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CORROSION INHIBITING COMPOSITION FOR COATING METAL, COATED METAL AND METHOD OF COATING

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This invention relates to inhibiting the corrosion of articles and objects having surfaces of metal which is normally corroded by the action of the moist atmosphere and in particular by contact with sea water or sea water spray.

The metals so corroded include in particular iron and steel, aluminum, magnesium, and copper, bi-metallic systems such as aluminum-magnesium or steel-aluminum, and alloys of these metals which are subject to corrosion as above indicated. Surfaces of other normally corrodible metals may also be treated effectively, to inhibit corrosion, in accordance with this invention.

The subject of corrosion inhibition has been studied extensively over many years, in an effort to minimize the very considerable economic losses which occur, during both use and storage, as a result of such corrosion of metallic surfaces, especially those of ferrous metals, but more recently also those of aluminum and magnesium. Various solutions to the problem have been advanced along many lines, including the plating of readily corrodible metals with metals which are more corrosion-resistant, the use of corrosion-resistant alloys, and the use of protective wrappings, coverings, and coatings or films. The present invention concerns corrosion inhibitors which fall within the broad class of protective coatings or films.

Paints of more or less conventional drying-oil-base types, and also greases and oils, have been used for many years as protective coatings for the surfaces of corrodible metals. Protective films, such as those formed by phosphatizing or "Bonderizing," have also been used for a number of years for such purposes. Such films are commonly made by treating the surface in an aqueous weakly acid solution containing the phosphating or other inhibiting chemicals. This latter procedure, which is time-consuming and involves a number of other difficulties in application, produces an adherent film or layer which is in the nature of a reaction product of the inhibitor and the metal of the surface. Although these coatings and films are satisfactory for a number of purposes, each one has one or more of a number of limitations. Many of them do not offer effective protection against the severe corrosive effects of sea or saline waters and spray; greases and oils collect dirt and grit and present difficult handling problems; conventional paints cannot be advantageously removed when it is desired to expose the original surface (for example the interior of the cylinders of internal combustion engines which are to be kept in storage and protected against corrosion); conventional films produced by aqueous methods require extended treatment in order to be effective.

The inhibitors of the present invention are distinctly superior, in effectiveness and in convenience of application, to any corrosion-inhibiting compounds or compositions of which I am aware. As these inhibitors are oil-soluble, they can be incorporated with suitable types of paints, with oils or greases, or with various kinds of strippable-film coating materials. The resulting coatings

may therefore be of a permanent nature (paints), or may be removable by wiping off (oils or greases) or by stripping. The inhibitors of this invention may be incorporated in priming coatings, which are applied to the metal surface to be protected and then covered by a paint, which may be a conventional paint or which may include a corrosion inhibitor. Alternatively, these inhibitors may be incorporated in a volatile solvent and applied to the metal surface to be protected, to form a film or layer which appears to be a reaction product of the inhibitor and the metal. This film may, if desired, be further protected, as by the above-described paints, oils, greases, or strippable films containing inhibitors of this invention, or by conventional paints, oils, greases or strippable films. Furthermore, some of the inhibitors of this invention are capable of being volatilized and thus can be used as vapor-phase inhibitors by exposing the surfaces to be protected to the vapors.

The corrosion inhibitors of this invention are organic esters of certain acidic oxides of metals, in particular of chromic acid H_2CrO_4, orthovanadic acid H_3VO_4, metavanadic acid $H_3V_3O_9$, and molybdic acid H_2MoO_4. These esters are representable by the formulas R_2CrO_4, R'_3VO_4, $R'_3V_3O_9$, and R'_2MoO_4. In the case of the chromates, R represents the radical of a tertiary alcohol ROH, while in the cases of the orthovanadates, the metavandates and the molybdates, R′ represents the radical of any alcohol, whether primary, secondary or tertiary. Each R, and also each R′, in any given compound, may be the same or different, and may be alkyl, aryl, aryl-alkyl, or heterocyclic, and is preferably although not necessarily a hydrocarbon radical. It will be noted that the primary and secondary esters of chromic acid are not included, due to the fact that these are oxidized to ketones and aldehydes in the presence of chromic acid.

Esters of acidic oxides of other metals, such as $RMnO_4$ and R'_2WO_4, where R and R′ are as defined above, may also be used as corrosion inhibitors in accordance with the present invention.

The most effective of the corrosion inhibitors of this invention are the esters of chromic acid with tertiary alcohols, as represented by the formula R_2CrO_4 given above. Typical of these compounds are the di-esters of chromic acid with any of the following tertiary alcohols: cedrol, 1-methyl borneol, methyl fenchol, alpha terpineol and other terpineols, triphenyl carbinol, tri (methyl-cyclohexyl) carbinol, diphenyl methyl carbinol, diphenyl pentadecyl carbinol, 5-ethyl 5-pentadecanol, 5-methyl 5-tetradecanol, 5-butyl 5-nonanol, 4,7-dimethyl 4,7-decandiol, octadecyl 1-cyclohexanol, tertiary butanol, and 2-methyl 2-butanol.

Examples of esters of acidic oxides of other metals hereinabove referred to include tribenzyl vanadate, tricyclohexyl vanadate, tricedryl vanadate, the lower alkyl ortho- and meta-vanadates (trimethyl, tripropyl, etc., vanadate), dimethyl molybdate, dipentadecyl molybdate, diamyl tungstate, and ditertiary butyl permanganate.

It should be noted that the ease of hydrolyzing increases as the molecular weight of the alcohol component of the ester decreases. This permits considerable latitude in selecting esters which will offer the desired ease of, or resistance to, hydrolysis.

For use, the corrosion inhibitors of this invention are incorporated, as already indicated, in appropriate coating or carrying media so that they may be applied, by brushing, spreading, spraying, dipping, or the like, to the surfaces to be protected. The coating or carrying media are preferably non-aqueous, although water may be present if more or less hydrolysis of the esters is desired.

The coating or carrying medium must of course be one which is not decomposed or otherwise adversely affected by the corrosion inhibitor. Drying oils are as a rule un-

satisfactory, since they set up so quickly in the presence of the corrosion inhibitor as to make their application to surfaces impractical or impossible. In fact, many of the corrosion inhibitors herein referred to are used, or usable, as paint driers. Non-drying oils and the like, such as the fatty glycerides and various petroleum oils and greases, are suitable.

Coating media which form solid protective layers, either of the paint type or the strippable-film type, are generally preferred, as they can be most readily and cleanly applied and become set to provide an effective sealing layer over the surface to be protected. These media include various synthetic resins, notably the vinyl resins, as well as natural resins such as shellac.

The corrosion inhibitor is most effective when present in solution in the coating or carrying composition, but may also be effective when present as a dispersion. While some of the coating media referred to above are solvents for some of the corrosion inhibitors of this invention, it is usually desirable to employ another substance which is a solvent for both. This solvent is volatilized as the coating sets. On the other hand, when the film-forming procedure is followed, the inhibitor may be dissolved in a solvent as a carrier, the resulting solution applied to the metal surface to be protected, and the solvent volatilized, as already pointed out.

The amount of corrosion inhibitor in such a coating composition or carrying solution, or other vehicle, may be varied over a wide range. Preferably, however, the amount of inhibitor should not be in excess of the maximum amount thereof which is soluble in the coating composition, carrying solution, or other vehicle during manufacture and in use.

A very effective corrosion-inhibiting coating composition, in accordance with this invention, may be prepared by mixing together cedryl chromate and a vinyl chloride-vinyl acetate (87%–13%) copolymer resin, each of which is in solution in a mutual solvent, of which various ones in the class of ketones and esters are known for the purpose. The proportions of chromate and resin are such as to provide 3.5 parts by weight CrO_4= to 90 parts by weight of the resin. The resulting product, after application to and setting upon a bimetallic magnesium-aluminum surface, protected the surface effectively against corrosion for over 1900 hours in the presence of salt spray, a very severe test, whereas conventional zinc chromate primer inhibitor failed in protective effect in less than 340 hours.

Another effective corrosion-inhibiting composition may be prepared by mixing cedryl chromate with lubricating oil, of viscosity SAE 50 for example, and in an amount such that the cedryl chromate is somewhat in excess of the amount that will dissolve in the oil. The resulting oily composition, when brushed onto an iron surface (e. g. an engine block or a cylinder surface) turns a brownish color, as though rust were present, but examination shows that rust is absent and that the surfaces thus coated are very effectively protected against corrosion. This composition may be removed, for example, by a solvent, leaving an invisible, highly corrosion-resistant film.

As another example of corrosion inhibition in accordance with this invention, a 30% solution of tertiary butyl chromate in tertiary butyl alcohol is prepared, and is applied to a clean magnesium surface by brushing, spraying or dipping, after which the surface is drained, and dried at room temperature. A brownish film (rather than a coating, as in the two preceding examples) is thus formed upon the surface, which latter is thereupon highly resistant to corrosion. In contrast, the best of the known chromate film treatments for magnesium require application by a hot aqueous solution which must be maintained in contact with the magnesium surface for at least 20 minutes.

I claim:

1. The combination of a metal surface normally corrodible by contact with moist atmospheres and with sea water, and a coating composition covering said surface, said coating composition consisting essentially of an effective corrosion-inhibiting amount of an ester selected from the group consisting of R_2CrO_4, R'_3VO_4, $R'_3V_3O_9$, R'_2MoO_4, and R'_2WO_4, wherein R and R' are hydrocarbon radicals of the alcohols ROH and R'OH respectively and are members of the group consisting of alkyl, aryl, aryl-alkyl and heterocyclic, and R is a tertiary radical, together with a carrier for said ester.

2. The combination of a metal surface normally corrodible by contact with moist atmospheres and with sea water, and a coating composition covering said surface, said coating composition consisting essentially of an effective corrosion-inhibiting amount of cedryl chromate and a carrier therefor.

3. The combination of a metal surface normally corrodible by contact with moist atmospheres and with sea water, and a film on said surface consisting essentially of a reaction product of said surface with an ester selected from the group consisting of R_2CrO_4, R'_3VO_4, $R'_3V_3O_9$, R'_2MoO_4, and R'_2WO_4, wherein R and R' are hydrocarbon radicals of the alcohols ROH and R'OH respectively and are members of the group consisting of alkyl, aryl, aryl-alkyl and heterocyclic, and R is a tertiary radical.

4. The combination in accordance with claim 3, wherein said ester is tertiary butyl chromate.

5. The combination in accordance with claim 3, wherein said metal surface is magnesium and said ester is tertiary butyl chromate.

6. A corrosion inhibiting composition consisting essentially of cedryl chromate, a vinyl resin, and a mutual solvent.

7. A corrosion inhibiting composition consisting essentially of cedryl chromate and a petroleum oil.

8. The method of inhibiting corrosion of a metal surface normally corrodible by contact with moist atmospheres and with sea water, which comprises applying to said surface a composition consisting essentially of a corrosion-inhibiting amount of an ester selected from the group consisting of R_2CrO_4, R'_3VO_4, $R'_3V_3O_9$, R'_2MoO_4, and R'_2WO_4, wherein R and R' are hydrocarbon radicals of the alcohols ROH and R'OH respectively and are members of the group consisting of alkyl, aryl, aryl-alkyl and heterocyclic, and R is a tertiary radical, together with a carrier for said ester.

9. The method of inhibiting corrosion of a metal surface normally corrodible by contact with moist atmospheres and with sea water, which comprises applying to said surface an ester selected from the group consisting of R_2CrO_4, R'_3VO_4, $R'_3V_3O_9$, R'_2MoO_4, and R'_2WO_4, wherein R and R' are hydrocarbon radicals of the alcohols ROH and R'OH respectively and are members of the group consisting of alkyl, aryl, aryl-alkyl and heterocyclic, and R is a tertiary radical, a medium which is inert to said ester and which is capable of forming a coating layer, and a mutual solvent for said ester and said medium, and then removing said solvent.

10. The method of inhibiting corrosion of a metal surface normally corrodible by contact with moist atmospheres and with sea water, which comprises applying to said surface a composition consisting essentially of cedryl chromate, a vinyl resin, and a mutual solvent for said ester and for said resin, and then volatilizing said solvent.

11. The method of inhibiting corrosion of a metal surface normally corrodible by contact with moist atmospheres and with sea water, which comprises applying to said surface a solution of tertiary butyl chromate in tertiary butyl alcohol, and then volatilizing said alcohol by exposure to normal room temperature.

12. The method of inhibiting corrosion of magnesium,

which comprises providing a clean surface on said magnesium, applying said surface a solution of about 30 percent tertiary butyl chromate in tertiary butyl alcohol, and then removing said alcohol by volatilization at normal room temperature.

13. The method of inhibiting corrosion of a metal surface normally corrodible by contact with moist atmospheres and with sea water, which comprises volatilizing adjacent to said surface an ester selected from the group consisting of R_2CrO_4, R'_3VO_4, $R'_3V_3O_9$, R'_2MoO_4, and R'_2WO_4, wherein R and R' are hydrocarbon radicals of the alcohols ROH and R'OH respectively and are members of the group consisting of alkyl, aryl, aryl-alkyl and heterocyclic, and R is a tertiary radical, together with a carrier for said ester.

14. The method of inhibiting corrosion of a metal surface normally corrodible by contact with moist atmospheres and with sea water, which comprises applying to said surface a solution consisting essentially of an ester selected from the group consisting of R_2CrO_4, R'_3VO_4, $R'_3V_3O_9$, R'_2MoO_4, and R'_2WO_4, wherein R and R' are hydrocarbon radicals of the alcohols ROH and R'OH respectively and are members of the group consisting of alkyl, aryl, aryl-alkyl and heterocyclic, and R is a tertiary radical, and a solvent for said ester, and then removing said solvent.

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