Corn oil also is usable because of its low saturated fatty acid content and its high oleic acid content even though there is a relatively large linoleic acid content. Lard oil is desirable despite its high saturated fatty acid content, inasmuch as the drying oil content is very small and the oil-insoluble materials can be separated.

In general, unsaturated non-hydroxy fatty acids in the class of saponifiable or high molecular weight fatty acids, or those containing at least about ten carbon atoms per molecule, may be used. Also their glycerides, such as are found in fatty oils may be employed for some purposes as herein described.

Example 3

Thus, according to one process where an unsaturated fatty oil was employed, 300 grams of lard oil were heated with 108 grams of diethanol amine in a liter glass beaker at atmospheric pressure under a temperature of about 300° F. for about twelve hours substantially as described in Example 1. Since lard oil is an ester of glycerol, the product contained a corresponding proportion of free glycerol as well as the resultant diethanol oleic amides and corresponding amides of the other fatty acids present. Since glycerol tends toward emulsification this product is not especially useful in turbine oils, but is useful for many of the other indicated purposes. This particular product also was liquid at normal temperatures and freely oil-soluble without subsequent clouding. It showed excellent corrosion resistance in compositions of the present invention and met the de-emulsification test fairly satisfactorily. After long standing, a solid material apparently from the saturated fatty acids forms and settles out of this product. This material dissolves in oil with heat, but settles out of the oil at normal temperatures. Therefore, in the preparation of liquid oils, any solid material should be removed from liquid amide products, from which it separates, before making up the oil.

As is apparent from the foregoing description, materials of this invention must be predominantly oil-soluble in order to be effective. As previously indicated, the oil-soluble amide products produced from the indicated unsaturated fatty acid materials must be produced with alkanol amines whose alkyl radicals have sufficient carbon content to render the product oil-soluble, a total of at least four carbons per molecule apparently being necessary. Thus, the methanol amines and the monoethanol amine produce relatively oil-insoluble products, whereas diethanol amine, dipropanol amines and the butanol amines produce soluble products as heretofore stated. By the term "oil-soluble" material is meant material that does not settle or cloud out of the oil at normal nor storage temperatures nor at temperatures of use.

Other variations coming within the scope of the appended claims will be apparent to those skilled in the art, such as the employment of other oil-soluble, unsaturated fatty acid materials and the employment of other available amines, including iso-products, as hereinbefore generally indicated.

We claim:

1. A non-aqueous anti-corrosion composition comprising mineral oil in which is dissolved in the order of 0.001% to 2.0% of a material containing an oil-soluble alkanol amide of an unsaturated non-hydroxy fatty acid, the alkanol constituent containing at least four carbon atoms and the fatty acid constituent containing at least ten carbon atoms.

2. A composition according to claim 1 in which the fatty acid is oleic acid.

3. A composition according to claim 1 in which the alkanol amide is an amide of diethanol amine.

4. A composition according to claim 1 in which the alkanol amide has the formula

$$R-\underset{\underset{O}{\|}}{C}-N(C_2H_4OH)_2$$

where

$$R-\underset{\underset{O}{\|}}{C}-$$

is the fatty acid residue.

5. A composition according to claim 1 in which the alkanol amide has the formula

$$R-\underset{\underset{O}{\|}}{C}-N(C_2H_4OH)\left(C_2H_4O-\underset{\underset{O}{\|}}{C}-R\right)$$

where both

$$R-\underset{\underset{O}{\|}}{C}-$$

groups are fatty acid residues.

6. A composition according to claim 1 in which said material is a normally liquid oil-soluble reaction product of oleic acid with diethanol amine.

7. A composition according to claim 1 in which the alkanol amide is diethanol oleic acid amide.

8. A turbine oil comprising mineral lubricating oil in which is dissolved in the order of 0.001% to 2.0% of a material containing a substantial proportion of an oil-soluble alkanol amide of an unsaturated non-hydroxy fatty acid of the non-drying type, the alkanol constituent containing at least four carbon atoms and the fatty acid constituent containing at least ten carbon atoms.

9. A composition according to claim 8 in which the alkanol amide is diethanol oleic acid amide.

10. A non-aqueous anti-corrosion composition comprising mineral oil in which is dissolved in the order of 0.01% to 0.5% of an oil-soluble alkanol amide of an unsaturated non-hydroxy fatty acid, the alkanol constituent containing at least four carbon atoms and the fatty acid constituent containing at least ten carbon atoms.

11. A composition according to claim 10 in which the fatty acid is oleic acid.

12. A composition according to claim 10 in which the alkanol amide is an amide of diethanol amine.

13. A composition according to claim 10 in which the alkanol amide is diethanol oleic acid amide.

14. A non-aqueous anti-corrosion composition comprising mineral oil in which is dissolved in the order of 0.001% to 2.0% of a normally liquid oil-soluble material containing an alkanol amide of an unsaturated non-hydroxy fatty acid and an esterified form of said alkanol amide, the alkanol constituent of said alkanol amide containing at least four carbon atoms and the fatty acid constituent of said alkanol amide containing at least ten carbon atoms.

15. A composition according to claim 14 in which the alkanol amide is diethanol oleic acid amide.

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