

UNITED STATES PATENT OFFICE

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CORROSION PROTECTION OF METALS

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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.

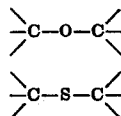
Metallic surfaces, particularly those containing iron, require protection against the hazard of corrosion in the presence of water. To illustrate: Moisture readily attacks finished or semi-finished metal objects unless the metal surface is covered during storage or shipment by a protective coating such 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.

We 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 wherein the carboxyl radicals are linked

by a carbon chain and wherein at least one ether type radical branches from this chain.

By ether type radical we mean a grouping wherein at least one atom of the elements O, S, Se or Te is attached to two separate carbon atoms, such as in



etc.

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 copper-lead, cadmium-nickel, silver-nickel, etc.

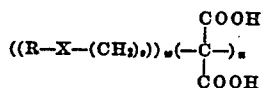
Articles containing these metals are too numerous to recite. However, it may be mentioned that the problem of rust prevention is critical, for example, where accurately machined parts are involved, such as piston rings, engine cylinders, bearing shafts, plungers of pumps, etc. In other instances, rust 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 also may occur in closed systems, as in internal combustion engines, steam turbines, pipe lines, etc., due to the corrosive influence of various impurities as water,

oxygen, CO₂, 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 falls.

The general formula of the corrosion-preventive acids of this invention is:

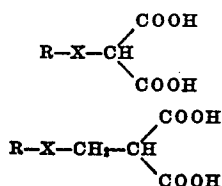


wherein u is an integer from 1 up to about 8 and preferably 2, v is an integer from zero up to about 8, preferably zero, w is at least 1, preferably 1 or 2, and never greater than u , X is an element of the class O, S, Se or Te, and R is a hydrocarbon radical. Unoccupied valences may be tied to the same or different hydrogen or hydrocarbon radicals.

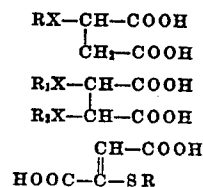
The several hydrocarbon radicals may be aliphatic, alicyclic, aromatic or mixed and may contain substituents which are preferably not too strongly polar, such as halogen, but are preferably free from highly polar substituents, such as hydroxyl, carboxyl, carbonyl, amino, hydrosulfide, etc. For maximum stability against deterioration by oxidation, the acid should contain not more than one aliphatic double bond per hydrocarbon radical, and preferably none.

As indicated above, the acid should contain not less than 16, and preferably at least 20 and up to 60, carbon atoms for good anti-corrosion properties. Also, the closeness of the O, S, Se or Te, as the case may be, to the carboxyl radicals has a bearing on this property, in general the closer they are, the greater the protective power. Because of this, homologues in which the ether linkage is in alpha or beta position to at least one and preferably both carboxyl radicals are most desirable.

The simplest of these acids are the malonic acid derivatives illustrated below:

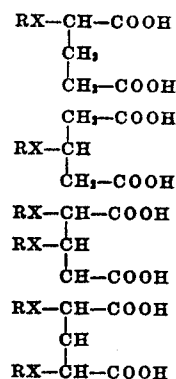


wherein again X is O, S, Se or Te and R is a hydrocarbon radical. However, this type of acid is thermally quite unstable, easily losing CO₂. Therefore, for many purposes it is not desirable. Succinic or fumaric (maleic) acid ether type derivatives, of which there are several, are very stable. They are:



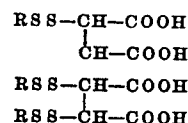
Any of these is very effective.

There are many derivatives of glutonic acid, a few of which are shown below:



From the above it can be readily seen what forms the dicarboxylic acid ethers may take, in which acids the carboxyl radicals are separated by four and more carbon atoms.

Where X stands for sulfur, two sulfur atoms may form the linkage. In other words, compounds of the following types are included in this invention:



As may be noted, there are two general groups of dicarboxylic acids among those listed above, those containing a single ether type radical and those containing two ether type radicals. Under many circumstances, the acids containing two ether type radicals are preferred because they have the ability of giving material corrosion protection in stagnant salt water. A form of corrosion which is probably most difficult to inhibit is that caused by a drop of salt water resting undisturbed on a metal surface. Few, if any, corrosion inhibitors which are not of the soap type are capable of effectively preventing this corrosion. However, the bis-ether type acids and particularly the bis sulfides of this invention have been proven to prevent corrosion against stagnant salt water for several days.

The compounds of this invention are quite soluble in many organic solvents. Wherever possible, true solutions are employed in preference to colloidal solutions for two reasons: first,

because colloids tend to cause emulsification of oleaginous substances with water; and second, colloids may precipitate, in which case at least a portion of the active ingredients would be lost.

The manufacture of most of the compounds of this invention is quite simple. For example, fumaric acid or maleic acid anhydride may be brominated and the resulting dibrom succinic acid is then reacted with an alcoholate, alkyl phenolate, mercaptide, selenide, telluride, etc., having a hydrocarbon radical of sufficient number of carbon atoms to insure that the reaction product has the required minimum of 16 carbon atoms. This hydrocarbon radical may be normal and/or cyclic, examples being heptyl, methyl cyclohexyl, normal or branched octyl, dimethyl cyclohexyl, ethyl cyclohexyl, nonyl, decyl, undecyl, dodecyl, lauryl, myristyl, cetyl, stearyl, oleyl, arachyl, benzyl, methyl phenyl, ethyl phenyl, dimethyl phenyl, propyl phenyl, butyl phenyl, octyl phenyl, naphthyl, alkyl naphthyl, tetrahydronaphthyl, C_{10} and higher dialicyclic, etc.

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 be evaporated, 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, thio-phosphates, carbonates; natural waxes as carnauba wax, candellilla 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, phenolformaldehyde 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 colloiddally 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-dichlor diethyl ether, antimony trichloride, etc.; treatment with $AlCl_3$, sulfuric acid, clay, etc.; as the treatment produces a sludge, special care must be taken to remove it very thoroughly and completely.

Example

The effectiveness of dicarboxylic acids of this invention in suppressing corrosion was determined by a modified test wherein a polished steel strip was subjected to the action of a vigorously stirred emulsion of a turbo raffinate having S. U. viscosity at 100° F. of 150 seconds with 10% by

volume sea water at 167° F. Below are some typical results:

Additive	Water	Time	Corrosion
		Hours	
.01% alpha beta dilauryl dithio succinic acid.	Synthetic sea water.	48	None — perfect protection. ¹
Mono thio lauryl succinic acid.	Distilled water....	48	Perfect.
	Synthetic sea water.	16	Partly corroded.

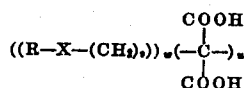
¹ After the test was completed, stirring was discontinued and the steel strip was allowed to drop into the sea water at the bottom of the container, remaining there undisturbed for four days. At the end of this period, only a few small rust spots had developed.

We claim as our invention:

1. A structural normally corrodible metal coated with a corrosion-preventive film of a free dicarboxylic acid having at least 16 carbon atoms and possessing at least one ether type radical of an element selected from the group consisting of O, S, Se and Te, which ether type radical branches from the carbon chain linking the carboxyl radical.

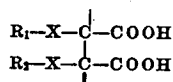
2. The coated material of claim 1, the film of which contains an acid having between 20 and 60 carbon atoms.

3. A structural normally corrodible metal coated with a corrosion-preventive film of a free dicarboxylic acid having at least 16 carbon atoms and having the formula



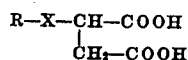
wherein u is an integer of 1 up to about 8, v is an integer of from 0 to about 8, w is at least 1 and not greater than u , X is an element selected from the group consisting of O, S, Se and Te, and R is hydrocarbon radical, and the unoccupied valences are tied to hydrogen or hydrocarbon radicals.

4. A structural normally corrodible metal coated with a corrosion-preventive film of a free dicarboxylic acid having at least 16 carbon atoms and having the formula



wherein X is an element selected from the group consisting of O, S, Se and Te, R_1 and R_2 are hydrocarbon radicals and the unoccupied valences are tied to hydrogen or hydrocarbon radicals.

5. A structural normally corrodible metal coupled with a corrosion-preventive film of a free dicarboxylic acid having at least 16 carbon atoms and having the formula



wherein X is an element selected from the group consisting of O, S, Se and Te and R is a hydrocarbon radical.

6. A structural normally corrodible metal coated with a corrosion-preventive film of a succinic acid ether having at least 16 carbon atoms.

7. A structural normally corrodible metal coated with a corrosion-preventive film of a succinic acid thio ether having at least 16 carbon atoms.

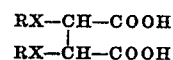
8. A structural normally corrodible metal coated with a corrosion-preventive film of a succinic acid di thio ether having at least 16 carbon atoms.

9. A ferrous metal coated with a rust-preventive film of a free dicarboxylic acid having at least 16 carbon atoms and possessing at least one ether-type radical of an element selected from the group consisting of O, S, Se and Te, which ether-type radical branches from the carbon chain linking the carboxyl radicals.

10. An article of manufacture comprising a structural normally corrodible metal treated with a fine dispersion in a substantially neutral vehicle of a dicarboxylic acid having at least 16 carbon atoms and possessing at least one ether-type radical of an element selected from the group consisting of O, S, Se and Te, which ether-type radical branches from the carbon chain linking the carboxyl radicals.

11. Method of protecting a normally corrodible structural metal 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 possessing at least one ether-type radical of an element selected from the group consisting of O, S, Se and Te, which ether-type radical branches from the carbon chain linking the carboxyl radicals.

12. Method of protecting a normally corrodible structural metal 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 and having the formula



wherein X is an element selected from the group consisting of O, S, Se and Te, and R is a hydrocarbon radical.

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