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ANTICORROSIVE

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The present invention relates to compositions having anti-corrosive, and especially rust-protective, properties, and more particularly deals with compositions comprising a substantially neutral vehicle, such as normally liquid or normally solid hydrocarbons, alcohols, esters (e. g., fatty oils and natural waxes), water, etc., containing finely dispersed small amounts of certain free dicarboxylic acids in which the acid radicals are linked through one or more elements selected from the group consisting of sulfur, selenium and tellurium.

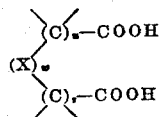
Metallic surfaces, particularly those containing iron, require protection against the hazard of corrosion in the presence of water. To illustrate: Moisture readily attacks finished or semi-finished metal objects unless the metal surface is covered during storage or shipment by a protective coating such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

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

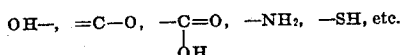
We have discovered that dicarboxylic acids having at least 16 carbon atoms in which the acid radicals are linked through a divalent sulfur, selenium or tellurium atom are such potent corrosion inhibitors that they are capable of effectively preventing rusting of ferrous metals and corrosion in general, affording protection not only

against pure water but against salt water, such as sea water as well. For use in rust-proofing and general corrosion prevention, small amounts of these acids are finely dispersed (as in true or colloidal solution) in a suitable vehicle. Inasmuch as many of them are quite soluble in many solvents, true solutions containing the necessary amounts can easily be prepared for most purposes.

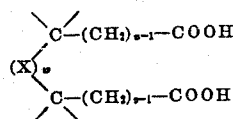
The general formula of these acids is:



wherein X is sulfur, selenium or tellurium, and u , v and w are integers, preferably 1 or 2. The unoccupied valences are tied to the same or different hydrogen or hydrocarbon radicals, the latter of which may be aliphatic, cycloaliphatic, aromatic or mixed and may contain substitution radicals which are not too strongly polar, such as halogen, etc., but should preferably be free from strong polar radicals, such as



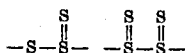
The above formula may take the following form:



As indicated before, the acid should have a total number of carbon atoms not less than 16, and preferably between about 20 and 60 for good anti-corrosive properties. Both true solutions and colloidal dispersions in various vehicles are effective in the matter of corrosion protection. However, true solutions are preferred for two reasons: first, colloidal solutions may under some circumstances coagulate, in which case at least a portion of the active protective agent is eliminated; and second, colloids tend to cause emulsification of oily vehicles with water, which in many instances, such as in the lubrication of steam turbines, is undesirable.

It is, of course, desirable that the acids be relatively resistant to oxidation, and therefore they should not contain more than one aliphatic double bond per hydrocarbon radical and preferably none.

Generally, in the presence of copper, acids containing a link of a single X atom (X being S, Se or Te) seem to impart to oils longer induction periods than acids having X—X linkage, while the latter impart lower rates of oxygen absorption after the induction period. Thus disulfide, diselenide or ditelluride acids may be preferred for some oils, while acids with mono linkages may be better for other oils. Polysulfide linkages of more than two sulfur atoms may also be used. They are, however, believed to contain only two sulfur atoms in the normal chain between the carboxyl radicals, the remaining sulfur being attached in the form of a branch, such as

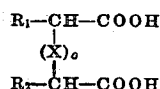


etc. If desired, the carboxyl radicals may be linked through a sulfone radical



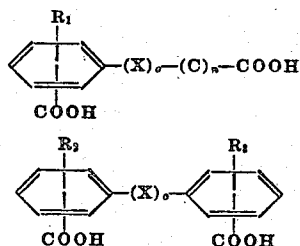
The closeness of the sulfur, selenium or tellurium to the carboxyl radical has some bearing on the corrosion-protective properties of the acids. In general, the closer they are, the more potent the compound is, other things being equal. Thus, from this angle, acids in which the sulfur, selenium or tellurium atoms are in alpha or beta position to at least one, and preferably both carboxyl radicals are the best anti-corrosives.

Accordingly, among the groups of acids are several which are particularly useful. For example, di-fatty acid alpha sulfides, selenides and tellurides having the formula



wherein o is 1 or 2, and R₁ and R₂ are alkyl radicals whose total number of carbon atoms is not less than 16 (one of them may be hydrogen). If desired, R₁ and R₂ may comprise alicyclic rings, in which case one or both of the carboxylic acids are naphthenic acids; or else R₁ and R₂ may contain aromatic rings as, for example, in phenyl or naphthyl acetic or corresponding propionic, stearic, etc. acids. Examples of individual acids of this group are dilauric or corresponding myristic, palmitic, stearic, arachic, behenic, etc., alpha sulfides including both mono-, di- and higher polysulfides; di-phenyl-stearic acid alpha sulfides; dicyclohexyl-stearic acid alpha sulfides, di-petroleum naphthenic acids alpha sulfides, etc. Obviously, the two fatty or naphthenic acids linked by the sulfur may be different as, for example, in phenyl stearic acid-acetic acid sulfides.

Groups of acids somewhat different from the above are represented by the formulae:



wherein R₁—R₃ are hydrogen or hydrocarbon

radicals, the latter preferably being aliphatic although they may comprise cycloaliphatic or aromatic groups. The unoccupied valences are tied to hydrogen or hydrocarbon radicals, which radicals may be the same or different in different



groups. X again is sulfur, selenium or tellurium; n is preferably 1 or 2; and o is 1 or preferably 2. The total number of carbon atoms is preferably 20 or more.

The dicarboxylic acids of this invention may be produced in several ways. One convenient method comprises reacting a chlorinated fatty acid or other suitable monocarboxylic acid with an alkali metal sulfide or polysulfide. Commercially available alkali metal sulfides are usually mixtures containing mono-, di- and sometimes higher polysulfides. Therefore this reaction may be utilized to produce mixtures of different sulfide dicarboxylic acids. Such mixtures are very excellent for the purpose of this invention, since they are usually more soluble in various vehicles and as oxidation stable as the best of the pure individual compounds.

Disulfides may be produced by first preparing a hydrosulfide derivative of a fatty acid or other suitable carboxylic acid by reaction of a chlorinated carboxylic acid with NaHS, KHS, etc., then oxidizing the hydrosulfide to the disulfide. Higher polysulfides may be obtained by oxidizing with sulfur in the presence of lead oxide.

Asymmetric dicarboxylic acids may be produced, for example, by reacting a suitable chlorinated monocarboxylic acid with an alkali metal salt of thioglycolic acid or of a fatty or other suitable monocarboxylic acid hydrosulfide.

Suitable monocarboxylic acids for the production of our dicarboxylic acids include fatty acids, such as acetic acid, 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, naphthol 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, tetralyl, dicyclohexyl fatty acids, or acids derived from naphthenes obtained by hydrogenation of isophorone, diisophorone and homologues, etc. In choosing a monocarboxylic acid from the list for use in a certain reaction, sight must not be lost of the fact that the dicarboxylic acid must have a minimum of 16 carbon atoms.

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 car-

riers 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 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-dichlorine diethyl ether, antimony trichloride, etc.; treatment with AlCl_3 , sulfuric acid, clay, etc. If the treatment produces a sludge, special care must be taken to remove it very thoroughly and completely.

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

Diesel fuels may cause corrosion of injection nozzles.

Lubricating oils and greases made of lubricating oils and soaps normally allow corrosion or even may cause corrosion of various metal parts with which they 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, antifreezes used in automobile radiators and the like may be mentioned. The dicarboxylic acids effectively eliminate their corrosiveness. Antifreezes usually comprise or consist of water-miscible alcohols, such as methanol, ethanol, isopropanol, glycol, glycerol, etc.

So-called hydraulic oils, damping oils, etc., which frequently are based on non-hydrocarbon liquids, such as various alcohols, esters, etc., have in the past introduced some corrosion 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.

Examples

The effectiveness of several dicarboxylic acids of this invention in suppressing corrosion was determined by a test which consists of subjecting a polished steel strip to the action of a vigorously stirred emulsion of a turbo raffinate of 150 S. U. viscosity at 100° F. with 10% by volume of water at 167° F. In some cases, distilled water was used, in others a 2% solution of NaCl, or sea water from the Pacific Ocean, or a synthetic sea water which had the same analysis as real sea water. When using distilled water protection was perfect in all cases for more than 48 hours. Brine waters gave the following results:

Additive	Water	Time	Corrosion
.01% alpha alpha dilauric acid sulfide.....	2% NaCl.....	Hours	None—perfect protection. Do.
	Synthetic sea water...	48	
.01% alpha alpha' dimyristic acid sulfide.....	2% NaCl.....	24	None—perfect protection. Perfect. Do.
	Sea water.....	25	
	Synthetic sea water...	48	
.01% alpha alpha' dipalmitic acid sulfide.....	Synthetic sea water...	48	Perfect.
.01% alpha alpha' distearic acid sulfide..... Do..... Do.....	2% NaCl.....	48	Perfect. Slight corrosion, less than 10%. None—perfect protection. Slight corrosion, less than 10%.
	Sea water.....	44	
	Synthetic sea water...	48	
.005% alpha alpha' distearic acid sulfide.....	do.....	25	
.01% alpha-lauric alpha-stearic acid sulfide.....	Synthetic sea water...	48	None—perfect protection.
.01% alpha alpha' distearic acid disulfide.....	2% NaCl.....	48	Perfect. Very slight corrosion.
	Synthetic sea water...	24	
.01% alpha hexadecyl thioglycolic acid.....	2% NaCl.....	24	Very slight corrosion.

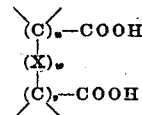
We claim as our invention:

1. A corrosion-preventive composition comprising predominantly an oleaginous vehicle containing finely dispersed a small corrosion inhibiting amount of a dicarboxylic acid having at least 16 carbon atoms, the two acid radicals in said acid being linked through an element selected from the group consisting of S, Se, and Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

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

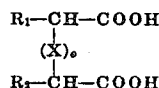
3. The composition of claim 1 wherein said acid is in colloidal solution.

4. A corrosion-preventive composition comprising predominantly an oleaginous vehicle containing finely dispersed a small corrosion inhibiting amount 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 S, Se and Te, u and v are each integers of less than three, and w is equal to one.

5. A corrosion-preventive composition comprising predominantly an oleaginous vehicle containing a small corrosion inhibiting amount of a dicarboxylic acid having at least 20 carbon atoms and the formula



wherein R_1 and R_2 are hydrogen or hydrocarbon radicals, X is an element selected from the group consisting of S, Se, and Te, and o is 1 or 2.

6. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous vehicle containing finely dispersed a small corrosion inhibiting amount of a dicarboxylic acid having at least 20 carbon atoms, the two carboxylic acid radicals in said acid being linked through a single divalent sulfur atom in alpha position with respect to each of said carboxylic acid radicals.

7. A corrosion-preventive composition comprising predominantly an oleaginous vehicle containing finely dispersed a small corrosion inhibiting amount of di-stearic acid alpha, alpha' monosulfide.

8. A corrosion-preventive composition com-

prising predominantly an oleaginous vehicle containing finely dispersed a small corrosion inhibiting amount of di-myristic acid alpha, alpha' mono-sulfide.

9. A corrosion-preventive composition comprising predominantly an oleaginous vehicle containing finely dispersed a small corrosion inhibiting amount of di-palmitic acid alpha, alpha' mono-sulfide.

10. 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 two acid radicals in said acid being linked through an element selected from the group consisting of S, Se or Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

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

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

13. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance free from resins containing finely dispersed .001%-.1% of a free dicarboxylic acid having at least 16 carbon atoms, the two acid radicals in said acid being linked through an element selected from the group consisting of S, Se or Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

14. 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 two acid radicals in said acid being linked through an element selected from the group consisting of S, Se or Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

15. A corrosion-preventive lubricating oil containing finely dispersed .001%-.1% of a free dicarboxylic acid having at least 16 carbon atoms, the two acid radicals in said acid being linked

through an element selected from the group consisting of S, Se or Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

16. 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 two acid radicals in said acid being linked through an element selected from the group consisting of S, Se or Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

17. 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 two acid radicals in said acid being linked through an element selected from the group consisting of S, Se or Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

18. 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 two acid radicals in said acid being linked through an element selected from the group consisting of S, Se or Te, said element being attached to a carbon atom not further removed from the carboxyl radical than the beta position.

19. A corrosion-preventive composition comprising predominantly an oleaginous vehicle containing finely dispersed a corrosion-inhibiting amount of a di-fatty acid having at least 20 carbon atoms, the two acid radicals in said acid being linked through a single divalent sulfur atom between two carbon atoms not further removed from each of the acid radicals than the beta position.

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