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COMPOSITION AND METHOD FOR PRODUCING CORROSION RESISTANT AND PROTECTIVE COATINGS ON ALUMINUM AND ALUMINUM ALLOYS

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ABSTRACT OF THE DISCLOSURE

A coating process for forming an adherent organic resin coating on metal substrate in which an organic resin, an inorganic hexavalent chromium compound, an oxidizable component, phosphoric acid and strontium chromate are mixed together, the chromium compound and the oxidizable compound are reacted to reduce the hexavalent chromium to trivalent chromium and in which the resulting mixture is applied to the substrate and the substrate and applied mixture is heated in an atmosphere of from 600 to 800° F. for a sufficient time in excess of about 26 seconds to achieve a metal temperature of at least about 450° F. to cause a portion of the trivalent chromium to be oxidized to hexavalent chromium resulting in a strongly adherent organic resin coating is described.

This invention relates to coating processes generally and, more specifically, to coating processes in which a metal substrate is coated with an organic resin.

The paint and coating industry, metal fabricators, builders, and others have long faced and recognized the problems incident to the formation of adherent weather resistant coatings of organic resins on metal substrates. Many solutions to the problems incident to obtaining an organic coating which will strongly adhere to the metal substrate have been proposed. Such proposals include pretreatment of the metal substrate, aluminum, alloys of aluminum, and steel, for example. Many such pretreatment processes involve treating the surface of the substrate with compositions which include either phosphoric acid or hexavalent chromium compound, or both.

Pretreatment of metal substrates with such compositions as chromic acid solutions, chromic acid-phosphoric acid solutions, fluoride containing chromic acid-phosphoric acid solutions, etc. are comparatively well known in the industry. In addition, it has been proposed to treat metal substrate surfaces with compounds of this general nature using particular techniques for applying, burnishing, or manipulating the surface of the metal.

Similar techniques using organic solvents and organic chromium compounds, etc., have also been proposed. The foregoing processes are generally effective to a lesser or greater extent but present serious disadvantages in actual practice. These processes, for example, are time and labor consuming in that they involve one or more preliminary steps, additional chemical mixing and handling equipment, plant space, etc. Water pollution is an inevitable problem with processes of this type since it is necessary, ultimately, to dispose of the treating solution. This disposal either results in water pollution or in significant expenditures in pretreatment of the spent treating liquid prior to disposal.

It has also been reported that advantageous results can be obtained by pretreating a metal surface with chromic acid, or other hexavalent chromium-containing compounds and a reducing agent in which a portion of the chromium is reduced to the trivalent state. In general, it has been previously found that there is a critical rela-

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tionship with respect to the hexavalent chromium-trivalent chromium ratio. It has been reported, for example, that it is necessary that at least 5% of the chromium remain in the hexavalent state. These processes generally have not overcome the major disadvantages and difficulties faced in the use of the processes previously discussed.

In an effort to overcome certain of these problems, it has been proposed to incorporate in the resin coating mixture certain compounds to enhance the ability of the resin, when cured, to adhere to the metal substrate. The inclusion of phosphoric acid, for example, in resin coating compositions is known. It is also known to include chromic oxide and other hexavalent chromium compounds in the resin mixture.

Proposals have also been made for treating certain surfaces with trivalent containing chromium compounds, but no resinous compositions including trivalent compounds have, to our knowledge, been reported. Prior experience indicated that at least some hexavalent chromium must be present if satisfactory results are to be obtained.

The previously believed necessity for maintaining hexavalent chromium in coating compounds which include organic resin coating materials has been discussed at some length as has the technique of introducing hexavalent chromium in a resin containing coating composition along with a reducing material sufficient to reduce a part, but not all, of the hexavalent chromium to trivalent chromium. It has, heretofore, been believed necessary to carefully control the relative proportions of hexavalent chromium and oxidizable compositions so as to ensure the presence of residual hexavalent chromium in the resin coating composition.

The prior art has also taught the use of techniques as just previously described in connection with heating for the purpose of reducing a specified proportion of the hexavalent chromium to trivalent chromium.

We have discovered, contrary to expectations and predictions based upon the prior art, that an extremely adherent, quick curing, highly flexible and formable corrosion resistant organic coating can be applied to metal substrates by including in the resin coating mixture hexavalent chromium, sufficient oxidizable material to completely reduce the hexavalent chromium to trivalent chromium and by heating the metal substrate with the coating mixture applied thereto to metal temperatures in excess of about 450° F. in a 600° F. to 800° F. heating atmosphere to thereby oxidize at least a portion of the trivalent chromium to hexavalent chromium. This approach, as will readily be seen, is opposite the approaches and techniques previously reported to be effective in the application of adherent corrosion resistant coatings.

The principal feature of this invention, therefore, resides in a new and unexpectedly effective method, which runs counter to prior teachings, for applying resin coatings which are unusually resistant to weathering and corrosion and which are flexible and formable to metal substrates.

This discovery is based primarily on the fact that pre-mixing by means of aqueous acid solutions, containing a salt or acid hexavalent chromium, phosphoric acid, water and a solvent with a variety of types of coatings such as epoxies, alkyls, organosols, etc., at a predetermined ratio, a conversion coating for metal substrates can be produced with the reaction of the coating with the metal occurring upon baking of the paint. Since no more chemicals are added than are necessary for completion of the reaction and the formation of the conversion coating, there is no need for rinses, bleed off, or other techniques for applying, handling, and disposing of pretreating solutions.

The invention in one of its features consists of pre-conditioning the paint system so that chromium substantially in the trivalent form is made available to this system. For reasons which have not yet been susceptible to explanation, the chromium must be added in hexavalent state and reduced, by means of an oxidizable component of the coating mixture, to the trivalent state. The trivalent chromium is subsequently oxidized by heat or by other means during the bake period to produce hexavalent chromium in the final coating and a chemical conversion bond between the substrate and the coating.

One of the features of the invention resides in the discovery that bake-conversion times can be substantially reduced by including in the coating mixture strontium chromate. Conversion coatings which result in good flexibility and strong adherence to the substrate can, therefore, be produced at high speeds using conventional continuous coating apparatus and techniques. High speed lines using electron beam or other curing means can result in even greater coating and conversion speeds.

In general, the coating process of this invention is carried out by mixing together ingredients consisting essentially of an inorganic hexavalent chromium compound, an organic resin containing an oxidizable component or an organic resin and a separate oxidizable component, phosphoric acid and strontium chromate, or equivalent. The oxidizable component is then reacted with the hexavalent chromium compound to reduce substantially all of the hexavalent chromium to trivalent chromium. The resulting mixture, characterized by the absence of detectable hexavalent chromium, is then applied to the substrate and the metal substrate and coating are heated in heating atmospheres having temperatures in the range of from about 600° F. to about 800° F. for a sufficient length of time to achieve a minimum metal temperature of 450° F. and to cause at least a portion of the trivalent chromium to be oxidized to hexavalent chromium. Usually, using conventional heat, the heating time in excess of about 26 seconds is required to form a coating in which the organic resin is bonded by reason of the conversion of trivalent chromium to hexavalent chromium during heating to the metal substrate such that the cured coating will withstand the effects of exposure to weather without cracking or peeling, is corrosion resistant, formable, flexible, etc. and possesses all necessary and desirable attributes for protective coatings for metals.

The mixing of the ingredients may be in any order, although it is most convenient to dissolve the chromium compound in a polar solvent such as water, phosphoric acid, etc. alone or in mixture with, e.g., acetone, prior to adding the resultant hexavalent chromium containing solution to the resin. The reaction may be caused or permitted to take place either during or subsequent to any of the mixing steps following intermixing of the hexavalent chromium and the oxidizable component.

In general, the nature of the resin is not critical but resins which contain an oxidizable component are preferred. Such resins as the epoxies, vinyls, alkyds, etc., are conveniently applied to substrates such as aluminum, aluminum alloys, iron, steel, etc. with highly advantageous results. The technique of this invention is most advantageously used in connection with the formation of primer coats on metal substrates. In these applications, best results are generally had using the epoxy resins as the organic resin component of the mixture.

The efficacy of the inventive process is illustrated in the examples described hereinafter which are summarized in the following table, along with certain comparative examples included to illustrate the salient features of the inventive process.

TABLE I

Experimental Number	Coat(s)	Resin	Percent					Bake Time, seconds	° F.	Notes	Results
			K ₂ Cr ₂ O ₇	Acetone	H ₂ O	H ₃ PO ₄	Other				
1(a)	Primer	do.	1	---	10	---	SrCrO ₄	30	600	0.25 bar drawdown	Peeled.
1(b)	Primer	do.	1	---	10	---	SrCrO ₄	60	600	do.	Do.
1(c)	Primer	do.	1	---	10	---	SrCrO ₄	90	600	do.	Do.
1(d)	Primer	do.	1	---	10	---	SrCrO ₄	120	600	do.	Do.
2(a)	Primer plus top coat	do.	1	---	10	---	4 SrCrO ₄	30	600	0.25 bar drawdown, no color change	Blistered.
3	Primer	do.	1	---	10	---	2 SrCrO ₄	60	600	No color change	Do.
4	Primer	do.	2	---	10	---	2 SrCrO ₄	90	600	Green-to-yellow	Very little blistering.
5	Primer plus top coat	do.	2	---	10	---	2 SrCrO ₄	90	600	Green-to-yellow	Minor blistering.
6	Primer	do.	2	---	2	---	2 SrCrO ₄	90	600	do.	Do.
7	Primer	do.	2	---	2	---	2 SrCrO ₄	90	600	do.	No blistering.
8	Primer	do.	2	---	2	---	2 SrCrO ₄	90	600	do.	Top coat lost gloss in boll test.
9(a)	Primer plus top coat	do.	2	---	0.5	---	2 SrCrO ₄	90	600	Green-to-yellow	Poor formability.
9(b)	Primer plus top coat	do.	2	---	0.5	---	2 SrCrO ₄	90	600	Green-to-yellow	Poor formability, no blistering.
9(c)	Primer plus top coat	do.	2	---	0.5	---	2 SrCrO ₄	26	600-600	140 f.p.m.	Blistered.
9(d)	Primer plus top coat	do.	2	---	0.5	---	2 SrCrO ₄	26	600-600	140 f.p.m.	Blistered.
9(e)	Primer plus top coat	do.	2	---	0.5	---	2 SrCrO ₄	50	600-600	73 f.p.m.	No blistering.
10(a)	Primer and top coat	do.	1	2	1	---	2 SrCrO ₄ +0.7%	60	600-600	73 f.p.m.	Do.
10(b)	Primer and top coat	do.	1	2	1	---	2 SrCrO ₄ +0.7%	30	600	do.	Primer failed boiling water test.
10(c)	Primer and top coat	do.	1	2	1	---	2 SrCrO ₄ +0.7%	45	600	do.	Primer better, failed boiling water test.
11(a)	Primer	do.	0.75	4	2	---	4 SrCrO ₄ +0.6%	60	600	do.	Primer passed boiling water test.
11(b)	Primer	do.	0.75	4	2	---	4 SrCrO ₄ +0.6%	45	600	do.	Do.
11(c)	Primer	do.	0.75	4	2	---	4 SrCrO ₄ +0.6%	60	600	do.	Do.
12	Primer	do.	0.75	4	2	---	4 SrCrO ₄ +0.6%	90	600	do.	Do.
13(a)	Primer	do.	0.75	4	2	---	4 SrCrO ₄ +0.25%	45	750	do.	Do.

See footnote at end of table.

TABLE I—Continued

Experimental Number	Coat(s)	Resin	Percent				Bake Time, seconds	° F.	Notes	Results
			K ₂ Cr ₂ O ₇	Acetone	H ₂ O	H ₃ PO ₄ Other				
13(b)	Primer	Epoxy	0.75	4	2	4	30	750		Primer passed boiling water test.
13(c)	Backer	do.	0.75	4	2	4	20	750		Do.
14(a)	Primer plus top coat	do.	0.33	1.7	.9	1.7	28	680-740	140	Blistered, failed boiling water test.
14(b)	Primer plus top coat	do.					31	680-740	130	Passed boiling water test.
14(c)	Primer plus top coat	do.					31	680-740	115	Do.
15	Primer plus top coat	do.	.65	2	2	2	30	750		Do.
16	Paint	Plastisol	0.75	4	2	4	45	750		Do.
17	Paint	Organosol	0.75	4	2	4	45	750		Do.
18	Alkyd	Vinyl	0.75	4	2	4	45	750		Do.
19	Primer plus top coat	Epoxy, 1 vinyl	0.75	4	2	4	45	750		Do.
20	Primer plus top coat	Epoxy, 1 vinyl	0.75	4	2	4	45	750		Do.
21	Primer plus top coat	Epoxy, 1 fluorocarbon	0.75	4	2	4	45	750		Do.

¹ Urea modified solution type epoxy containing TiO₂ (approx. 2.0 lb./gal.), SrCrO₄ (approx. 0.2 lb./gal.), filler, primary diacetone alcohol and Carbitol. Sold by Celanese Corporation, H.C.I. Chemicals & Coatings, as Epoxy Primer HF-51 and HF-59.

² 101 white melamine modified dehydrated ester oil resin base paint. Sold by Celanese, Sherwin Williams and other paint manufacturers. This is a standard white paint in the industry and is applied in the standard way.

³ Dichromate solution changed from yellow to green with evolution of heat when added to primer.

⁴ Coating machine test run—140 feet per minute, corresponds to about 28 seconds dwell time in drying oven. In general, dwell time can be determined as follows: dwell time (seconds) = 3,600/l.p.m. for the primer, and dwell time = 4,200/l.p.m. for the stop coat.

⁵ Backer is the same epoxy composition except that it contains no filler or pigment.

⁶ Weight/volume percent; gms. additive/100 mls. primer.

⁷ Solution polyvinyl chloride, Sherwin Williams grade VO#2.

⁸ Plastisol finish, Sherwin Williams polyvinyl chloride, Type PL-101 white.

⁹ Solution polyvinyl acetate, Sherwin Williams vinyl finish paint.

¹⁰ Polyvinylidene fluoride resin, Sherwin Williams.

Unless otherwise indicated, in each of the examples summarized in Table I, the following materials were used:

Concentrated (85%) phosphoric acid was used in all cases. Phosphoric acid proportions are stated in volume/volume percent; i.e. volume of phosphoric acid to volume of primer.

High purity commercial grade potassium dichromate was used in all cases. Potassium dichromate was added on a weight/weight basis; i.e. weight of potassium dichromate per weight of primer.

High purity industrial water was used and was added on a volume/volume basis, based on primer.

Organic primer compositions, unless otherwise specified, were urea modified epoxy resin type solution grade resins produced by Celanese Corporation-H.C.I. Chemicals and Coatings sold under the designations HF-51 and HF-59. The primer contains titanium dioxide and strontium chromate, along with inert filler and a solvent consisting primarily of diacetone alcohol and Carbitol. The primer contained not less than about 2.0 lbs. of TiO₂ and 0.2 lb. of SrCrO₄ per gallon. This pigment comprises not less than about 75% of the total pigment present in the primer. The pigments, inert fillers, etc., in the amounts normally present in paints and primers, do not affect the essential characteristics of the compositions and coatings involved in this invention and may be included or omitted as desired without affecting the essential characteristics of the final product.

Where a top coat is indicated, unless otherwise specified, the top coat is a dehydrated castor oil based resin modified with melamine to form a film when baked. Resins of this type are supplied by H.C.I. Chemicals & Coatings, Celanese Corporation, Sherwin Williams and others. The coating composition contains about 44-46% solids.

As will be more fully demonstrated hereinafter, and as shown in the table, the precise nature of the resins involved is of no particular significance since the same results can be accomplished using all conventional coating resins. If the resins include an oxidizable component, so as to reduce substantially all of the hexavalent chromium to trivalent chromium, then no specific additive for this purpose is necessary. If, on the other hand, the resin is of the type which does not include such an oxidizable component, then an oxidizable component in the form of a solvent or other compound may be included in the mixture.

The experiments summarized in the preceding table are described briefly as follows:

EXAMPLE 1

One percent potassium dichromate was dissolved in 10% water and blended with the primer. The color of the chromium containing primer mixture changed from the yellow-orange color of hexavalent chromium to the green color characteristic of trivalent chromium. Draw-downs were made, applying the mix to precleaned aluminum panels, using a 0.025 bar. The panels were baked at 600° F. for, respectively, 30 seconds, 60 seconds, 90 seconds and 120 seconds. The panels were tested for adhesion by placing them in boiling water for one hour. Blistering and peeling started within ten minutes, showing the lack of adhesion.

EXAMPLE 2

The potassium dichromate was dissolved in water, the phosphoric acid was added to the water solution of dichromate and the aqueous dichromate-phosphoric acid solution was added to the primer. The solution had a yellowish color before its addition to the primer, indicative of the presence of hexavalent chromium. After mixing with the primer, the mix turned green indicating reduction of hexavalent chromium to trivalent chromium. This reaction occurred with emission of heat. The reaction of the hexavalent chromium with the oxidizable component of the

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resin can, therefore, be carried out simply by permitting the mixture containing the chromium and the oxidizable component to stand for a sufficient period before applying it to the metal substrate. Drawdowns were made in the manner described previously and the panels were baked at 600° F. for, respectively, 30 seconds, 60 seconds and 90 seconds. The 30 second and 60 second panels failed and the 90 second baked panel showed very little blistering. These data indicate that phosphoric acid is necessary for the improvement of the adhesion, that at a longer bake there is a chemical reaction occurring indicated by a change in color from green to yellowish during the baking period. A top coat was put over each of the three panels which were then baked at 600° F. for 30 seconds. All panels failed except the one in which the primer coat had been baked for 90 seconds at 600° F., which showed very little blistering.

EXAMPLE 3

Example 3 indicates the effect of reduced amounts of phosphoric acid. Phosphoric acid was reduced from 2 to 4% in an effort to increase pot life. Drawdowns made, as previously described, were baked at 600° F. for 90 seconds. After boiling in water for 90 minutes, the panel showed only minor blistering. The pot life increased from 15 minutes, as in Example 2, to 24 hours, at which time the mix solidified.

EXAMPLE 4

Doubling the amount of potassium dichromate in the mixture, as indicated in the data shown for Example 4 in the table, did not improve adhesion.

EXAMPLE 5

It was felt that large amounts of water were undesirable. Accordingly, the water content was decreased from 10% to 2%. This necessitated heating of the water and phosphoric acid so as to dissolve all of the potassium dichromate. When the phosphoric acid-potassium dichromate solution was cooled, it was added to the primer and the hexavalent chromium was reacted with the oxidizable component of the epoxy resin by letting the mixture stand for 30 minutes before drawdowns were made. Drawdowns were then made after one-half hour and after four hours and baked at 600° F. for 90 seconds. A top coat was added and baked at 600° F. for 30 seconds.

All of the panels showed no blistering or loss of adhesion after boiling for 90 minutes in water. These panels were sent to Suntest in Florida for actual weather exposure and were exposed in Riverside, Calif. Similar samples were submitted to a salt spray test in the laboratory for 1,000 hours. No loss of adhesion and only very minute isolated blistering occurred in any of the tests.

EXAMPLE 6

An effort was made to replace phosphoric acid with concentrated high purity commercial grade hydrofluoric acid, in the proportions shown in the table, using the procedures described with respect to Example 5. No loss of adhesion was observed but the top coat lost its gloss in a one hour boil test.

EXAMPLE 7

The effect of acetone in the mixture was evaluated. The mixture was prepared by adding the potassium dichromate to the boiling water, adding phosphoric acid to the water solution of potassium dichromate and continuing to heat the solution until all of the potassium dichromate was dissolved. The solution was then cooled and acetone was added. The acetone and chromium containing phosphoric acid solution was then added to the primer. The addition of acetone in this formulation made mixing of the chemicals to the primer easier, since acetone is a solvent compatible with both the chromate, phosphoric acid and the primer.

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At this point, comparisons were made between pre-cleaned metal coated with the formulation shown in the table and baked for 90 seconds at 600° F., and aluminum treated conventionally with commercial pretreatments and coated with the same epoxy primer. It was concluded from exposure tests, salt spray tests, and boiling water tests, that the new system of Example 7 was of at least as good a quality as any of the known treatments. The only disadvantage at this point was that the material treated with the composition of Example 7 did not have as good formability of the coating.

EXAMPLE 8

The formulation shown in the table for Example 8 was attempted; however, with 2% potassium dichromate, 0.5% water and 2% acetone all of the potassium dichromate cannot be dissolved.

EXAMPLE 9

The same mixing sequence was used in this example, using 1% potassium dichromate. Panels were coated and baked at 600° F. for 90 seconds for the primer and top coated with white alkyd paint and baked for 30 seconds at 600° F. The panels showed no blistering after 90 minutes boiling and the formability was considerably increased as compared with Example 7, although some fractioning occurred on a 180° bend.

Two epoxy primers, identical with the exception that one of them contained strontium chromate, were compared. The primer containing strontium chromate gave much better results, insofar as adhesion is concerned, than the identical primer without strontium chromate. As previously indicated, the primer used in the examples reported contained strontium chromate. In order to evaluate the effect of strontium chromate, a series of examples were run.

EXAMPLE 10

With 0.7% strontium chromate added, in addition to the 0.2 lb. per gallon strontium chromate already in the primer, drawdowns made with a 0.015 bar on pre-cleaned aluminum and baked at 600° F. for 60 seconds passed the boiling water tests. When top coated, however, all panels failed the boiling water test.

Strontium chromate first and then potassium dichromate were dissolved in phosphoric acid and water. The solution was cooled and filtered and acetone added. This acetone-water-phosphoric acid solution of potassium dichromate and strontium chromate was permitted to stand for one hour and filtered. Twenty milliliters of the filtered solution was added to one pint of epoxy backer, which is the same as the primer except that the fillers and pigments are omitted. The panels coated with this backer mixture were cured at, respectively, 45 seconds, 60 seconds and 90 seconds at 600° F. All panels passed the three hour boiling water test. When top coated with alkyd paint and baked for 45 seconds, the top coat failed the boiling water test. It appeared that a loss of adhesion existed between the primer coat and the top coat, possibly due to water penetration at the interface of the two coatings.

EXAMPLE 11

Example 10 was repeated except that the primer coat was cured for 90 seconds at 600° F. Both the primer coated and the primer and top coated panels passed a three hour boiling test. It was determined that a cure time of at least about 75 seconds at 600° F. was required for curing the primer coat and a cure, at 600° F., in excess of 30 seconds was required for the top coat.

It was believed that higher temperatures would be required to minimize cure time. Higher temperature cures were studied in the following series of experiments.

9 EXAMPLE 13

The previously described formulation procedure was followed and the panels were coated with primer and backer and baked for, respectively, 45 seconds for the primer at 750° and 30 seconds for the top coat at 750°. The same formulation added to epoxy backer was baked for 30 seconds at 750° F. All of the panels passed tests of four hours in boiling water. These experiments demonstrate that equivalent results can be obtained using a 90 second bake at 600° F. and a 45 second bake at 750° F.

It was also determined that strontium chromate is necessary for good adhesion and corrosion protection. It was concluded from observation of these experiments that hexavalent chromium added to the coating was being reduced to trivalent chromium, and that subsequently it is essential to have sufficient bake time and temperature to oxidize at least a portion of the trivalent chromium to hexavalent chromium. This oxidation occurs during the bake in the oven.

In order to establish that all of the hexavalent chromium added to the coating was reduced to trivalent chromium, samples were prepared as follows and analyzed. Fifteen grams of strontium chromate and 22 grams of potassium dichromate were dissolved in 50 milliliters of phosphoric acid, 25 milliliters of water and 50 milliliters of acetone. The solution was cooled and filtered and 20 milliliters of this solution was added to one pint of clear epoxy resin backer and 20 milliliters of this same solution was added to one pint of clear alkyd resin coating material.

Both samples were sent to an independent testing laboratory, E. S. Babcock & Sons, Analytical Laboratories, for analysis of hexavalent chromium. Both samples showed absence of hexavalent chromium. 0.2 gram of hexavalent chromium was added by E. S. Babcock & Sons and the mixtures were retested. Again, the analysis showed the absence of hexavalent chromium. Hexavalent chromium (dichromate) was determined by the diphenyl carbazide method (J. vander Walt and A. J. Vandermerwe, Analyst; 63, 809 (1938)). This method is suitable for the detection of microgram quantities of chromium.

EXAMPLE 14

Strontium chromate and potassium dichromate proportions were increased with respect to the phosphoric acid in this example. 300 grams of strontium chromate and 500 grams of potassium dichromate were dissolved in 2400 milliliters of phosphoric acid, 1200 milliliters of water and 2400 milliliters of acetone. 4000 milliliters of this solution was added to 25 gallons of primer. After application and bake of the primer, an alkyd top coat was painted over the primer coat. The coated aluminum sheet was cured by passing it through a coating oven. The initial line speed was 140 feet per minute, corresponding to 26 seconds bake time. The first station oven temperature was 740° at the intake and 680° at the exit. Incomplete cure was observed at 140 feet per minute. The line speed was reduced to 130 feet per minute. Blistering tests disappeared and boiling water tests were satisfactory. As a precaution, the line speed was further reduced to 115 feet per minute, corresponding to approximately 31 seconds cure time. 5000 lbs. of aluminum coiled sheet was processed at this speed. Samples of this metal were exposed in Riverside, Calif., and in Florida. Six months exposure showed no defects. A number of pieces were formed using conventional roll formers and, upon examination, no defects were discovered. Roll formed shutters were fabricated and exposed to weather testing. After six months no defects were noticed and after twelve months the coating was stripped with methylethyl ketone. No corrosion was observable on the aluminum surface under the paint films.

Using the formulation of this example, some salting out of the strontium chromate-potassium dichromate solution was observed. To correct this problem, the proportion of water was increased and, as an aid to operating personnel,

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the basis for measurement was changed. Strontium chromate and potassium dichromate were measured on a weight/volume basis and phosphoric acid, water and acetone were measured on a volume/volume basis, based on the primer volume. This approach is satisfactory if the primers and paints have relatively small differences in their weight per gallon of solids, see Experiment No. 15.

Because epoxy primers and alkyd paints are widely used in the industry, most of the work done with respect to this invention was done using these materials. There is no chemical or other reason, however, why one coating material should be different from another insofar as this invention is concerned. Of course, the different coating materials will have different characteristics resulting inherently from the characteristics of the material involved but the invention is equally applicable to all coating resins, as demonstrated by the following series of experiments.

EXAMPLE 16

The dichromate-strontium chromate solution described in Example 13 was added to a plastisol primer. The primer was baked for 45 seconds at 750°. A plastisol top coat was added and baked at 750° for 30 seconds. No blistering or cracking was observed after four hours in boiling water. The plastisol primer is solution grade polyvinyl acetate identified as organosol plastisol primer VO No. 2 supplied by Sherwin Williams Corporation. The plastisol finish coat was a polyvinyl chloride resin supplied by Sherwin Williams Corporation identified as organosol plastisol finish coat PL-101 white pigmented.

EXAMPLE 17

The formulation used in Example 13 was added to an organosol primer paint, the same primer paint used in Example 17 but containing a volatile solvent. The organosol primer paint was applied to test panels and baked at 750° F. for 45 seconds. No blistering or cracking was observed after boiling in water for four hours.

EXAMPLE 18

The alkyd paint previously used as a top coat was used as the primer in this example. To this alkyd paint, the strontium chromate-potassium dichromate solution used in Example 13 was added. A solvent system which was satisfactory in all respects was found through routine compatibility tests. Solvesso 150 was used as the solvent and no adverse effect was observable. A single coat of this alkyd paint, without primer, was found to be equal or superior to one coat alkyls used in conventional processes using conventional pretreatment techniques.

EXAMPLE 19

The same tests were run using a vinyl paint, solution grade polyvinyl acetate supplied by Sherwin Williams Corporation. A one coat system, without primer, gave satisfactory results.

EXAMPLE 20

Good results were also obtained using the same technique but using an epoxy primer and a trivalent chromium containing vinyl top coat.

EXAMPLE 21

Satisfactory results were also obtained using the same formulation and technique with an epoxy primer and a strontium chromate-potassium dichromate containing fluorocarbon finish coat. Polyvinylidene fluoride resin, sold by DeSoto Chemical Company and Sherwin Williams Corporation, based upon Kynar 500 resin from Pennsalt Corporation were used in this example.

It is quite significant, from the foregoing, that the invention can be applied with a variety of coatings. It works well with epoxies, organosols, plastisols, alkyls, vinyls, fluorocarbons, etc., with a one coat system and, of course, in a two coat system. The only reservation in the two

coat system is that the primer and top coat must be compatible.

In the foregoing examples, the resins used included an oxidizable component. In such cases then the addition of a neutral solvent would have no effect on the end product, which is the creation of a chemical bond between the paint and the metal during the oxidation period of the bake.

If, however, the resin-pigment composition has no chemical activity so as to reduce Cr_6 to Cr_3 as it stands, then the addition of a solvent which is compatible with the resin and which is oxidizable to reduce chromium from the +6 to the +3 valence will result in the same system.

Tests using the formulation of Example 13 and a variety of solvents were run. The solvents used were carbitol, butyl carbitol and isophorone. Two milliliters of Formula No. 13 was added to 50 milliliters of the respective solvents. The results of the oxidation reduction reaction are shown in the following table:

TABLE 2

Solvent	Temperature, ° F.	Time of Reaction
Carbitol.....	32	22 minutes.
	90	5 minutes.
	150	10 seconds (approx.).
Butyl carbitol.....	32	23 minutes.
	90	5.8 minutes.
	150	10 seconds (approx.).
Isophorone.....	32	23 minutes.
	90	4.3 minutes.
	150	10 seconds (approx.).

These types of solvents are very reactive in reducing Cr_6 to Cr_3 . If small amounts of solvents ran into large amounts of the formulation, Cr_6 is reduced to Cr_3 without gelling.

The same test was conducted using isopropyl alcohol at room temperature. Reduction occurred immediately and the mixture gelled with time.

The same test was repeated using diacetone alcohol, methylethyl ketone, diacetone alcohol-high flash naphtha in 50/50 mixture, toluene and xylene. In each of the above cases there was no reduction of Cr_6 to Cr_3 and the solution remained orange without gelling. These solvents, then, must be regarded as neutral.

It is apparent from the foregoing that the oxidizable component may be either an integral part of the resin or may be added to the resin mixture as, for example, a solvent. Primary alcohols and aldehydes form excellent oxidizable solvents for use in this invention. Secondary alcohols and ketones are more stable, but can also be used if the reaction time of the Cr_6 with the oxidizable solvent is long enough.

In the preceeding examples, aluminum and aluminum alloys, types 5005, 5010, 3003 and 5052 were used. No difference between the various substrate were noted.

EXAMPLE 22

Drawdowns were made on cold rolled steel of 0.050 gauge using the same techniques previously described. In these particular examples, the epoxy based primer and the formulation specified in Example 14 was used.

While the greatest use of the invention is expected to be in connection with the coating of aluminum and aluminum alloy, it is plain that the invention is also suitable for use in coating iron, steel and other alloys of iron and other substrates as well.

The preceding examples are intended only to illustrate a few of the various applications and the principal points of the invention and are not to be construed as limiting the invention.

What is of great significance in the preceding examples is that in each case the Cr_6 was reduced to Cr_3 in the coating mixture prior to application. The substrate with the coating mixture applied thereon was then baked at such a temperature, between about 600° and about 800° F. for a sufficient length of time to insure that at least a portion of the chromium was oxidized to the +6

valance state thereby forming a chemical bond between the coating and the metal. Heretofore it has been believed necessary to retain at least a portion of the chromium in the +6 valence state. We have found, contrary to the prior art teachings, that superior results can be obtained through reduction of the chromium to the +3 state followed by baking at sufficient temperatures for sufficient lengths of time to oxidize the chromium back to the +6 state.

The exact parameters of the baking condition have not been determined. It has been determined, however, that, at least for economically feasible coating speeds, the temperature must be in the range of from about 600° F. to about 800° F. Perhaps slightly higher temperatures could be used for very short periods of time but above about 800° F., depending upon the resin involved, some resin degradation would be expected to occur. The upper limit of usable temperature, then, is fairly broad but is in the range of about 800° F. A few, routine experiments to determine the point at which resin degradation occurs is all that is required to determine the maximum temperature usable in connection with this invention.

The bake time, the time for oxidizing the Cr_3 to Cr_6 , is, of course, related to the bake temperature. The lower the temperature, i.e. 600° F., the longer the bake time that is required. Conversely, at higher temperatures, shorter bake times may be used. Strontium chromate is also important in obtaining maximum adhesion, corrosion resistance, etc., with short bake times. In general, the bake time must be at least 26 seconds, even in a continuous coating process and, in general, bake times of at least 30-45 seconds is required. The metal substrate must reach at least about 450° F., irrespective of the exact oven temperature. The optimum bake time can, of course, be determined through a few routine experiments to determine the bake time required at the specified temperature to accomplish the necessary adhesion using, for example, boil tests, exposure tests, salt spray tests, etc.

It will be understood, therefore, that it is not practical to specify a precise bake time and temperature which will give optimum results for all possible resins. It is sufficient to enable one skilled in the art to carry out the invention, however, to specify that the bake temperature must be in the range of from about 600° F. to about 800° F. and the bake time must usually be in excess of about 26 seconds to achieve a metal substrate temperature of about 450° F., and, while the upper limit of bake time is not critical, practical considerations dictate that the bake time not exceed about 200 seconds. Within these ranges, a few routine laboratory tests will define, rather precisely, the optimum bake time and temperature variables for a specified resin.

Insofar as the formulations are concerned, no special criticality is involved. It is generally correct, and is quite sufficient for the practice of the invention, to specify the addition of from 0.2 to about 4.0 grams of potassium chromate and from about 0.1 to about 2.0 grams of strontium chromate, or the equivalents of these compounds, to 100 milliliters of primer or resin based coating compound. In general, the mixture should also contain from about 0.5 to about 10 parts of water, from 0.1 to about 10 parts of acetone or other solvent, and from about 1.0 to about 10.0 parts of phosphoric acid, on a volume/volume basis. It is critical that the components include an oxidizable component sufficient to reduce the Cr_6 to Cr_3 such that the final mixture is characterized by the substantial absence of chromium in the +6 state, substantially all of the chromium being in the +3 state. The oxidizable component may be an integral part of the resin or it may be added in the form of a solvent, diluent, or otherwise.

Attempts were made to accomplish the same results as were accomplished in the preceding examples by the addition of organic and inorganic chromium in the +3 state directly to the mixture, without the necessity of

reducing +6 chromium to the +3 state. Results were quite unsatisfactory in every case. From the prior art there was no reason to expect that +3 chromium in a coating mixture would accomplish the desired results, whether added directly or resulting from reduction of +6 chromium and, indeed, the prior art strongly indicated that the presence of at least some +6 chromium was essential to successful coating. As the foregoing examples clearly illustrate, however, this is not the case.

With the principles and examples of the foregoing specification in mind, it will be apparent that various modifications and adaptations, including the addition of components which do not enter into the chromium-resin-substrate interaction, may be made without departing from the spirit and scope of the invention, as defined in the following claims.

I claim:

1. A coating process for forming an adherent organic resin coating to metal substrate, comprising the steps of:

- (a) mixing together ingredients, in the following proportions, consisting essentially of 0.2 to 4.0 grams of an inorganic hexavalent chromium compound, to 100 milliliters of an organic resin containing an oxidizable component, 1.0 to 10.0 parts of phosphoric acid on a volume/volume basis and 0.1 to 2.0 grams of strontium chromate;
- (b) reacting the oxidizable component and the hexavalent chromium compound thereby reducing substantially all of the hexavalent chromium to trivalent chromium;
- (c) applying the mixture resulting from steps (a) and (b) characterized by the absence of detectable hexavalent chromium to a metal substrate; and
- (d) heating the applied resulting mixture and metal substrate to from about 600° F. to about 800° F. for a sufficient time in excess of about 26 seconds to achieve a minimum metal substrate temperature of at least about 450° F. to cause at least a portion of the trivalent chromium to be oxidized to hexavalent chromium thereby forming a coating in which the organic resin is bonded to the metal substrate so as to withstand the effects of an exposure to weather without cracking or peeling.

2. The coating process as defined in claim 1 wherein the organic resin is selected from the group consisting of epoxies, vinyls and alkyds, and wherein the metal substrate is selected from the group consisting of aluminum, alloys of aluminum, and steel.

3. The coating process as defined in claim 1 wherein the organic resin is epoxy resin.

4. A coating process for forming an adherent organic resin coating to metal substrate, comprising the steps of:

- (a) mixing together ingredients, in the following proportions, consisting essentially of 0.2 to 4.0 grams of an inorganic hexavalent chromium compound, to 100 milliliters of an organic resin containing an oxidizable component, 1.0 to 10.0 parts of phosphoric acid on a volume/volume basis and 0.1 to 2.0 grams of strontium chromate;
- (b) reacting the oxidizable component and the hexavalent chromium compound thereby reducing substantially all of the hexavalent chromium to trivalent chromium;
- (c) applying the mixture resulting from steps (a) and (b), characterized by the absence of detectable hexavalent chromium, to a metal substrate; and
- (d) heating the applied resulting mixture and metal substrate to from about 600° F. to about 800° F. for a sufficient time in excess of about 26 seconds to achieve a minimum metal substrate temperature of at least about 450° F. to cause at least a portion of the trivalent chromium to be oxidized to hexavalent chromium thereby forming a coating in which the organic resin is bonded to the metal substrate so as to withstand the effects of and exposure to weather without cracking or peeling.

5. The coating process as defined in claim 1 wherein the organic resin is selected from the group consisting of epoxies, vinyls and alkyds, and wherein the metal substrate is selected from the group consisting of aluminum, alloys of aluminum, and steel.

6. The coating process as defined in claim 1 wherein the organic resin is epoxy resin.

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