Patented Jan. 30, 1945 2,368,606

UNITED STATES PATENT OFFICE

2,368,606

CORROSION PROTECTION OF METALS

Ellis R. White, Albany, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application February 8, 1943, Serial No. 475,203

15 Claims. (Cl. 148—6.5)

This is a continuation-in-part of my copending application Serial No. 439,929, filed April 21, 1942. 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 certain free dicarboxylic acids 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 radiation, 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.

It has been 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 carboxyl radicals comprising a trivalent nitrogen atom.

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.

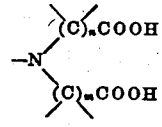
Articles containing these metals are too numerous to recite. However, it may be mentioned that the problem of rust prevention is critical, for example, where accurately machined parts are involved, such as piston rings, engine cylinders, bearing shafts, plungers of pumps, etc. In other instances, rust 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, 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 formula of the corrosion-preventive acids of this invention is:

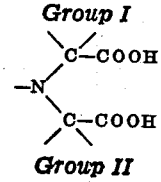


wherein n and m are integers ranging from 1 up to about 8 and preferably are 1 or 2. The unoccupied valences shown are tied with hydrogen or hydrocarbon radicals. The latter may be aliphatic, alicyclic, aromatic or mixed and may contain substituents which are preferably not too strongly polar, such as 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.

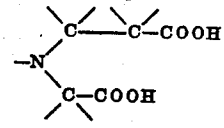
As indicated above, the acid should have not less than 16 carbon atoms and preferably at least 20 and up to about 60 carbon atoms for good anti-corrosive properties. Also the closeness of the nitrogen to the carboxyl radicals has a bearing on this property; in general the closer they are, the greater the protective power. Thus from this angle, homologues in which the nitrogen atom is in alpha position to at least one carboxyl radical and preferably to both are most desirable. Compounds of this type are the N-amino diacetic acids, and more specifically the N-amino alpha-alpha di-fatty acids. However, a disadvantage of the N-diacetic acids is their relatively low thermal stability which causes loss of CO_2 upon heating to moderately elevated temperatures. For this reason, it is often desirable to have at least one carboxyl radical separated from the nitrogen atom by 2 or even more carbon atoms. In general, N-amino alpha-beta di-fatty acids or N-amino beta-beta di-fatty acids are very nearly as potent corrosion inhibitors as the corresponding alpha-alpha compounds, and have a somewhat greater thermal stability.

Accordingly, depending upon the conditions of use, any one of the following three groups of my acids may be preferred:

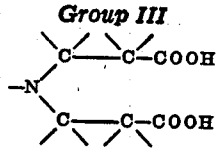
Group I



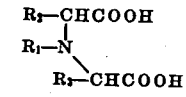
Group II



Group III



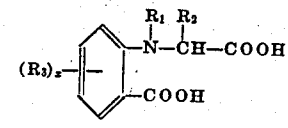
In Group I are the N-amino alpha-alpha di-fatty acids or corresponding naphthenic or aromatic fatty acids:



wherein R_1 is a hydrogen or a hydrocarbon radical, and R_2 and R_3 are hydrocarbon radicals, which in the case of ordinary fatty acids are aliphatic, in the case of naphthenic acids comprise cycloaliphatic rings, and in the case of aromatic fatty acids are aromatic or alk-aromatic.

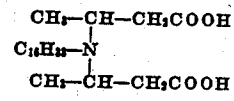
These dicarboxylic acids may be produced by reacting a primary amine with an alpha halogenated fatty acid, aromatic fatty acid or naphthenic acid as the case may be. Suitable primary amines to be used in this reaction are, for example, ammonia, various alkyl or cycloalkyl amines as methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, iso-octyl, cyclopentyl, methyl cyclopentyl, cyclohexyl, dimethyl cyclohexyl, decyl, tetrallyl, dodecyl, myristyl, cetyl, stearyl, oleyl, etc., amines; or aromatic amines as aniline, toluidine, xylidines, cumidine, naphthylamine, etc. Suitable fatty acids include 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. Obviously, the two acids attached to the nitrogen may be different.

In Group II are the N-amino alpha-beta di-fatty acids and the N-anthranilic alpha-mono fatty acids. The latter have the formula



wherein R_1 is hydrogen or a hydrocarbon radical, R_2 and R_3 are hydrocarbon radicals and X is an integer of 0–4. These acids may be produced by reacting anthranilic acid or homologues thereof with an alpha halogen fatty acid, naphthenic acid, or aromatic fatty acid of the classes described above. Homologues of anthranalic acid are alkyl anthranilic acids, ortho naphthylamine carboxylic acid, alkyl derivatives thereof, etc.

Compounds of Group III may be prepared, for example, by reacting HBr with crotonic acid and then condensing the resulting brom-butyric acid with a relatively high-molecular weight primary amine, say a C_{16-18} aliphatic amine. The resulting compound is, for example:



Still another type of compound is based on

alkylated diphenylamine, said phenyl radical having a carboxyl radical.

Inasmuch as the acids are relatively little soluble in most vehicles, at least at ordinary room temperatures, it is usually necessary to produce suitable colloidal dispersions. These may be obtained, for example, by first producing a solution in the vehicle by heating mixtures of the vehicle with the acid to moderately elevated temperatures, and then allowing the solution to cool. This procedure, for instance, is applicable to hydrocarbon oils of sufficiently high boiling temperatures as kerosene, gas oils, Diesel fuels, range fuels, lubricating oils, etc.

In other cases, a solution may be formed in a solvent, such as a lower alcohol, benzene, etc., which is then poured into the liquid body of the desired vehicle. In this manner, colloidal dispersions of the acid in oils may be obtained.

The vehicles to which the N-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, troweling, 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, n-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 acetones, 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 mono-methyl 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, phosphites, phosphates, thiophosphates, carbonates; natural waves as carnauba wax, candelilla 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 N-amino 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.

Example I

The effectiveness of several N-amino dicarboxylic acids in suppressing corrosion was determined by a modified Kuebler test which consists of subjecting a polished steel strip to the action of a vigorously stirred emulsion of an oil under test with 10% by volume of distilled water or of a 2% solution of sodium chloride in distilled

water at 75° C. for 48 hours. Results were as follows:

Oil	Additive	Conditions	Corrosion
Refined lube oil, 150 S. U. at 100° F.	None	Distilled water	100% rusted.
Do	.001% N-toluidino di-alpha stearic acid	NaCl	Do.
Do	do	Distilled water	5% rusted.
Do	.002% N-toluidino di-alpha stearic acid	NaCl	100% rusted.
Do	do	Distilled water	0% rusted.
Do	.005% N-toluidino di-alpha stearic acid	NaCl	No corrosion.
Do	do	Distilled water	Do.
Do	.003% N-octadecyl amino di-alpha stearic acid	NaCl	Do.
Do	Less than .01% [1] N-toluidino alpha stearic acetic acid	do	Do.
Do	Less than .01% [1] N-anthranilic alpha stearic acid	do	Do.
Do	Less than .01% [1] N-octadecyl amino beta-beta' dipropionic acid.	do	Do.
Do	Less than .01% [1] N-octadecyl amino alpha propionic beta-butyric acid.	do	Do.

[1] Samples impure, hence amount of active ingredient less than weighed out amount of .01%.

Example II

The effectiveness of toluidino di-alpha stearic acid in enhancing the anti-corrosion properties of a slushing oil was determined by the following test:

Two strips of steel ¾" x 3" were carefully polished and cleaned to give a bright surface. One strip was coated with a rust-proofing grease by immersion in a bath consisting of a 50–50 mixture of paraffin wax and petrolatum dissolved in a volatile hydrocarbon solvent. The second strip was coated by immersing it in the above bath after 1% of toluidino di-alpha stearic acid had been dissolved therein. The two coated strips were then placed in a horizontal position in a glass dish and 30 drops of a 3% salt solution were deposited on the upper surface of the strips. A loose fitting cover was placed over the dish and it was allowed to stand at room temperature.

The rusting was determined by counting the number of drops that showed signs of rust in any period of time. Results were as follows:

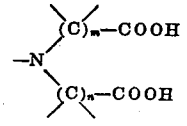
Coating	Per cent rusted	
	5 days	10 days
50% paraffin wax 50% petrolatum	80	83
49.5% paraffin wax 49.5% petrolatum 1% toluidino di-alpha stearic acid	10	50

Example III

Of two polished steel strips, the first was inserted in a lubricating oil containing .01% N-toluidino alpha di-stearic acid. The other was coated in the same lubricating oil not containing a rust-preventive compound. Both steel strips were then touched with the bare fingers and left exposed to the atmosphere. The first strip did not develop fingerprints in many days, while the second one developed fingerprints within a few hours.

I claim as my invention:

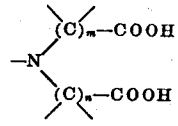
1. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by a dicarboxylic acid having at least 16 carbon atoms and having the formula



wherein n and m are integers ranging from 1 to 8, and the unoccupied valences are tied to hydrogen or hydrocarbon radicals.

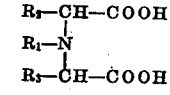
2. The coated metal of claim 1, the film of which contains an acid having between 20 and 60 carbon atoms.

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



wherein R_1 is a radical selected from the group consisting of hydrogen and hydrocarbons, and R_2 and R_3 are hydrocarbon radicals.

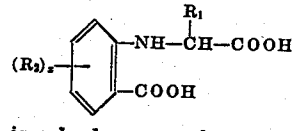
5. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by a free N-amino alpha-alpha' di-fatty acid having at least 16 carbon atoms.

6. A solid metal corrodible by salt solution coated with a corrosion-preventive film formed by N-aromatic amine di-fatty acid containing at least 16 carbon atoms.

7. A solid metal corrodible by salt solution coated with a corrosion preventive film formed by an N-amino alpha-alpha' di-stearic acid.

8. A solid metal corrodible by salt solution coated with a corrosion preventive film formed by an N-amino alpha-alpha' di-naphthenic acid containing at least 16 carbon atoms.

9. 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

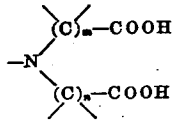


wherein R_1 is a hydrogen or hydrocarbon radical and R_2 are hydrocarbon radicals and x is 0–4.

10. A solid metal corrodible by salt solution coated with a corrosion preventive film formed by N-anthranilic alpha stearic acid.

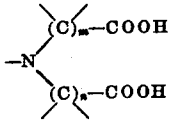
11. A ferrous metal coated with a rust-preven-

tive film formed by a dicarboxylic acid having at least 16 carbon atoms and having the formula



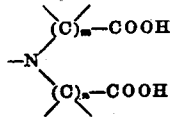
wherein n and m are integers ranging from 1 to 8, and the unoccupied valences are tied to hydrogen or hydrocarbon radicals.

12. An article of manufacture comprising a solid metal corrodible by salt solution treated with a fine dispersion in a substantially neutral vehicle of a free dicarboxylic acid having at least 16 carbon atoms and having the formula



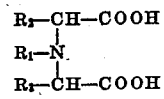
wherein n and m are integers ranging from 1 to 8, and the unoccupied valences are tied to hydrogen or hydrocarbon radicals.

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



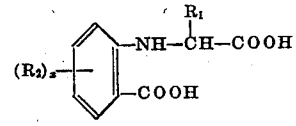
wherein n and m are integers ranging from 1 to 8, and the unoccupied valences are tied to hydrogen or hydrocarbon radicals.

14. 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 free dicarboxylic acid having at least 16 carbon atoms and having the formula



wherein R_1 is a radical selected from the group consisting of hydrogen and hydrocarbons, and R_2 and R_3 are hydrocarbon radicals.

15. 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 free dicarboxylic acid having at least 16 carbon atoms and having the formula



wherein R_1 and R_2 are hydrocarbon radicals and x is an integer of 0–4.

ELLIS R. WHITE.