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ANTICORROSIVE

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23 Claims. (Cl. 252—48.6)

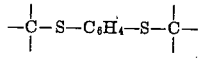
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The present invention relates to compositions having anti-corrosive, and especially rust-protective properties, and more particularly deals with compositions comprising a substantially neutral vehicle, such as normally liquid or normally solid hydrocarbons,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

Metallic surfaces, particularly those containing iron, require protection against the hazard of corrosion in the presence of water. To illustrate: Moisture readily attacks finished or semi-finished metal objects unless the metal surface is covered during storage or shipment by a protective coating such as a slushing oil; water in Diesel engine fuels often corrodes closely fitted parts such as are found in Diesel engine unit type injectors; water in turbines corrodes turbine lubricant circulatory systems, particularly the governor mechanisms of steam turbines; and water in hydrocarbon oils such as gasoline rusts steel storage tanks and drums; water in anti-freeze 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 oxidantion catalysts increasing the rate of deterioration of various organic compounds with which they come in contact or may enter between moving parts of machinery where they act as abrasives.

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

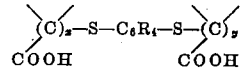
I have discovered that dicarboxylic acids in which the two carboxyl radicals have a total of at least about 24 carbon atoms, and are linked through a bridge comprising the structure



are very efficient corrosion inhibitors capable of effectively preventing rusting of ferrous metals against pure water and even against dilute salt water, such as sea water, to some extent. These dicarboxylic acids having between about 30 and 60 carbon atoms are preferred. For use in rust-

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proofing and corrosion prevention in general, small amounts of these acids are finely dispersed as in true or colloidal solution in a suitable vehicle. Inasmuch as they are quite soluble in many solvents, true solutions containing the necessary amount can normally be prepared for most purposes. The compounds of this invention can be represented by the following general formula:



wherein x and y are integers from 1 to about 8 and preferably 1 or 2, and R is hydrogen or alkyl. The unoccupied valences are tied to 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., 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.

The closeness of the sulfur to the carboxyl radicals has a bearing on corrosion-protective properties of the acids; in general, the closer they are, the greater the protective power. Thus, from this angle, homologues in which the two sulfur atoms are in alpha position to the two carboxyl radicals, respectively, are the most desirable.

These compounds may be prepared by reacting the alkali (preferably sodium or potassium) salt of dithio hydroquinone (or a homologue or analogue thereof) with a halo carboxylic acid (preferably the bromo iodo or chloro derivative). To prevent the alkali salt from reacting with the free carboxylic radical the latter is first converted to a salt, for example an alkali salt, and then hydrolyzed back to the free carboxylic acid after the reaction with the aromatic disulfide is completed.

Among the hydrocarbon carboxylic acids, the halogen alkali salts of which are suitable for this synthesis, are fatty acids, including 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, etc. acids. 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 bridge may be different. These oil soluble corrosion inhibiting compounds are also new compositions of matter.

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: Colloidal solutions may under some circumstances coagulate, in which case at least a portion of the active agent is eliminated; and, second, colloids tend to cause emulsification of oily vehicles with water, emulsification being undesirable in many instances as in the lubrication of steam turbines.

The vehicles to which dicarboxylic acids of this invention may be added for the purpose of producing corrosion-protective compositions may be divided into several groups. In the first place, they may be liquids or plastics, the only requirements as to their physical state being (in addition to their being able to act as carrier for the acids under normal atmospheric conditions) that they be spreadable over metal surfaces. Spreading may be accomplished by immersing, flooding, spraying, brushing, trowelling, etc.

After being applied, all or part of the vehicle may evaporate, or it may be more or less permanent. In other words, both volatile carriers may be used, or substances which do not materially volatilize under normal atmospheric conditions. As to chemical requirements, the vehicle must be stable under ordinary conditions of storage and use and be inert to the active inhibitors.

Thus the vehicle should preferably be substantially neutral, although it may be weakly acidic or basic, preferably having dissociation constants not above about 10^{-8}. In vehicles of low dielectric constant, as hydrocarbon oils, which are not conducive to ionization of dissolved electrolytes, relatively small amounts, i. e., about 0.1%–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 ethers, 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, 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, particulary 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 0.001% up to about 0.1%, 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 0.1% 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 0.1% 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 a selective solvent for aromatic hydrocarbons as liquid SO_2, phenol, furfural, nitrobenzene, aniline, beta-beta-dichloro diethyl ether, antimony trichloride, etc.; treatment with $AlCl_3$, sulfuric acid, clay, etc. If the treatments produce a sludge, special care must be taken to remove it very thoroughly and completely.

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

Diesel fuels may cause corrosion of injection nozzles.

Lubricating oils and greases made of lubricating oils and soaps normally allow corrosion or even may cause corrosion of various metal parts with which they come in contact, such as bearings, crank-cases, shafts, etc. This problem arises in many types of engines and is often particularly serious in steam turbines. The presence of the inhibitors of this invention will afford

excellent protection in all of the above instances.

Rusting of ferrous metals exposed to the atmosphere during usage or storage is a serious problem. This is of particular importance where accurately machined parts must be preserved. Slushing oils comprising various types of liquid or plastic hydrocarbons, fats, waxes, lanolin, are employed to protect the metals against this attack, and the inhibitors of this invention have great value as active components 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 present 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.

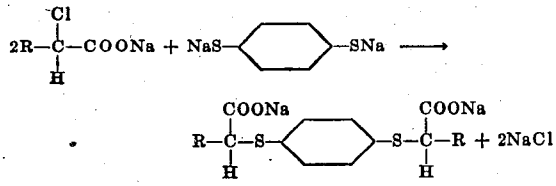
It is understood that the corrosion-protective compositions of this invention may contain other ingredients in addition to the vehicle and the dicarboxylic acids. However, such additional ingredients must be chemically inert to the acid and the vehicle employed. Thus strong oxidizing agents as chlorine, 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 di-acids 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 mono-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; 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, antifreezes, etc. may contain anti-oxidants.

Example

The corrosion inhibitors of the present invention may be prepared as follows:

One mol of the alkali salt of dithio hydroquinone is reacted with two mols of the halo carboxylic acid. The latter two mols may be the same or different carboxylic acids which may contain the same or different halogens. In order to yield a corrosion inhibitor in which the phenylene sulfide atoms are each joined to a carbon atom adjacent to the carboxyl group, the alpha halogen carboxylic acids should be employed. The reaction thus may be exemplified by the equation



Two tenths mols of the sodium salt of alpha brom stearic acid were reacted with $\frac{1}{10}$ mol of the sodium salt of dithio hydroquinone dissolved in 500 cc. of approximately 90% ethyl alcohol. Heat was evolved by the reaction begun at room temperature and the reaction was completed in about half an hour. The solution was then acidified with tenth normal acid to release the free distearic acid derivative which precipitated. This was recrystallized from ligroin (a petroleum fraction used as a rubber solvent) and then from acetone. Conversion and yield of para phenylene dithio alpha alpha' distearic acid were practically the theoretical amount. A molecular weight determination showed a molecular weight of 352 which corresponds to the theoretical molecular weight.

The effectiveness of 0.01% para phenylene dithio alpha alpha' distearic acid in suppressing corrosion was determined by a test wherein a polished steel strip was subjected to the action of virgorously stirred emulsion of a turboraffinate having a S. U. viscosity at 100° F. of 150 seconds with 10% by volume of water at 167° F. When using distilled water, the protection was perfect for 48 hours. In salt water, slight corrosion began after about one hour of exposure.

This is a continuation-in-part of my copending application Serial No. 475,200, filed February 8, 1943.

I claim as my invention:

1. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle and finely dispersed therein a corrosion inhibiting amount of a phenylene bis sulfide dicarboxylic acid having a total of at least 24 carbon atoms in both carboxylic acid chains.

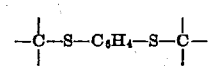
2. The composition of claim 1 wherein the number of carbon atoms in said dicarboxylic acid is between 30 and 60.

3. The composition of claim 1 wherein said vehicle has a dissociation constant below 10^{-8}.

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

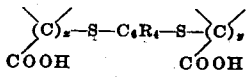
5. The composition of claim 1 wherein said acid is in colloidal solution.

6. A corrosion-preventive composition comprising predominantly a stable, substantially neutral vehicle and finely dispersed therein a corrosion inhibiting amount of a free dicarboxylic acid having at least 30 carbon atoms wherein the carboxyl radicals are linked through a bridge comprising the following structure:



7. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle

and finely dispersed therein a corrosion inhibiting amount of a phenylene bis sulfide dicarboxylic acid having at least 30 carbon atoms and having the formula



wherein x and y are integers of 1 up to about 8 and the R radicals are selected from the group consisting of hydrogen and alkyl radicals.

8. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle and finely dispersed therein a corrosion inhibiting amount of a phenylene bis sulfide dilauric acid.

9. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle and finely dispersed therein a corrosion inhibiting amount of a phenylene bis sulfide dimyristic acid.

10. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle and finely dispersed therein corrosion inhibiting amount of a phenylene bis sulfide distearic acid.

11. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance and finely dispersed therein a corrosion inhibiting amount of a free dicarboxylic acid having at least 30 carbon atoms, the carboxyl radical in said acid being linked through a phenylene bis sulfide radical.

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

13. The composition of claim 11 in which said substance is normally plastic.

14. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance free from resins and finely dispersed therein 0.001% to 0.1% of a free dicarboxylic acid having at least 30 carbon atoms, the carboxyl radical in said acid being linked through a phenylene bis sulfide radical.

15. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance containing resins and finely dispersed therein 0.1% to 5% of a free dicarboxylic acid having at least 30 carbon atoms, the carboxyl radical in said acid being linked through a phenylene bis sulfide radical.

16. A corrosion-preventive lubricating oil containing finely dispersed therein 0.001% to 0.1% of a free dicarboxylic acid having at least 30 carbon atoms, the carboxyl radical in said acid being linked through a phenylene bis sulfide radical.

17. A corrosion-preventive composition comprising predominantly a carboxylic acid ester and finely dispersed therein a corrosion inhibiting amount of a free dicarboxylic acid having at least 30 carbon atoms, the carboxyl radical in said acid being linked through a phenylene bis sulfide radical.

18. A corrosion-preventive composition comprising predominantly a fat and finely dispersed therein a corrosion inhibiting amount of a free dicarboxylic acid having at least 30 carbon atoms, the carboxyl radical in said acid being linked through a phenylene bis sulfide radical.

19. As an additive in fluid and plastic compositions having corrosive tendencies, a para phenylene dithiodicarboxylic acid in which the two carboxylic acid radicals have a minimum total of 24 carbon atoms.

20. As an additive for fluid and plastic compositions having corrosive and rusting tendencies when in contact with metal surfaces, a free dicarboxylic acid having at least 30 carbon atoms, the carboxyl radical in said acid being linked through a phenylene bis sulfide radical.

21. As an additive for fluid and plastic compositions having corrosive and rusting tendencies when in contact with metal surfaces, phenylene bis sulfide dilauric acid.

22. As an additive for fluid and plastic compositions having corrosive and rusting tendencies when in contact with metal surfaces, phenylene bis sulfide dimyristic acid.

23. As an additive for fluid and plastic compositions having corrosive and rusting tendencies when in contact with metal surfaces, phenylene bis sulfide distearic acid.

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