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ANTICORROSIVE

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The present invention relates to compositions having anti-corrosive, and especially rust-protective, properties, and more particularly deals with compositions comprising a substantially neutral vehicle, such as normally liquid or normally solid hydrocarbons, alcohols, esters (e. g., fatty oils and natural waxes), water, etc., containing finely dispersed a small amount of certain free dicarboxylic acids which are very potent corrosion inhibitors, possess high thermal stability and are relatively inexpensive.

Metallic surfaces, particularly those containing iron, require protection against the hazard of corrosion in the presence of water. To illustrate: Moisture readily attacks finished or semi-finished metal objects unless the metal surface is covered during storage or shipment by a protective coating such as a slushing oil; water in Diesel engine fuels often corrodes closely fitted parts such as are found in Diesel engine unit type injectors; water in turbines corrodes turbine lubricant circulatory systems, particularly the governor mechanisms of steam turbines; and water in hydrocarbon oils such as gasoline rusts steel storage tanks and drums; water in anti-freeze compositions causes corrosion in automobile radiators, etc. Corrosion not only has a deleterious effect upon the metal surfaces, but also frequently loosens finely divided metal oxides which may act as oxidation catalysts increasing the rate of deterioration of various organic compounds with which they come in contact or may enter between moving parts of machinery where they act as abrasives.

It is a purpose of this invention to produce potent corrosion-protective compositions of wide applicability. Another purpose is to produce slushing compositions of improved corrosion-protective properties. A specific purpose is to produce rust-protective hydrocarbon compositions, i. e., including various Diesel oils, steam turbine oils, greases, etc. Still another purpose is to provide anti-freeze compositions free from a tendency to cause rusting. Further, it is a purpose to produce a non-oily composition which can be used for rust-protection of ferrous metals and in general for protecting various metals against corrosion.

I have discovered that condensation products between maleic acid and rosin acids such as abietic acid in which the abietic acid carboxyl radical is esterified, are extremely potent corrosion inhibitors of high thermal stability, being stable up to about 650° F., particularly when finely dispersed in low concentration in a suitable vehicle.

It is known that the relatively high molecular weight condensation products between maleic acid and olefins are potent corrosion inhibitors when dissolved in low concentrations in hydrocarbon oils. However, one of their disadvantages is that they begin to decompose when their solution is heated to above about 500° F. This has the effect that in internal combustion engines, for instance, oils containing this anti-corrosive agent will gradually lose their corrosion-protective properties. Therefore, an anti-corrosive of better thermal stability would definitely be desirable.

The manufacture of my condensation product is very simple. About equimolal quantities of maleic acid anhydride, unsaturated rosin acid and a suitable alcohol are mixed, and the mixture is first heated under total reflux to about 450° F. for an hour or so. Water is removed. The temperature is then raised to about 600° F. for approximately two hours. At the end of this period, the temperature is lowered to about 450° F. and steam or other inert gas is blown through the reaction mixture to remove unreacted ingredients. The steaming should be continued for about two hours at 450° F. and for one hour at 280°–300° F. because it also serves to convert the anhydride radical of the condensation product to the free dicarboxylic acid. When this is accomplished, the reaction product may be used as such or may, if desired, be purified for example by crystallization from a lower alcohol having not more than about 6 carbon atoms.

The reaction product is stable up to about 600° F. even though it contains at least 1 and probably 2 olefinic double bonds. If desired, this product may be hydrogenated to eliminate these double bonds, thereby making the compound still more resistant to decomposition and oxidation. Instead of saturating the olefinic double bonds with hydrogen, they may be saturated with sulfur or chlorine or both, thereby imparting to the compound mild extreme pressure properties.

Rosin acids are unsaturated polyalicyclic hydrocarbon carboxylic acids, abietic acid being a typical rosin acid. They are obtained from tall oil, Swedish rosin and other by-products of the pulp paper industry.

Alcohols suitable for the esterification should be aliphatic, preferably having 10 or more carbon atoms, i. e., 12 to 24 carbon atoms. If the alcohol is relatively low-boiling, considerable pressure may have to be applied during the reaction, and

the resulting condensation product is relatively insoluble in hydrocarbon oils. Cyclic alcohols do not readily react, and it is difficult to effect the desired esterification with any alcohol other than aliphatic alcohol.

Instead of rosin acids, other hydrocarbon carboxylic acids of 10 or more carbon atoms having 2 or more olefinic double bonds, such as polyolefinic unsaturated fatty acids, may be employed. However, it is usually necessary to carry out the condensation with a smaller amount of the maleic acid anhydride than would be required to react with all of the double bonds of the fatty acid molecules, otherwise a resinous acid of high melting point and high neutralization number will form which is not only totally insoluble in hydrocarbon oils and most other solvents, but is also difficult to disperse colloidally. For this reason, it is desirable, at least when using polyolefinic fatty acids, that the mol ratio of maleic acid anhydride to the fatty acid in the reaction mixture be such to obtain a product having a neutralization number of not more than about 300 and preferably less than 275. If this precaution is observed, the reaction products are soft, plastic masses of relatively low melting temperatures which are considerable soluble in hydrocarbon oils.

Suitable polyolefinic fatty acids include geranic acid, linoleic acid, linolenic acid, eleaostearic acid, fish oil fatty acids, seal oil fatty acids, tung oil fatty acids, fatty acids separated as the extract in the selective solvent extraction of mixed fatty acids from various drying and semi-drying oils, e. g., linseed oil, rapeseed oil, cottonseed oil, soya bean oil, corn oil, rice oil, sesame oil, mustardseed oil, etc.

To produce the anti-corrosive composition, a small amount of the esterified condensation product is finely dispersed in a suitable vehicle. The dispersion may be a true or colloidal solution. True solutions are in general preferred whenever they can possibly be obtained, first because colloidal solution may cause emulsification between an oleaginous vehicle and water which may be very undesirable, and second, because colloids may precipitate, in which case at least a portion of the active ingredient is removed.

The vehicles to which the dicarboxylic acids of this invention may be added for the purpose of producing corrosion-protective compositions may be divided into several groups. In the first place, they may be liquids or plastics, the only requirements as to their physical state being (in addition to their being able to act as carrier for the acids under normal atmospheric conditions) that they be spreadable over metal surfaces. Spreading may be accomplished by immersing, flooding, spraying, brushing, trowelling, etc.

After being applied, all or part of the vehicle may evaporate, or it may be more or less permanent. In other words, both volatile carriers may be used, or substances which do not materially volatilize under normal atmospheric conditions. As to chemical requirements, the vehicle must be stable under ordinary conditions of storage and use and be inert to the active inhibitors.

Thus the vehicle should preferably be substantially neutral, although it may be weakly acidic or basic, preferably having dissociation constants not above about 10^{-8}. In vehicles of low dielectric constant, as hydrocarbon oils, which are not conducive to ionization of dissolved electrolytes, relatively small amounts, i. e., about .1%–5% of various carboxylic acids, such as fatty or naphthenic acids, may be present, and in many instances this may even be beneficial.

Both polar and non-polar vehicles may be employed. Among the former are water, alcohols, such as methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, cyclohexyl, heptyl, methyl cyclohexyl, octyl, decyl, lauryl, myristyl, cetyl, stearyl, benzyl, etc., alcohols; polyhydric alcohols as ethylene glycol, propylene glycol, butylene glycol, glycerol, methyl glycerol, etc.; phenol and various alkyl phenols; ketones as acetone, methyl ethyl ketone, diethyl ketone, methyl propyl, methyl butyl, dipropyl ketones, cyclohexanone and higher ketones; keto alcohols as benzoin, ethers as diethyl ether, diisopropyl ether, diethylene dioxide, beta-beta dichlor diethyl ether, diphenyl oxide, chlorinated diphenyl oxide, diethylene glycol, triethylene glycol, ethylene glycol monomethyl ether, corresponding ethyl, propyl, butyl ethers; neutral esters of carboxylic and other acids as ethyl, propyl, butyl, amyl, phenyl, cresyl and higher acetates, propionates, butyrates, lactates, laurates, myristates, palmitates, stearates, oleates, ricinoleates, phthalates, phosphates, phosphites, thiophosphates, carbonates; natural waxes as Carnauba wax, candellila wax, Japan wax, jojoba oil, sperm oil; fats as tallow, lard oil, olive oil, cottonseed oil, perilla oil, linseed oil, tung oil, soya bean oil, flaxseed oil, etc.; weak bases as pyridine, alkyl pyridines, quinolines, petroleum bases, etc.

Vehicles of little or no polarity comprise hydrocarbons or halogenated hydrocarbons as liquid butanes, pentanes, hexanes, heptanes, octanes, benzene, toluene, xylenes, cumene, indene, hydrindene, alkyl naphthalenes; gasoline distillates, kerosene, gas oil, lubricating oils (which may be soap-thickened to form greases), petrolatum, paraffin wax, albino asphalt; carbon tetrachloride, ethylene dichloride, propyl chloride, butyl chloride, chlor benzol, chlorinated kerosene, chlorinated paraffin wax, etc.

The amounts of the dicarboxylic acids which must be incorporated in the above vehicles to produce corrosion-protective compositions vary considerably with the type of vehicle used. As a general rule, the presence of resinous materials, particularly those of a colloidal nature, calls for relatively larger amounts of inhibitors. Resinous materials which interfere with the activity of the inhibitors comprise asphaltenes, petroleum resins, various other natural resins, as rosin, resins formed by polymerization of drying fatty oils, phenol-formaldehyde resins, glyptal type resins formed by esterification of polyhydric alcohols with polycarboxylic acids, etc.

In the absence of such resinous materials, amounts required of the dicarboxylic acids vary from about .001% up to about .1%, although larger amounts may be used. However, where the acids are in colloidal dispersion, rather than in true solution, a concentration in excess of about .1% may result in relatively quick loss of part of the inhibitor by precipitation and settling.

In the presence of resins and other colloids, amounts in excess of .1% and up to 5% may be required. Inasmuch as resins may act as protective colloids, compositions containing these large amounts of colloidally dispersed inhibitors, together with resin, may be quite resistant to precipitation and settling.

Since resinous and gummy substances in the vehicles do call for greater amounts of inhibitors, it is usually desirable to refine normally liquid vehicles thoroughly and free them from gummy

substances, thereby imparting to them maximum inhibitor susceptibility. This is of particular importance, for example, in lubricating oils, specifically steam turbine oils, which are advantageously highly refined before the inhibitor is introduced. Suitable refining treatments include, for example, extraction with selective solvent for aromatic hydrocarbons as liquid SO_2, phenol, furfural, nitrobenzene, aniline, beta-beta-dichlorine diethyl ether, antimony trichloride, etc.; treatment with $AlCl_3$, sulfuric acid, clay, etc. If the treatment produces a sludge, special care must be taken to remove it very thoroughly and completely.

Applications of the various corrosion-protective compositions vary over a wide range. Hydrocarbon compositions are of special importance. For example, gasolines stored in drums may cause rusting of the drums because of the accumulation of water. This is particularly bad in tropical countries where the moisture content of the air is high and wide variations in temperature over a 24-hour cycle cause considerable breathing of the drums.

Diesel fuels may cause corrosion of injection nozzles.

Lubricating oils and greases made of lubricating oils and soaps normally allow corrosion or even may cause corrosion of various metal parts with which they came in contact, such as bearings, crank-cases, shafts, etc. This problem arises in many types of engines and is often particularly serious in steam turbines. The presence of the inhibitors of this invention will afford excellent protection in all of the above instances.

Rusting of ferrous metals exposed to the atmosphere during usage or storage is a serious problem. This is of particular importance where accurately machined parts must be preserved. Slushing oils comprising various types of liquid or plastic hydrocarbons, fats, waxes, lanolin, are employed to protect the metals against this attack, and the inhibitors of this invention have great value as an active component in such slushing oils.

Cutting oils, EP lubricants, due to their content of sulfur and/or chlorine in various active forms, frequently are quite corrosive. The dicarboxylic di-fatty acids effectively inhibit this corrosion.

Among the non-hydrocarbon compositions which frequently cause corrosion difficulties, antifreezes used in automobile radiators and the like may be mentioned. The dicarboxylic acids effectively eliminate their corrosiveness. Antifreezes usually comprise or consist of water-miscible alcohols, such as methanol, ethanol, isopropanol, glycol, glycerol, etc.

So-called hydraulic oils, damping oils, etc., which frequently are based on non-hydrocarbon liquids, such as various alcohols, esters, etc., have in the past introduced some corrosion dificulties which can effectively be prevented by the acids of this invention.

Dispersions of the dicarboxylic di-fatty acids in water may be useful in the rust-proofing of metals which after treatment must not be greasy as, for example, various machine parts in the textile industries, particularly in the knitting of fine dry goods. If desired, solutions or dispersions in low-boiling alcohols, etc., may be used for the same purpose.

It is understood that the corrosion-protective compositions of this invention may contain other ingredients in addition to the vehicle and the dicarboxylic acids. However, such additional ingredients must be chemically inert to the acid and the vehicle employed. Thus strong oxidizing agents as chlorine, peroxides, etc., must be avoided as they tend to destroy the inhibitors. Strong bases, particularly in ionizing vehicles, as in water, alcohols, etc., will neutralize the diacids and thereby render them relatively ineffective. Likewise, strong acids may reduce their effectiveness. However, in non-ionizing solvents, i. e., in hydrocarbon compositions, chlorinated hydrocarbons, etc., the presence of relatively small quantities of primary, secondary and tertiary nitrogen bases and/or carboxylic acids will not normally interfere with the activity of the inhibitor. On the other hand, even in these vehicles very strong bases as various onium bases, or very strong acids as sulfonic acids, should not be present.

Accordingly, hydrocarbon compositions and the like may contain various types of oxidation inhibitors as alkylated phenols, aromatic amines, preferably secondary amines, amino phenols; as well as various EP compounds containing halogen, S, P, As, etc., anti-wear compounds, detergents, sludge-preventing compounds, pour point reducers, thickeners, such as soaps, etc. Likewise, fats, anti-freezes, etc., may contain anti-oxidants.

Example

Equimolal quantities of maleic acid anhydride, abietic acid and stearyl alcohol were reacted in the manner described before. .01% of the reaction product was dissolved in a highly refined steam turbine oil having a Say. Univ. viscosity of 100° F. of 150 seconds. Two polished steel strips were immersed in vigorously stirred emulsions of said oil with 10% distilled water and sea water, respectively, for 48 hours at 167° F. Both strips remained blank, showing no signs of corrosion.

I claim as my invention:

1. A corrosion-preventive composition comprising predominantly a stable, substantially neutral vehicle containing finely dispersed a corrosion inhibiting amount, less than 5% of a free dicarboxylic acid being the hydrolyzed condensation product between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of said hydrocarbon carboxylic acid being esterified with an aliphatic alcohol.

2. The composition of claim 1 wherein the alcohol has at least 10 carbon atoms.

3. The composition of claim 1 wherein the alcohol has from 12–24 carbon atoms.

4. The composition of claim 1 wherein the carboxylic acid is abietic acid.

5. The composition of claim 1 wherein said vehicle has a dissociation constant below 10^{-8}.

6. The composition of claim 1 wherein said acid is in true solution.

7. The composition of claim 1 wherein said acid is in colloidal solution.

8. A corrosion-preventive composition comprising predominantly a stable, substantially neutral vehicle containing finely dispersed a corrosion inhibiting amount, less than 5% of a free dicarboxylic acid being the hydrolyzed condensation product between maleic acid anhydride and an unsaturated rosin acid, the carboxyl radical of the rosin acid being esterified with an aliphatic alcohol.

9. A corrosion-preventive composition comprising predominantly a stable, substantially neutral vehicle containing finely dispersed a corrosion inhibiting amount, less than 5% of a free dicar-

boxylic acid being the hydrolyzed condensation product between maleic acid anhydride and a polyolefinic fatty acid having at least 10 carbon atoms, the carboxyl radical of the fatty acid being esterified with an aliphatic alcohol.

10. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance containing a corrosion inhibiting amount, less than 5% of a free dicarboxylic acid being the hydrolyzed condensation product between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of the hydrocarbon carboxylic acid being esterified with an aliphatic alcohol.

11. The composition of claim 10 in which said substance is normally liquid.

12. The composition of claim 10 in which said substance is normally plastic.

13. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance free from resins containing finely dispersed .001%–.1% of a free dicarboxylic acid being the hydrolyzed product of condensation between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of the hydrocarbon carboxylic acid being esterified with aliphatic alcohol.

14. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance containing resins and finely dispersed .1%–5% of a free dicarboxylic acid being the hydrolyzed product of condensation between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of the hydrocarbon carboxylic acid being esterified with aliphatic alcohol.

15. A corrosion-preventive lubricating oil containing finely dispersed .001%–1% of a free dicarboxylic acid being the hydrolyzed product of condensation between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of the hydrocarbon carboxylic acid being esterified with aliphatic alcohol.

16. A corrosion-preventive composition comprising a carboxylic acid ester containing finely dispersed a corrosion inhibiting amount, less than 5% of a free dicarboxylic acid being the hydrolyzed product of condensation between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of the hydrocarbon carboxylic acid being esterified with aliphatic alcohol.

17. A corrosion-preventive composition comprising a fat and finely dispersed therein a corrosion inhibiting amount, less than 5% of a free dicarboxylic acid being the hydrolyzed product of condensation between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of the hydrocarbon carboxylic acid being esterified with aliphatic alcohol.

18. A non-corrosive anti-freeze composition comprising a water-soluble alcohol and finely dispersed therein a corrosion inhibiting amount, less than 5% of a free dicarboxylic acid being the hydrolyzed product of condensation between maleic acid anhydride and a polyolefinic hydrocarbon carboxylic acid having at least 10 carbon atoms, the carboxyl radical of the hydrocarbon carboxylic acid being esterified with aliphatic alcohol.

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