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CORROSION PROTECTION OF METALS

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13 Claims. (Cl. 148—6.5)

The present invention relates to metals or metal-containing articles of manufacture which are normally subject to corrosion and which have been rendered substantially non-corrodible by treatment with a dispersion of a certain free dicarboxylic acid in a suitable vehicle.

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 treat metals or articles of manufacture containing metals in a way so that they become resistant to their normal corrosion. It is a specific purpose to treat in a simple manner accurately machined metal parts so that they may be handled without developing corrosion, particularly in places where fingerprints have been left. Another purpose is to protect iron or steel equipment exposed to the atmosphere so that its rusting is prevented or at least retarded. Still another purpose is to protect mechanical equipment from rusting, which equipment stands idle and/or is shipped over long distances.

I have discovered that structural metals which are used in the construction of various articles of manufacture and are subject to a normal corrosion can be protected simply and effectively by treating them with a fine dispersion of a dicarboxylic acid having at least 16 carbon atoms and a linkage between the alpha or beta carboxyl radicals comprising an ether radical.

The dispersion may be a true or colloidal solution in a suitable vehicle which is capable of flowing under the conditions of the treatment, i. e., is liquid or plastic at the temperature of the treatment.

The treating temperature is preferably about atmospheric if the vehicle is normally liquid, although lower or higher temperatures may be employed. The lower temperature limit is usually determined by the solidification temperature of the liquid, and temperatures should be below the boiling temperature of the vehicle and below the decomposition temperatures of both the vehicle and the dicarboxylic acid.

Metals capable of being thus protected are in particular the ferrous metals, e. g. soft iron, various steels, cast iron, and to a lesser extent copper, brass, bronze, zinc, aluminum, magnesium alloys, various bearing metals as coper-lead, cadmium-nickel, silver-nickel, etc.

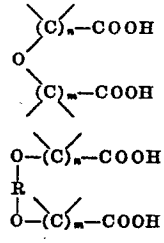
Articles containing these metals are too numerous to recite. However, it may be mentioned that the problem of rust prevention is critical, for example, where accurately machined parts are involved such as piston rings, engine cylinders, bearing shafts, plungers of pumps, etc. In other instances, rust prevention may perhaps not be critical, but of vast economic importance as, for example, in the mass production of steel castings which are piled up and often set in the open for months before being finished.

Corrosion may be due not only to atmospheric exposure, but may be caused or accelerated by contact with acidic materials, for example by touching with the fingers. It may also occur in closed systems, as in internal combustion engines, steam turbines, pipe lines, etc., due to the corrosive influence of various impurities such as water, oxygen, CO_2, salts, inorganic or organic acids, etc.

The treatment according to this invention for the prevention of corrosion may consist of a single contact of the metal to be protected with the dispersion containing the dicarboxylic acid, or may comprise repeated contacts effected at intervals, or may consist of a continuous treatment lasting as long as the use of the particular dispersion or piece of equipment or both. The choice of any particular type of these treatments is usually dictated by circumstances. For example, if newly machined and finished machine parts are to be rust-proofed, they may be dipped or sprayed with a suitable dispersion, and then stored away. On the other hand, if rust prevention in a steam turbine is desired, it is preferable that the circulating lubricating oil contain the active rust preventive compound and contact is made as long as this oil is used. Should, after

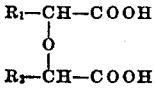
a while, this oil be discarded and be replaced by another one not containing a rust-preventive, then corrosion protection usually lasts for a long time thereafter, due to the protective film left behind. In cases where this film is mechanically destroyed, as in bearings or gears, etc., running under extreme loads, the protective film must be renewed continuously; otherwise rust protection fails.

The general formulae of the corrosion-preventive acids of this invention are:



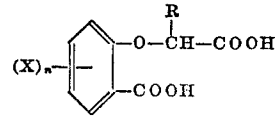
wherein n and m are 1 or 2, i. e., not further removed from the carboxylic radicals than the beta carbon atoms and R is a hydrocarbon radical of 2 to about 10 carbon atoms. The unoccupied valences shown are tied to hydrogen or hydrocarbon radicals. The several hydrocarbon radicals may be aliphatic, alicyclic, aromatic or mixed and may contain substituents which are preferably not too strongly polar, such as halogen, carbosulfide sulfur, etc., but 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



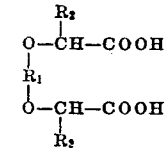
wherein R_1 and R_2 are the same or different hydrocarbon radicals, such as alkyl, cyclo alkyl, aryl or mixed radicals. Alpha alpha' di-fatty acid ethers of fatty acids containing 12 to 20 carbon atoms and not more than one olefinic double bond per fatty acid comprise the preferred group within the above 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 a 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 by reacting the di-alkali salt of an alpha hydroxy carboxylic acid with an alpha or beta monochlor or monobrom fatty acid as shown, for example, by Merriman, J. Chem. Soc. 99:911(1911). Di-ethers may be produced by reacting, for example, an alkali metal salt of a dihydroxy benzene with an alpha halogen fatty acid.

Alpha or beta hydroxy carboxylic acids may be obtained from the corresponding 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. Spread-

ing 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, 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.

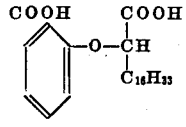
In the absence of such resinous materials, amounts required of the dicarboxylic acids vary from about .001% up to about .1%, although larger amounts may be used. However, where the acids are in colloidal dispersion, rather than in true solution, a concentration in excess of about .1% may result in relatively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

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



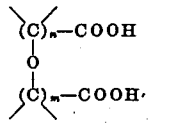
No corrosion occurred, the protection being perfect.

I claim as my invention:

1. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by a free dicarboxylic acid having at least 16 carbon atoms, the two acid radicals of said acid being linked through an ether group not further removed from the carboxylic radicals than the beta carbon atoms.

2. The coated material of claim 1, the film of which contains an acid having between 20 and 60 carbon atoms.

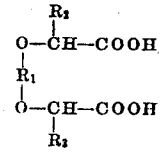
3. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by a free dicarboxylic acid having at least 16 carbon atoms and having the formula



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

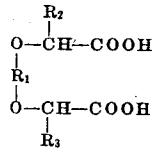
4. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed

by a free dicarboxylic acid having at least 16 carbon atoms and having the formula



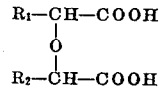
wherein R_2 and R_3 are hydrogen or hydrocarbon radicals and R_1 is a hydrocarbon radical.

5. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by 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 comprises a benzene ring.

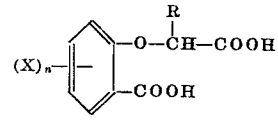
6. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by a free dicarboxylic acid having at least 16 carbon atoms and having the formula



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

7. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by an alpha-alpha' di-fatty acid ether having 20–40 carbon atoms and containing not more than two olefinic double bonds per fatty acid radical.

8. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by a free dicarboxylic acid having at least 16 carbon atoms and having the formula



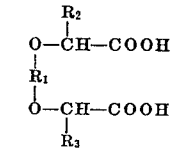
wherein R is a hydrocarbon radical, X represents one or several optional alkyl radicals, and n is a number from 1 to 4.

9. A ferrous metal coated with a rust-preventive film formed by a free dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals of said acid being linked through an ether group not further removed from the carboxylic radicals than the beta carbon atoms.

10. An article of manufacture comprising a solid metal corrodible by salt solution treated with a fine dispersion in a substantially neutral vehicle of a dicarboxylic acid having at least 16 carbon atoms, the carboxyl radicals of said acid being linked through an ether group not further from the carboxylic radicals than the beta carbon atoms.

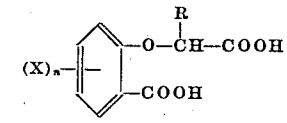
11. Method of protecting a solid metal corrodible by salt solution from corrosion comprising spreading over its surface a fine dispersion in a substantially neutral vehicle of a dicarboxylic acid having at least 16 carbon atoms to deposit on said metal a protective coating of said acid, the carboxyl radicals in said acid being linked through an ether radical not further removed from the carboxylic radicals than the beta carbon atoms.

12. Method of protecting a solid metal corrodible by salt solution from corrosion comprising spreading over its surface a fine dispersion in a substantially neutral vehicle of a dicarboxylic acid having at least 16 carbon atoms to deposit on said metal a protective coating of said acid, said acid having the formula



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

13. Method of protecting a solid metal corrodible by salt solution from corrosion comprising spreading over its surface a fine dispersion in a substantially neutral vehicle of a dicarboxylic acid having at least 16 carbon atoms to deposit on said metal a protective coating of said acid, said acid 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.

EMMETT R. BARNUM.