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COATING COMPOSITION AND METHOD

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ABSTRACT OF THE DISCLOSURE

The subject matter of this invention is a coating composition particularly for magnesium consisting essentially of a slurry of finely divided inorganic solid particulate material in an aqueous solution containing substantial amounts of phosphate, nitrate, and dissolved metal. The addition of chromate is desirable and the most preferred particulate material is spherical aluminum powder.

This invention relates to a coated article and coating composition and method for making same and more specifically to an improved corrosion resistant and decorative coating for metal or other substrates which are subject to deterioration by water, salt spray or the like. The invention has special advantages as a protective coating for magnesium and will be described in detail with reference thereto; however, it will be understood that the coating compositions will also serve to advantage on other basis materials, for example, aluminum, ferrous base metals, ceramics, organic plastics and the like.

Magnesium has advantages over other metals, such as aluminum and zinc, particularly for the manufacture of die castings. Magnesium is lighter than the other metals and on a volume for volume basis often has a cost advantage. Also, magnesium is relatively simple and therefore inexpensive to cast as compared, for example, with aluminum. Excellent non-porous castings can be obtained with minimum problems of quality control. However, magnesium has the serious disadvantage of being subject to rapid corrosion. Hence, it is essential that the magnesium, be it a die casting or otherwise, have a coated or treated surface to protect it from corrosion. Various coatings and dip treatments have been proposed for magnesium to provide the needed protection, however, at the present state of the art there is no commercially practical low cost treatment or coating for magnesium which will provide more than about eighteen hours of protection in a standard five percent salt spray chamber. The lack of such a coating has been a serious detriment to more widespread use of magnesium by the automobile and marine industries, for example, since experience has shown that albeit the metal has other advantages over aluminum and zinc, it is noncompetitive where the need for corrosion resistance is a serious factor.

Coatings formulated in accordance with the present invention provide well upwards of fifty hours protection in either a five percent or a twenty percent salt spray accelerated corrosion test, and this with a coating thickness of only about 2 to 3 mils. Such protection is fully adequate for almost all uses of the metal however, if more is needed it can be attained by applying two or more coatings to a total coating thickness of about 2 to 4 mils whereby corrosion protection upwards of 100 hours in either five percent or twenty percent salt spray can be provided.

In United States patent application Ser. No. 291,271 filed June 28, 1963, now Patent No. 3,248,251, in the name of Charlotte Allen and assigned to the assignee of the present invention there are disclosed and covered coating compositions consisting essentially of a slurry of finely divided solid particulate material in an aqueous acidic solution containing substantial amounts of phosphate,

chromate and metal ions. I have now discovered that if nitrate ion is included in place of or preferably in addition to the chromate, a marked improvement is attained particularly as regards coating magnesium.

Briefly, then, the present invention comprehends a coating composition comprising a slurry of finely divided particulate material in an aqueous solution containing metal ion, phosphate ion, nitrate ion and preferably also chromate ion. The solid particulate material should preferably have a grain size of 325 mesh or less, and can be any of a wide variety of metallic or nonmetallic materials as hereinafter described. However, for optimum corrosion protection by far the outstanding solid particulate material is aluminum powder, preferably spherical aluminum powder having a grain size on the order of 10 microns or less. The amount of solid particulete material included can be from 10 to 2000 grams per liter of solution. For most applications, however, and particularly where aluminum powder is used, the preferred range is from 300 to 2000 grams per liter of solution, 800 grams per liter being ideal.

In all of the preferred compositions of this invention, the concentration of the metal ion is from .5 to 6 mols per liter, ideally from 3 to 5 mols per liter. Magnesium ion provides the best results. The metal ion can be added to the solution either in the form of a metal salt, i.e., a metal nitrate, phosphate, chromate or dichromate, or it can be added in a form which will dissolve in the aqueous acid solution by way of an acid-base reaction to provide the metal salt and hence the metal ion. For example, some or all of the metal can be added in the form of its oxide, hydroxide, or carbonate. Of course where the metal is so added, it is necessary that the other ingredients provide the acidity required to take the metal compound into solution. For example, the phosphate can be added as phosphoric acid, the nitrate as nitric acid or the chromate as chromic acid. It will be obvious from the specific examples which follow that the compositions of this invention are strongly acidic having a pH under 3.

The phosphate ion should be present in the solution in the amount of about .2 to 4 mols per liter, preferably about 1 to 3 mols per liter. The term "phosphate" is intended to comprehend not only the PO_4^{---} but also the HPO_4^{--} and $H_2PO_4^{-}$ ions. The phosphate can be added either as phosphoric acid or as a metal phosphate which is sufficiently soluble to be taken into solution in sufficient amounts to provide the phosphate concentration desired. Of course, it is not essential that the metal phosphate be highly soluble in water since the solution is acidic and most of the metal phosphates even though not highly soluble in water are nevertheless sufficiently soluble in acid to be useful in the practice of the present inventon. Typical of phosphates which can be used are monobasic, dibasic and tribasic orthophosphates of magnesium, zinc, ferrous or ferric iron, calcium or the alkali metals such as sodium, potassium, or lithium. Of course the magnesium compounds are excellent for the reason that the magnesium ion is preferred as mentioned above. Where the phosphate ion is added as phosphoric acid, the ortho acid is preferred, though meta, pyro or hypo phosphoric acid can be used if desired.

The nitrate ion should be present in an amount of about .5 to 6 mols per liter, the best results being attainable with a concentration of 2 to 6 mols per liter. The nitrate can be added as nitric acid, which is preferred, or it can be added as a metal nitrate, for example, magnesium nitrate, zinc nitrate, etc.

For optimum results in the way of good adhesion and corrosion protection it is preferred that the aqueous solution also contain chromate ion, the term "chromate" being

intended to comprehend both the CrO_4^{--} and the $Cr_2O_7^{--}$ ions as will be noted from the examples which follow. Such ion can advantageously be present in an amount up to 3 mols per liter and in the preferred solutions is present in an amount of .5 to 1.5 mols per liter. The molar concentrations for the chromate ion specified herein are on the basis that all the ion is present as CrO_4^{--} though some or all may be present as Cr_2O_7 as indicated above. The chromate ion can be added as chromic acid or as a metal chromate or dichromate, for example, the chromate or dichromate of magnesium, zinc or sodium.

The following examples of preferred embodiments of the invention will serve to further illustrate:

EXAMPLE 1

$Mg(H_2PO_4)_2.3H_2O$ ----------grams--	10
MgO ----------do----	9
CrO_3 ----------do----	10
HNO_3 (70% by weight) ----------cc--	25
Aluminum powder (spherical, 5 to 10 microns) grams--	80

H_2O to 100 cc.

EXAMPLE 2

$Mg(H_2PO_4)_2.3H_2O$ ----------grams--	10
MgO ----------do----	7
$MgCr_2O_7.6H_2O$ ----------do----	10
HNO_3 (70%) ----------cc--	25
Aluminum powder (spherical, 5 to 10 microns) grams--	75

H_2O to 100 cc.

EXAMPLE 3

CrO_3 ----------grams--	8
H_3PO_4 (85%) ----------cc--	12
HNO_3 (70%) ----------cc--	20
MgO ----------grams--	15
Aluminum powder (spherical, 5 to 10 microns) grams--	80

H_2O to 100 cc.

EXAMPLE 4

CrO_3 ----------grams--	10
H_3PO_4 (85%) ----------cc--	20
HNO_3 (70%) ----------cc--	20
$NaNO_3$ ----------grams--	60
MgO ----------do----	15
Aluminum powder (spherical, 5 to 10 microns) grams--	70

H_2O to 100 cc.

The prepared composition is applied, as by spraying, dipping, rolling or brushing, to the surface or surfaces to be coated or bonded and is subsequently cured by heating, a temperature of about 500° to 1000° F. generally being required. The optimum curing temperature will vary depending upon the precise composition being cured; in general, however, the preferred curing temperature is from about 600 to 650° F. After complete curing, the coating or bond will be insoluble in water even on prolonged exposure thereto. If there is an incomplete cure, the solution ingredients in the composition will leach out when exposed to water and this will be evidenced by the yellow or orange color of the chromate ion when, for example, a damp rag is wiped across an uncured or incompletely cured surface. The time required for curing is dependent upon the temperature used; the higher the temperature the less time needed. For example, for a relatively slow cure of a given coating at low temperature, about 15 to 60 minutes at 600° F. would be desirable. Where a fast cure is required, about 5 to 10 minutes at 700° F. could be used. For an extremely fast cure radiant heating at even higher temperature can be used to advantage; this is particularly useful where the substrate is of a material not highly heat resistant since by high temperature radiant heating the coating can be fully cured without developing excessive temperature in the substrate. In general, the compositions cannot be overcured, with relatively wide limits, and hence except for cost and any temperature limitation on the solid particulate material being used or on particular substrate material involved, there is no disadvantage in curing for longer periods of time or at higher temperatures than required.

Heat curing of the composition to water insolubility is essential to the attainment of the desirable physical characteristics and from this it will be manifest that the solid particulate material used must be capable of withstanding the curing temperature without disintegrating.

The thickness of the coating or bond after curing should preferably be from about .0005 to .02 inch and hence the precise concentration of the liquid composition applied and the amount applied should preferably be adjusted accordingly. For optimum corrosion protection it will be desirable to apply two or more coatings. The compositions of this invention exhibit excellent surface tension characteristics and thoroughly wet the substrate, even though it be of a material difficult to wet with water. The surface being coated should of course be clean and while there is no requirement to roughen an otherwise smooth surface prior to coating, such will often be desirable to obtain maximum bond strength.

In addition to providing excellent corrosion protection, the coatings wherein aluminum powder is used as the particulate additive can be polished to a high gloss, comparable to that of chromium plating, by just light buffing after the curing step. The advantages of this unusual feature will be manifest; magnesium die castings coated and then buffed can be used for decorative parts on automobiles and the like. If desired, other metal powders, for example, antimony powder, can be used in combination with the aluminum powder to attain different gloss effects, and colored pigments can be included in the composition to provide some color in the high gloss finish. For example, cobalt oxide can be added to give a blue color.

Whereas the chief utility for the coatings is for corrosion protection, especially for magnesium, and the best powdered additive for such purpose is aluminum, it will be understood that coatings with other special physical properties can be attained by using other materials or combinations of materials as the particulate additive. For example, particulate refractory oxides such as aluminum oxide (corundum) refractory silicides such as molybdenum disilicide, nitrides such as boron nitride or carbides such as silicon carbide can be used as the powdered additive for high heat resistant coatings and dry lubricants such as graphite, molybdenum disulfide, tungsten disulfide, lead oxide and the metal fluorides such as calcium fluoride can be used for high lubricity or anti-galling coatings. Teflon (polytetrafluoroethylene) can also be used as the particulate additive to provide lubricity and other desirable qualities, the Teflon preferably being added as an aqueous dispersion thereof. Of course, the powdered additive should be substantially unreactive with the solution, i.e., at least sufficiently unreactive to remain in the form in which added through the coating operations. Aluminum powder is nonreactive in the solution for indefinitely long periods. Where such materials as molybdenum disulfide or graphite are used, however, it is preferrable to admix them into the solution no more than a week or so prior to use since they may undergo a slow oxidation reaction in the solution and hence not have an indefinitely long shelf life.

It will be understood that while the invention has been described in detail with reference to certain embodiments thereof various changes and modifications can be made fully within the intended scope of the claims which follow.

I claim:

1. A coating and bonding composition consisting essentially of a dispersion of inorganic solid particulate material having a grain size less than 325 mesh in an aqueous solution the solute of which consists essentially

of a combination of inorganic compounds from the group consisting of phosphoric acid, chromic acid, nitric acid, and the magnesium salts of said acids, the combination of compounds in said solution being such as will provide at least .2 mol per liter dissolved phosphate, at least .5 mol per liter dissolved chromate, at least .5 mol per liter dissolved nitrate, and at least .5 mol per liter dissolved magnesium, said solid particulate material being substantially insoluble in said solution and being present in an amount of from about 10 to 2000 grams per liter of said solution, said composition being heat curable upon drying thereof to a substantially water insoluble material with said solid particulate material being bonded therein.

2. A coating and bonding composition as set forth in claim 1 wherein said solid particulate material is predominantly spherical aluminum powder.

3. A coating and bonding composition consisting essentially of a dispersion of inorganic solid particulate material having a grain size less than 325 mesh in an aqueous solution the solute of which consists essentially of a combination of inorganic compounds from the group consisting of phosphoric acid, chromic acid, nitric acid and the magnesium salts of said acids, the combination of inorganic compounds in said solution being such as will provide from about 1 to 3 mols per liter dissolved phosphate, from about .5 to 1.5 mols per liter dissolved chromate, from about 2 to 6 mols per liter dissolved nitrate, and from about 3 to 5 mols per liter dissolved magnesium, said inorganic solid particulate material being present in an amount of from about 10 to 2000 grams per liter of said solution, said composition being heat curable upon drying thereof to a substantially water insoluble material with said solid particulate material being bonded therein.

4. A coating and bonding composition as set forth in claim 3 wherein said solid particulate material is predominantly spherical aluminum powder.

5. A method for coating a surface comprising the steps of applying to the surface a composition consisting essentially of a uniform mixture of spherical aluminum powder having a grain size not exceeding about 10 microns in an aqueous solution the solute of which consists essentially of a combination of inorganic compounds from the group consisting of phosphoric acid, chromic acid, nitric acid and the magnesium salts of said acids, the combination of compounds in said solution being such as will provide at least .2 mol per liter dissolved phosphate, at least .5 mol per liter dissolved chromate, at least .5 mol per liter dissolved nitrate, and at least .5 mol per liter dissolved magnesium, said spherical aluminum powder being substantially insoluble in said solution and being present in an amount of from about 10 to 2000 grams per liter of said solution; drying said composition, and then curing said composition.

6. The method of claim 3 wherein said curing is achieved by heating to a temperature of at least about 500° F. for a time sufficient to cause said composition to become insoluble in water with said spherical aluminum powder being bonded therein.

7. An article of manufacture comprising a solid substrate having deposited thereon a layer formed by coating said substrate and then drying and heat curing to water insolubility, a composition consisting essentially of a mixture of spherical aluminum powder having a grain size not greater than 10 microns in an aqueous solution the solute of which consists essentially of a combination of inorganic compounds from the group consisting of phosphoric acid, chromic acid, nitric acid and the magnesium salts of said acids, the combination of compounds in said solution being such as will provide at least .2 mol per liter dissolved phosphate, at least .5 mol per liter dissolved chromate, at least .5 mol per liter dissolved nitrate, and at least .5 mol per liter dissolved magnesium, said spherical aluminum powder being substantially insoluble in said solution and being present in said solution and being bonded in said article after curing thereof.

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