Patented Feb. 20, 1945

2,369,640

UNITED STATES PATENT OFFICE

2,369,640

ANTICORROSIVE

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No Drawing. Application February 8, 1943, Serial No. 475,199

22 Claims. (Cl. 252—56)

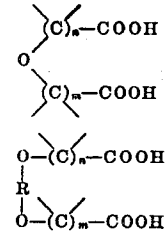
The present invention relates to compositions having anti-corrosive, and especially rust-protective, properties, and more particularly deals with compositions comprising a substantially neutral vehicle, such as normally liquid or normally solid hydrocarbons, alcohols, esters, e. g., fatty oils and natural waxes, water, etc., containing finely dispersed small amounts of certain free dicarboxylic acids in which the carboxyl radicals are linked through an ether radical.

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 composition causes corrosion in automobile radiators, etc. Corrosion not only has 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.

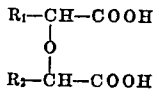
I have discovered that dicarboxylic acids having at least 16 carbon atoms in which the carboxyl radicals are linked through an oxygen radical attached to an alpha or beta carbon atom are potent corrosion inhibitors, such that many of them are capable of effectively preventing rusting of ferrous metals, affording protection not only against fresh water, but against diluted salt water, such as sea water, as well. For use in rust-proofing and corrosion-prevention in general, small amounts of these acids are finely dispersed as in colloidal or true solution in a suitable vehicle.

The general formulae of these acids are:



wherein n and m are 1 or 2, and R is a hydrocarbon radical of 2 to about 10 carbon atoms. The unoccupied valences shown are tied to hydrogen or hydrocarbon radicals. The several hydrocarbon radicals may be aliphatic, alicyclic, aromatic or mixed and may contain substituents which are preferably not too strongly polar, such as halogen, carbosulfide sulfur, etc., which should preferably be free from highly polar substituents, such as hydroxyl, carboxyl, carbonyl, amino, hydrosulfide, etc. For maximum stability against deterioration by oxidation, the acid should not contain more than one olefinic double bond per hydrocarbon radical, and preferably none.

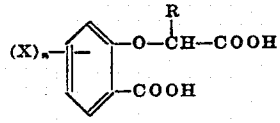
As indicated above, the acid should have not less than 16 carbon atoms and preferably at least 20 and up to about 60 carbon atoms for good anti-corrosive properties. Also, the closeness of the oxygen to the carboxyl radicals has a bearing on the protective powers, and from this angle, homologues in which the oxygen is in alpha position to at least one carboxyl radical and preferably to both are most desirable. Compounds of this type are homologues of di-acetic acid ethers having 16 or more carbon atoms, and more specifically, the alpha alpha di-fatty ethers. Accordingly, a very desirable group of compounds is represented by the formula



wherein R_1 and R_2 are the same or different hydrocarbon radicals, such as alkyl, cyclo alkyl, aryl, or mixed radicals. Alpha alpha' di-fatty acid ethers of fatty acids containing 12 to 20 carbon atoms and not more than one olefinic dou-

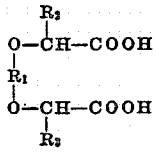
ble bond per fatty acid comprise the preferred group within the above group, particularly the alpha alpha' di-lauric, di-myristic, di-palmitic, di-stearic, di-arachic and di-oleic acid ethers.

Another group which may be looked upon as salicylic acid derivatives is represented by the formula:



wherein R is a hydrocarbon radical and the aromatic ring may, if desired, contain one or several alkyl radicals as indicated by the symbol X, n being an integer from 3 to 4.

Still another group are di-ethers having the following general formula:



wherein R_2 and R_3 are hydrogen or hydrocarbon radicals, and R_1 is a hydrocarbon radical, preferably benzene ring.

Both true solutions and colloidal dispersion in various vehicles are effective in the matter of corrosion protection. However, true solutions are preferred for two reasons: first, colloidal solutions may, under many circumstances, coagulate, in which case the active protective agent would be eliminated; and second, colloids tend to cause emulsification of oily vehicles with water, emulsification in many instances being very undesirable as in the lubrication of steam turbines.

The ether dicarboxylic acids of this invention may be produced for example, by reacting the di-alkali salt of an alpha hydroxy carboxylic acid with an alpha or beta monochlor or monobrom fatty acid. Di-ethers may be produced by reacting, for example, an alkali metal salt of an ortho dihydroxy benzene with an alpha halogen fatty acid as shown, for example, by Merriman J. Chem. Soc. 99:911 (1911).

A large group of hydroxy carboxylic acids may be obtained from halogen monocarboxylic acids which in turn are produced by simple halogenation of suitable monocarboxylic acids.

Suitable monocarboxylic acids for the above purpose include fatty acids such as acetic, propionic butyric, isobutyric, valeric, caproic, caprylic, decylic, undecylic, lauric, myristic, palmitic, stearic, arachic, behenic, oleic, phenyl acetic, phenyl propionic, phenyl stearic, tolyl stearic, naphthyl acetic, naphthyl stearic, acids, etc. Naphthenic acids, such as are obtained by caustic alkali extraction of relatively high-boiling straight-run petroleum oils, such as kerosene, gas oil, lubricating oils, etc., may be used; or synthetic naphthenic acids, such as cyclohexyl acetic, cyclohexyl propionic, cyclohexyl stearic acids, corresponding alkyl cyclohexyl, tetrallyl, dicyclohexyl fatty acids, or acids derived from naphthenes obtained by hydrogenation of isophorone, diisophorone, and homologues, etc. When choosing carboxylic acids from the above list, sight must not be lost of the fact that the ether thiocarboxylic acid must possess a minimum of 16 carbon atoms.

Another group of hydroxy carboxylic acids comprises the group of hydroxy benzoic, hydroxy naphthenic, etc., acids and the alkyl homologues thereof, typical representatives being the salicylic acids.

The vehicles to which 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 treatments produce 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 come 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 acids effectively inhibit this corrosion.

Among the non-hydrocarbon compositions which frequently cause corrosion difficulties, anti-freezes used in automobile radiators and the like may be mentioned. The dicarboxylic acids effectively eliminate their corrosiveness. Anti-freezes 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 difficulties which can effectively be prevented by the acids of this invention.

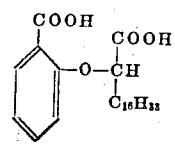
Dispersions of the dicarboxylic di-fatty acids in water may be useful in the rust-proofing of metals which after treatment must not be greasy as, for example, various machine parts in the textile industries, particularly in the knitting of fine dry goods. If desired, solutions or dispersions in low-boiling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

The effectiveness of a typical ether-dicarboxylic acid was determined by a test wherein a polished steel strip was subjected to the action of a vigorously stirred emulsion of a turboraffinate having a S. U. viscosity at 100° F. of 150 seconds and containing .01% of the acid with 10% by volume of synthetic sea water at 167° F. for 48 hours. The acid was alpha (2-carboxy phenoxy) alpha stearic acid having the formula



No corrosion occurred, the protection being perfect.

I claim as my invention:

1. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small corrosion inhibiting amount of a free dicarboxylic acid having at least 16 carbon atoms, the two carboxyl radicals of said acid being linked through an ether group which is joined to an alpha or beta carbon atom.

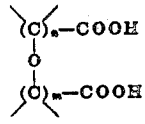
2. The composition of claim 1 wherein the number of carbon atoms in said acid is between 20 and 60.

3. The composition of claim 1 wherein said vehicle has a dissociation constant below 10^{-2}.

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

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

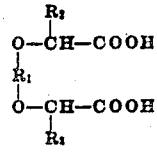
6. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small corrosion inhibiting amount of a free dicarboxylic acid having at least 16 carbon atoms and having the formula



wherein n and m are integers of 1 to 2 and the unoccupied valences are tied to hydrogen or hydrocarbon radicals.

7. The composition of claim 6 wherein n plus m amounts to 2 to 3.

8. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small corrosion inhibiting amount of a free dicarboxylic acid having at least 16 carbon atoms and having the formula

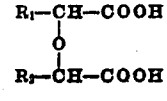


wherein R_2 and R_3 are hydrogen or hydrocarbon radicals and R_1 is a hydrocarbon radical.

9. The composition of claim 8 wherein R_1 comprises an ortho connected benzene ring.

10. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small corrosion inhibiting amount of a dicarboxylic acid ether having at least 16 carbon atoms said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

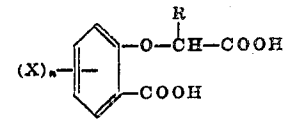
11. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small corrosion inhibiting amount of a dicarboxylic acid ether having at least 16 carbon atoms and the formula



wherein R_1 and R_2 are hydrocarbon radicals containing not more than one olefinic double bond.

12. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small corrosion inhibiting amount of alpha alpha' di-fatty acid ether having 20 to 40 carbon atoms and containing not more than one olefinic double bond per fatty acid radical.

13. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small corrosion inhibiting amount of alpha beta di-fatty acid ether having at least 16 carbon atoms and having the formula



wherein R is a hydrocarbon radical, X represents one or several optional alkyl radicals, and n is a number from 1 to 4.

14. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance containing a small corrosion inhibiting amount of a free dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals in said acid being linked through an ether group said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

15. The composition of claim 14 in which said substance is normally liquid.

16. The composition of claim 14 in which said substance is normally plastic.

17. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance free from resins containing finely dispersed .001%–.1% of a free dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals in said acid being linked through an ether group said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

18. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance containing resins and finely dispersed .1%–5% of a free dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals in said acid being linked through an ether group said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

19. A corrosion-preventive lubricating oil containing finely dispersed .001%–.1% of a free dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals in said acid being linked through an ether group said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

20. A corrosion-preventive composition comprising predominantly a carboxylic acid ester containing finely dispersed a small corrosion inhibiting amount of a free dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals in said acid being linked through an ether group said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

21. A corrosion-preventive composition comprising predominantly a fat and finely dispersed therein a small corrosion inhibiting amount of a free dicarboxylic acid having at least 16 carbon

atoms, the carboxyl radicals in said acid being linked through an ether group said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

22. A non-corrosive anti-freeze composition comprising predominantly a water-soluble alcohol and finely dispersed therein a small corrosion inhibiting amount of a free dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals in said acid being linked through an ether group said ether joining carbon atoms no further removed than the beta position from the carboxyl radicals.

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