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ANTICORROSIVE METAL ARTICLE AND
METHOD OF MAKING SAME

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13 Claims. (Cl. 117—127)

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This invention relates to corrosion inhibitors for protecting various metal surfaces, such as ferrous and non-ferrous metals, metal alloys, and the like, from corrosive and oxidative action of air, moisture, salt brines, acids, gases such as SO₂ and SO₃, and the like. Corrosion inhibitors of this invention in addition to protecting the metal surfaces from attack by corrosive materials, inhibit formation of acidic and deterioration products from forming in initially non-corrosive liquids which act as carriers for corrosion inhibitors, as coolants, penetrants, hydraulic fluids, anti-freeze compositions and the like, thereby additionally protecting the metal surface from corrosion by these metal contacting liquids.

Metallic surfaces exposed to corrosive gases or when in contact with corrosive liquids or liquids which tend to decompose and form corrosive bodies which readily attach and corrode metal surfaces with which they are in contact, require protection against such damage. Thus moisture entering the cooling, fuel and lubricating systems of internal combustion engines, steam turbines, and the like, readily attack and corrode various metal parts of such systems, this not only has a deleterious effect upon the metal surface, but also frequently loosens finely divided metal oxides which may act as oxidation catalysts, increasing the rate of deterioration of the contacting liquids, or which oxides may enter movable parts of the engine and act as abrasives, causing fouling and plugging of the circulating systems.

Moisture is not the only agent which causes corrosive damage to metal surfaces. Acidic decomposition materials formed in engine liquids during use attack metal surfaces and in addition to causing corrosion, result in gumming and sticking of movable metal parts as well as formation of lacquer, varnish and carbonaceous materials. Thus anti-freeze compositions for automobile radiators, hydraulic brake and shock-absorbing fluid deteriorate and corrode metal surfaces. In addition metal chemical equipment, steel drums, structures, instruments in contact with moisture, corrosive gases and liquid compositions, are readily attacked and corrode.

Various substances have been tried for preventing corrosion of metal surface. In the majority of cases such compositions comprise an oleaginous base, such as mineral lubricating oils, fatty oils, greases, and the like, containing minor amounts of corrosion inhibitors, such as natural or synthetic resins or waxes, cellulose esters or ethers, wool fat, paraffin wax, asphalt bitumen, metal soaps, such as metal stearate; metal naph-

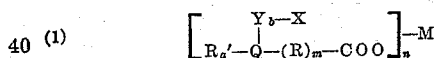
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thenate; metal resins, preferably the barium magnesium and aluminum resins; pigments such as chromate yellow, ochre, zinc oxide, titanium oxide, etc.; and substances with bacteriocidal or algacidic properties, such as copper arsenate, and the like. In the majority of cases compositions of this type have proved to be of little value due to their relatively short life as corrosion inhibitors and their inability to prevent deterioration of organic liquid with which they are admixed.

It is an object of this invention to treat metals in a simple and convenient manner so that they may resist corrosion. Another object is to protect ferrous and non-ferrous metals and their alloys from rusting and corroding when exposed to corrosive conditions. Still another object is to protect from corrosion chemical and mechanical metal equipment in contact with various organic compositions which are susceptible to deterioration and acidic formations by stabilizing such compositions. Furthermore, it is an object to chemically rust-proof metal surfaces and stabilize contacting liquids by dispersing therein a rust-proofing agent of this invention.

It has now been discovered that metals subjected to corrosive influences can be protected simply and effectively by dispersion in a non-lubricating liquid, preferably a non-lubricating petroleum hydrocarbon liquid, boiling below about 600° F., a polyvalent metal salt or soap of an aromatic monocarboxylic acid, having, if desired, attached to the aromatic nucleus various substituent groups.

Corrosion inhibitors and metal rust-proofing polyvalent salts of aromatic monocarboxylic acid applicable for this invention can best be illustrated by the general structural formulas:

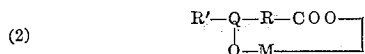


wherein Q represents a mono or polyaromatic radical; R is an alkyl or aryl group; *m* is either one or zero, in which latter case the carboxylic acid radical would be attached directly to the aromatic ring Q; Y represents a radical selected from the group consisting of oxygen or SO₃; R' represents an alkyl, alkaryl, aryl, aralkyl, amino, nitro, alkoxy, or aroxy group; X can be hydrogen or acid equivalent metal; *a* and *b* are integers, one sum of which should be equal to the number of available nuclear carbon atoms on the ring Q and M is a polyvalent metal selected from groups II, III and VIII of the periodic table.

Polyvalent salts of aromatic monocarboxylic

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acids can also be represented by the inner salt formula:



wherein the symbols correspond to those used in Formula 1.

The polyvalent metal salts of aromatic mono carboxylic acids can be prepared by any convenient method. Among the polyvalent metals which can be used are: beryllium, magnesium, calcium, zinc, strontium, cadmium, barium, aluminum, indium, iron, cobalt and nickel. Preferred polyvalent metals are calcium, cobalt, zinc and nickel. The aromatic monocarboxylic acids may be mono or polynuclear, having attached to said nucleus, if desired, substituent groups such as alkyl, aryl, alkoxy, aroxy, alkaryl, hydroxy, amino, nitro, or sulfo radicals. Examples of aromatic monocarboxylic acids and substituted monocarboxylic acids are: benzoic acid, nitrobenzoic acid, aminobenzoic acid, tertiary butyl benzoic acid, 5 hydroxy-1,3 dimethyl benzoic acid, 6 hydroxy-1,2 dimethyl benzoic acid, 3,6 dimethyl-2-hydroxy benzene-1-carboxylic acid, anthrandic acid, thymotic acid, cresotic acid, octyl cresotic acid, oxyphenyl cresotic acid, 5-ethyl-2,4 cresotic acid, sulfobenzoic acid, alkyl sulfobenzoic acid, salicylic acid, isomeric methyl isopropyl salicylic acid, diisopropyl salicylic acid, dimethyl salicylic acid, carvacrotic acid, oxytoluic acid, cinnamic acid, phenylstearic acid, phenyl propionic acid, diphenyl glycollic acid, atropic acid, gallic acid, vanillic acid, protocatechuic acid and alkyl protocatechuic acid, resorcylic acid and alkyl resorcylic acids, anthroic acid and alkyl anthroic acids and the like.

Of the acids mentioned, not only the neutral salts come into consideration, but also the salts which contain more metal bound than corresponds with the composition of the neutral salt, such as the basic salts, their anhydrous compounds and the inner salts; examples are the basic zinc salt of tertiary butyl benzoic acid, the inner calcium and zinc salts of diisopropyl salicylic acid. The basic cobalt salt of thymotic acid and the like.

A typical salt of this invention can be made as follows:

(A) Preparation of diisopropyl salicylic acid

Approximately 4.8 mols of 92% H_2SO_4 is stirred into a reaction vessel containing approximately 2.4 mols of di-isopropyl ether and mixed for about 10 minutes at which time the mixture attains a temperature of about 70° C. The temperature of the mixture is increased to around about 90° C. and about 2 mols of salicylic acid is slowly added to the mixture, care being taken that the temperature does not rise above about 100° C. This composition is maintained at between about 95-100° C. for about 15 hours after which it is cooled and admixed with gasoline and water under agitation. The sulfuric acid layer is removed and the gasoline layer washed with an approximate equivalent volume of water.

The diisopropyl salicylic acid is removed from the gasoline by mixing with a 10% caustic solution. The sodium salt solution thus obtained is washed with gasoline and subsequently acidified with 4N sulfuric acid. The di-isopropyl salicylic acid is separated off, filtered, washed with water and dried.

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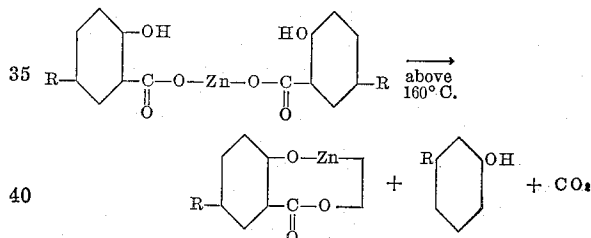
(B) Preparation of zinc salt of diisopropyl salicylic acid

Di-isopropyl salicylic acid prepared in the manner indicated above is heated to around about 115-118° C. and a quantity of zinc oxide, preferably around about 20% higher than is necessary to neutralize the acid is added and the mixture carefully heated to about 120-125° C. for about half an hour. The mixture is then dissolved in ether or some other solvent, filtered and the solvent evaporated.

The zinc salt can be made from the dilute caustic soda solution referred to in part A by converting the sodium salt into the zinc salt by addition of zinc sulfate. The zinc salt of diisopropyl salicylate can then be extracted from the aqueous solution with the aid of gasoline and obtained in the dry state by evaporation of the solvent.

(C) Preparation of inner ring salts of zinc diisopropyl salicylate

A salt as prepared in part B is dispersed in a suitable diluent having a boiling point above 200° C. and the mixture heated above about 160° C. and preferably between about 190-200° C. until carbon dioxide evolution has ceased. The transformation of the zinc salt from an open salt to an inner salt is believed to take place as follows:



The inner salt is removed from the diluent by any convenient manner such as distillation, etc. Inner salts are preferable especially when dispersed in non-lubricating petroleum hydrocarbon boiling below 600° F. since they dissolve more readily therein.

The vehicles to which the polyvalent metal aromatic mono-carboxylic acids of this invention may be added for the purpose of producing corrosion-protecting compositions may be polar and non-polar vehicles which are spreadable over metal surfaces. Spreading may be accomplished by immersing, flooding, spraying, brushing, trowelling, flushing, contacting, etc.

After being applied all or part of the vehicle may evaporate, or it may be more or less permanent. It is preferable to use as a carrier 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.

Among the vehicles which can be used are normally liquid petroleum hydrocarbons of non-lubricating range boiling below about 600° F. such as normal hexane, 2,2,4 trimethyl pentane, 2,2,5,3, tetra methylbutane, 2,5 dimethylhexane, normal octane, nonane, decane, dodecane, ethyl cyclohexane, isopropylcyclohexane, toluene, p-xylene, o-xylene, m-xylene, cumene, petroleum naphtha, mineral spirits which are distillates obtained from petroleum having a boiling range of between about 150-216° C. and a flash point

of 100° C., kerosene, Stoddard solvent, mineral seal oil, gas oil, gasoline, other light petroleum distillates; turpentine, halogenated hydrocarbons such as ethylene dichloride, trichloroethylene, propyl chloride, butyl chloride, chlorinated kerosene, 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, such as glycols, glycerols, etc, esters of monohydric alcohols and aliphatic mono and dicarboxylic acids such as oleic, ricinoleic, adipic sebacic, succinic, phthalic acids.

The amounts of corrosion inhibiting polyvalent metal-aromatic monocarboxylic acids which must be incorporated into the above vehicles to stabilize the vehicle and produce a corrosion-protective composition depends upon the vehicle, the condition under which the composition is used and the metal being protected. Generally between about 0.1 to 2% by weight and preferably about 1% is all that is required. The addition of larger quantities being superfluous from the point of view of activity.

The following examples will serve to illustrate the manner of practicing the present invention, although they are not to be considered as limiting the scope of the appended claims.

EXAMPLE I

Test pieces of iron plaque were coated with:

- A. 3% seawater emulsified in a Venezuelan refined petroleum distillate.
- B. Composition A containing 0.1% zinc salt of di-isopropyl salicylate.

The iron plaques were kept at a temperature of about 90° C. and the formation of rust observed.

Rust-inhibiting composition	Appearance of iron plaque
A. 3% seawater emulsified in a refined petroleum distillate.	Intensive rust formation observed after 2 hours.
B. 3% seawater emulsified in a refined petroleum distillate containing 0.1% wt. of Zn salt of diisopropyl salicylate.	No rusting observed.

EXAMPLE II

A Venezuelan refined distillate was admixed with aluminum stearate and heated until a clear solution was obtained. This was brushed on an iron pipe and exposed to very corrosive atmosphere. Another iron pipe was brushed with the same composition to which was added 0.1% Calcium diisopropyl salicylate. After 16 days of exposure to corrosive atmosphere the coated pipe which did not contain the corrosion inhibitor rusted badly while only slight rust formations were observed on the pipe which was coated with the aluminum stearate composition containing calcium diisopropyl salicylate only after 100 days.

EXAMPLE III

A series of tests were conducted for a period of two weeks in which test pieces of clean steel were exposed to the atmosphere, some were exposed to the atmosphere after being brushed or sprayed with liquids enumerated below while still others were coated with the same liquid vehicles but contained from 0.1 to 2% by wt. of polyvalent-metal-monocarboxylic acid corrosion inhibitors of this invention.

Metal	Diluent	Additive	Appearance of steel test piece after 2 weeks
5 1. Steel...	None.....	None.....	Rusted badly.
2. Steel...	Kerosene.....	do.....	Do.
3. Steel...	do.....	0.1% Ca salt of diisopropyl salicylate	No rust after 2 weeks.
4. Steel...	do.....	2.0% Zn salt of diisopropyl salicylate.	Do.
5. Steel...	do.....	2.0% cobalt salt of thymotic acid.	Do.
10 6. Steel...	do.....	2.0% Zn salt of tert. butyl benzoic acid.	Do.
7. Steel...	Trichloroethylene.	do.....	Rusted badly.
8. Steel...	do.....	2.0% Zn Salt of diisopropyl salicylate.	No rust after 2 weeks.
9. Steel...	do.....	2.0% Co salt of thymotic acid.	Do.
15 10. Steel...	do.....	2.0% Zn salt of tert. butyl benzoic acid.	Do.

If desired other corrosion inhibitors can be added to compositions of this invention. Among them can be included sulfonated castor oil, blown vegetable and fish oils, waxes, organic derivatives of acids of phosphorus such as aliphatic and aromatic esters of acid of phosphorus, organic derivatives or inorganic acids, e. g. sulfuric, silicic and nitric acid; mercapto and cyano monocarboxylic acids; fatty acid amides and the like.

When difficulty is encountered in dispersing salts of this invention in a particular carrier, a solubilizer can be used such as sulfonates, alcohols, esters, acids and the like.

Many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim as my invention:

1. In a method of inhibiting corrosion and rusting of a metal surface which normally is subjected to oxidation and corrosion conditions by applying to said metal surface a corrosion protective composition comprising a relatively volatile non-polar liquid carrier and an effective corrosion-inhibiting agent, the improvement which comprises utilizing as the corrosion-preventive composition a composition consisting essentially of a normally liquid petroleum hydrocarbon of non-lubricating range boiling below about 600° F. and from about 0.1 to 2% by weight of zinc diisopropyl salicylate.

2. In a method of inhibiting corrosion and rusting of a metal surface which normally is subjected to oxidation and corrosion conditions by applying to said metal surface a corrosion protective composition comprising a relatively volatile non-polar liquid carrier and an effective corrosion-inhibiting agent, the improvement which comprises utilizing as the corrosion-preventive composition a composition consisting essentially of a normally liquid petroleum hydrocarbon of non-lubricating range boiling below about 600° F. and from about 0.1 to 2% by weight of calcium diisopropyl salicylate.

3. In a method of inhibiting corrosion and rusting of a metal surface which normally is subjected to oxidation and corrosion conditions by applying to said metal surface a corrosion protective composition comprising a relatively volatile non-polar liquid carrier and an effective corrosion-inhibiting agent, the improvement which comprises utilizing as the corrosion-preventive composition a composition consisting essentially of a normally liquid petroleum hydrocarbon of non-lubricating range boiling below about 600°

F. and from about 0.1 to 2% by weight of cobalt diisopropyl salicylate.

4. In a method of inhibiting corrosion and rusting of a metal surface which normally is subjected to oxidation and corrosion conditions by applying to said metal surface a corrosion protective composition comprising a relatively volatile non-polar liquid carrier and an effective corrosion-inhibiting agent, the improvement which comprises utilizing as the corrosion-preventive composition a composition consisting essentially of a normally liquid petroleum hydrocarbon of non-lubricating range boiling below about 600° F. and from about 0.1 to 2% by weight of calcium salt of thymotic acid.

5. In a method of inhibiting corrosion and rusting of a metal surface which normally is subjected to oxidation and corrosion conditions by applying to said metal surface a corrosion protective composition comprising a relatively volatile non-polar liquid carrier and an effective corrosion-inhibiting agent, the improvement which comprises utilizing as the corrosion-preventive composition a composition consisting essentially of a normally liquid petroleum hydrocarbon of non-lubricating range boiling below about 600° F. and from about 0.1 to 2% by weight of cobalt salt of thymotic acid.

6. In a method of inhibiting corrosion and rusting of metal surfaces by applying to said metal surfaces a corrosion-protective composition comprising a relatively volatile non-polar liquid carrier and an effective corrosion-inhibiting agent, the improvement which comprises utilizing as the corrosion-preventive composition a composition comprising normally liquid polar and non-polar vehicle boiling below 600° F. and from about 0.1% to 2% by weight of a polyvalent metal-hydroxy aromatic monocarboxylic acid salt.

7. An article of manufacture, a corrodible metal protected with a coating of corrosion-preventive composition consisting essentially of a normally liquid polar and non-polar vehicle and from about 0.1% to 2% by weight of a polyvalent metal-hydroxy aromatic mono-carboxylic acid salt.

8. An article of manufacture, a corrodible metal protected with a coating of corrosion-preventive composition consisting essentially of a normally liquid polar and non-polar vehicle and from about 0.1% to 2% by weight of zinc diisopropyl salicylate.

9. An article of manufacture, a corrodible metal protected with a coating of corrosion-preventive composition consisting essentially of a normally liquid polar and non-polar vehicle and from about 0.1% to 2% by weight of a calcium diisopropyl salicylate.

10. An article of manufacture, a corrodible metal protected with a coating of corrosion-preventive composition consisting essentially of a normally liquid polar and non-polar vehicle and from about 0.1% to 2% by weight of a cobalt diisopropyl salicylate.

11. An article of manufacture, a corrodible metal protected with a coating of corrosion-preventive composition consisting essentially of a normally liquid polar and non-polar vehicle and from about 0.1% to 2% by weight of a calcium salt of thymotic acid.

12. An article of manufacture, a corrodible metal protected with a coating of corrosion-preventive composition consisting essentially of a normally liquid polar and non-polar vehicle and from about 0.1% to 2% by weight of a cobalt salt of thymotic acid.

13. In a method of inhibiting corrosion and rusting of metal surfaces by applying to said metal surfaces normally liquid polar and non-polar vehicle and from about 0.1% to 2% by weight of a polyvalent metal hydroxy aromatic monocarboxylic acid salt.

JOHANNES A. VAN MEUSEN.

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