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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 mercapto-monocarboxylic acids.

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 corrosion-protective compositions of wide applicability. Another purpose is to produce slushing compositions of improved rust-protective properties. A specific purpose is to produce lubricating oils which protect against rusting and at the same time possess a very high degree of oiliness as measured by the coefficient of friction. Still another purpose is to produce extreme pressure lubricants, particularly greases having rust-preventive properties. A further purpose is 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 mercapto-monocarboxylic acids containing at least 10, and preferably 12—30, carbon atoms are potent corrosion inhibitors, such that they are capable of effectively preventing rusting of ferrous metals, affording protection not only against pure water, but against salt water such as sea water as well. For use in rust-proofing and corrosion prevention in general, small amounts of these acids are finely dispersed, such as in true or colloidal solution in a suitable vehicle.

In addition, when dissolved in lubricants in the amounts required for corrosion protection, the mercapto-carboxylic acids impart to the lubricants remarkable extreme pressure properties, reducing the coefficient of friction between various metals and particularly between steel against steel very remarkably. It was found that in this respect the sulfur in the mercapto-carboxylic acids of this invention is far more active than so-called "corrosive sulfur," heretofore employed for this purpose. In addition, the mercapto sulfur has the added advantage of being not only non-corrosive but positively corrosion-preventive in spite of its enhanced activity.

Due to the fact that these mercapto acids have such pronounced E. P. properties in extremely low concentrations, they are especially useful in soap-thickened greases which in general do not permit high concentration of free acid. On the other hand, these greases should be free from free alkali. Soaps particularly suitable for grease-making are Li, Na, K, Mg, Ca, Ba and Al soaps.

Moreover, since these mercapto acids combine E. P. properties with corrosion-protective properties, they are also very well suited for breaking in engines, say gasoline engines or Diesel engines.

Mercapto-carboxylic acids suitable for my purpose are primarily hydrocarbon carboxylic acid hydrosulfides, wherein the hydrosulfide radical is in alpha or beta position to the carboxyl radical. If desired, the acids may contain inorganic substituents which are not too strongly polar, such as ether, etc., radicals, but should preferably be free from highly polar substituents, such as hydroxyl, amino, nitro, carbonyl, or additional carboxyl and hydrosulfide radicals. For maximum stability against deterioration by oxidation, the acids should contain not more than one olefinic double bond, and preferably none.

These mercapto-carboxylic acids can be produced quite readily by reacting an alpha or beta halogenated hydrocarbon carboxylic acid with KSH or NaSH.

Examples of suitable hydrocarbon carboxylic acids are fatty acids, such as undecylic, lauric, myristic, palmitic, stearic, oleic, arachic, behenic, etc., acids; naphthenic acids such as may be recovered from petroleum oils by extraction with caustic alkali; synthetic naphthenic acids, such as cyclohexyl-heptylic, -nonylic, -undecylic, -lauric, -palmitic, -stearic, etc., acids, corresponding methyl, cyclohexyl, ethyl cyclohexyl, dimethyl cyclohexyl, higher alkyl cyclohexyl, etc., fatty acids; fatty acids having two or more cyclohexyl radicals; aromatic fatty acids, such as phenyl-, tolyl-, xylyl-, benzyl-, benzal-, naphthyl-, tetrallyl, etc., lauric, myristic, palmitic, stearic, arachic, etc., acids.

The mechanism by which the mercapto-carboxylic acids assert their corrosion-protective and extreme pressure properties is believed to be as follows:

The carboxylic acid radical being highly polar is attracted to the metal surface, where as a re-

sult of this attraction, a relatively high concentration of the acid exists and a protective film of the acid is formed. Because of the high concentration, two things happen: First, the sulfur becomes far more active than could normally be expected by taking into consideration its concentration in suspension; and, second, a portion of the mercapto acid is oxidized to bis-carboxylic acid disulfide, which is a very potent corrosion inhibitor.

The vehicles to which the mercapto-carboxylic 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^{-3}. 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 mercapto-carboxylic 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 mercapto-carboxylic acids vary from about .001% up to about .1%, although larger amounts, say 1.0%, 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.; as 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 mercapto-carboxylic acids 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 mercapto-carboxylic acids effectively inhibit this corrosion, and in addition, enhance their effectiveness.

Among the non-hydrocarbon compositions which frequently cause corrosion difficulties, anti-freezes used in automobile radiators and the like may be mentioned. The mercapto-carboxylic acids effectively eliminate their corrosiveness. Anti-freezes 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 mercapto-carboxylic 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 mercapto 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 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.

Example I

The effectiveness of alpha mercapto stearic acid in suppressing corrosion was determined by a test wherein a polished steel strip was subjected to the action of a vigorously stirred emulsion of a turbo raffinate oil having S. U. viscosity at 100° F. of 150 seconds, with 10% by volume of water at 167° F. When using distilled water, .01% of the acid in the oil gave perfect protection. In synthetic sea water spots appeared in 24 hours, and in 48 hours about 5% was corroded.

Example II

The extreme pressure property of alpha mercapto lauric acid was tested by making solutions of different concentrations of this acid in a 55 V. I. light motor oil having a Say. Univ. viscosity of 155 at 100° F., and running them in the four-ball machine described in "Engineering," vol. 136 (1933), page 46, for 2 hours at 7 kg. load at 130° C. The scar diameters on the top balls were then measured and found to be as follows:

Per cent alpha mercapto lauric acid	Scar diameter
	Mm.
None	.70
.005	.59
.01	.32
.025	.32
.05	.36
.1	.37
.25	.39
1.0	.42

I claim as my invention:

1. A corrosion-preventive composition comprising predominantly a substantially neutral vehicle containing finely dispersed a small amount, sufficient to inhibit corrosion, of a halogen-free hydrocarbon monocarboxylic acid alpha or beta hydrosulfide having from 10–30 carbon atoms.

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

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

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

5. The composition of claim 1 wherein said acid is a mercapto fatty acid.

6. The composition of claim 1 wherein said acid is alpha mercapto stearic acid.

7. The composition of claim 1 wherein said acid is a mercapto naphthenic acid.

8. The composition of claim 1 wherein said acid is a mercapto aromatic fatty acid.

9. A corrosion-preventive composition comprising predominantly a substantially neutral oleaginous substance containing a small amount, sufficient to inhibit corrosion, of an unsubstituted hydrocarbon monocarboxylic acid alpha or beta hydrosulfide having from 10–30 carbon atoms.

10. The composition of claim 9 wherein said substance is normally liquid.

11. The composition of claim 9 wherein said substance is normally plastic.

12. A corrosion-preventive extreme pressure lubricant comprising predominantly a refined lubricating oil containing dissolved .001% to 1% of a halogen-free hydrocarbon monocarboxylic acid alpha or beta hydrosulfide containing 10–30 carbon atoms.

13. A corrosion-preventive grease comprising predominantly a lubricating oil thickened with a soap free from free alkali and containing .001% to 1% of a halogen-free hydrocarbon monocarboxylic acid alpha or beta hydrosulfide having from 10–30 carbon atoms.

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