

PATENT SPECIFICATION (11)

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(54) IMPROVEMENTS IN OR RELATING TO COATED SUBSTRATES

(71) We, DIAMOND SHAMROCK CORPORATION, of 1100 Superior Avenue, Cleveland, Ohio, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Coating compositions, especially for metal substrates, which are applied prior to painting and are then heat-cured are often used to impart corrosion-resistance to metal surfaces, as well as to enhance adhesion of subsequently applied paints. Such coating compositions typically contain a metal in non-elemental form, which metal can exhibit multi-valency and is susceptible to reduction to a lower valency state during curing of the applied composition. For example, in our Patent Specification 1,273,413 chromium bonding compositions are disclosed which contain, in liquid medium, a hexavalent-chromium-providing compound and reducing agent therefor.

Such compositions exhibit excellent adherence to metal substrates and offer many desirable characteristics, including the formation of a firm bond between subsequently applied topcoats and the underlying metal substrate. Some of these topcoats can themselves be compositions containing a multi-valent metal in aqueous medium. A coating such as disclosed in our aforesaid specification can also be top-coated with a chromium bonding coating. Such a topcoating can contain a hexavalent-chromium-providing compound in a liquid medium containing water.

After the pre-paint coating and then the topcoat application and curing, the resulting coated article is usually required to ex-

hibit good corrosion resistance. In addition, prior to application of the topcoating, the initially coated metal should, most desirably, be water-resistant. This water-resistance not only maintains coating integrity during application of a subsequent coating, but also permits water quenching to be used for the purpose of cooling the initially-coated article. Water quenching can provide most economical cooling. This cooling is most desirable where the subsequent coating is to be applied by an immersion coating technique and also when the subsequent coating composition is heat-sensitive.

It has now been found that the corrosion resistance of coated composites can be desirably enhanced when both the pre-paint and the topcoating compositions are formulated with multi-valent metal and careful control is exercised over cure conditions. Additionally, water-sensitivity of the pre-paint or base coating can be sufficiently suppressed not only to permit topcoating with compositions which are water-based, but also to permit water quenching after heat curing of base coatings.

According to one aspect, therefore, the present invention provides a process in which a substrate is provided with a protective coating composite, wherein a portion of the coating composite comprises both an undercoating and a subsequent coating, each established from a heat-curable composition which before curing contains, in liquid medium, a hexavalent-chromium-providing substance and a reducing agent therefor, the hexavalent chromium being susceptible to valency reduction to a lower valence state during curing of the applied composition and being present in the composition at least partially in a higher valency state, which comprises:

(A) establishing the undercoating of the



coating composite in a non-water-resistant condition;

(B) pre-curing the undercoating at elevated temperature to a dry and water-resistant coating, under precuring conditions selected to orient the undercoating towards reduction of the chromium in the higher valency state;

(C) establishing the subsequent coating of the coating composite in a non-water-resistant condition; and

(D) curing the subsequent coating at elevated temperature under curing conditions to subject the subsequent coating firstly to the pre-curing conditions, thereby initially orienting the chromium of the subsequent coating towards reduction from the higher valency state, and with the elevated temperature conditions, by continuation thereof, then orienting the chromium of the subsequent coating towards a return to the higher valency state chromium.

The present invention is also directed to composite coated substrates, as well as to subsequently painted substrates which can thereby be obtained.

The known pre-paint coatings, each of which may also be termed herein as an "undercoating" or "base-coating", need not be complex. Such coatings, which may be of the chromate type, may form highly adherent coatings on the substrate metal surface. Such compositions are susceptible to curing at elevated temperature. Some of the very simple undercoating compositions, such as disclosed in US Patent Specification 3,687,738 merely contain chromic acid and a particulate metal, for instance aluminium, manganese, zinc and magnesium. Further, these particulate metals are known from our aforesaid patent specification to be useful in bonding coating compositions, containing a hexavalent - chromium - providing substance and a reducing agent therefor.

Of particular interest in the present invention are the bonding coatings, i.e., coatings obtained from compositions containing a hexavalent-chromium-providing substance and a reducing agent therefor. Preferred bonding coating compositions contain as the reducing agents succinic acid and other dicarboxylic acids having up to 14 carbon atoms as has been disclosed in US Patent Specification 3,382,081. These acids (with the exception of succinic) can be used alone and also these acids can be used in admixture with one another or in admixture with other organic substances exemplified by aspartic acid, acrylamide or succinimide. Additional combinations which are particularly useful include mono-, tri- or polycarboxylic acids, together with additional organic substances, as disclosed in US Patent Specification 3,519,501. Also of particular interest are the disclosures in regard to re-

ducing agents, which may be acidic in nature, contained in US Patent Specifications 3,535,166 and 3,535,167. Further, glycols and glycol-ethers are of particular interest many representative compounds being disclosed in US Patent Specification 3,679,493.

Substantially all pre-paint or undercoating compositions are simply water based, ostensibly for economy. Additional or alternative substances comprising the liquid medium, at least for some of these compositions, include those disclosed in US Patent Specification 3,437,531 namely blends of chlorinated hydrocarbons and a tertiary alcohol, including tertiary butyl alcohol as well as alcohols other than tertiary butyl alcohol. It would appear, in the selection of the liquid medium, that economy is of major importance and thus such medium usually contains readily commercially available liquids.

The undercoating, although it may contain elemental metal, e.g., the pulverulent metals mentioned hereinabove will also contain metal in non-elemental form, which also can exhibit multi-valency and is present in the undercoating composition at least partially in a higher valency state. In the compositions of the present invention, this component is provided by chromium in the hexavalent state, incorporated into the undercoating compositions, for instance, as chromic acid or dichromate salts. During the curing of the applied coating composition, the chromium is susceptible to reduction to a lower valence state. Such reduction is generally enhanced by the presence of the reducing agent in the composition.

When the undercoating is established, typically by application directly to the surface of the substrate to be coated, (although such substrate might be a precoated metal substrate, for example, a phosphatized metal substrate), the applied coating will be non-water-resistant. This means that, prior to curing, the applied coating can be easily removed by rubbing with a damp cloth. The undercoating thus established is then subjected to elevated temperature precuring conditions. These conditions are selected so as initially to transform the established undercoating into a dry and water-resistant coating. Rubbing with a damp cloth in the same way is typically a ready means for testing the water-resistant nature of the precured coating, after precuring and cooling of the coating.

Further, the conditions used for precuring at elevated temperature are selected to orient the chromium of the resultant undercoating towards reduction from the higher valency state. Although multi-valent metals other than chromium can additionally be present in the cured undercoating, for example molybdenum and tungsten, and even such multi-valent metals as manganese are

contemplated to be present in the undercoating, chromium is selected as representative for determination of the appropriate cure conditions. In general, the preferred pre-cure conditions for chromium-containing undercoatings are an air temperature below 550°F. for a time less than about 10 minutes. However, a lower temperature, e.g. 450°—500°F., with a commensurately longer cure time, e.g. up to 25 minutes or more, can also be typically used. The resulting undercoated article can then be subjected to testing for determining orientation of the valency state of the chromium (and any additional multi-valent metal) in the undercoating.

For chromium, such testing can proceed by first contacting the cured undercoat with a slightly basic aqueous medium. The resulting medium, after acidification, can then be subjected to the standard potassium iodide/starch titration test for determining hexavalent chromium. If hexavalent chromium is found to be present, the amount can be determined by titrating against thiosulphate. This titration measures the free iodine of the sample which is quantitatively associated with the hexavalent chromium present. This test will thus indicate if the heat cure conditions have been appropriately selected for orienting the undercoating towards a minimum of higher valency state chromium in accordance with the process of the invention. The application of this test has been more particularly described hereinafter in connection with an illustrative embodiment of the invention. Representative tests of this nature, for other multi-valent metals of the undercoatings, are well known to persons skilled in the art, as also is the above-discussed test.

The resulting undercoated substrate can then be cooled before being topcoated, particularly prior to application of a heat-sensitive topcoat composition. Although this cooling can be simple air drying, appropriate control of the undercoat curing will form it into a water-resistant coating and thereby allow the use of economical water-quenching or, in general, quenching in or with a liquid medium containing water, for at least a part of the cooling procedure. Typically, a cured, undercoated article can proceed directly to water quenching, from the cure operation, and then go from such quenching right on to a topcoating operation. Also, removal of residual quench water from the article before topcoating may be desired.

The undercoated metal surface then has applied thereto a subsequent coating, also termed herein for convenience a "top-coating". Although the nature of this topcoating can vary over very broad limits, it also contains a multi-valent metal in liquid medium, with the metal being at least partially present in a higher valency state, like

the undercoating. For example, it has been shown in US Patent Specification 3,718,509 that a hexavalent-chromium-containing bonding coating provides a highly serviceable topcoating for a metal substrate which is first treated with such a chromium-containing bonding coating composition which further contains a pulverulent metal. It is also contemplated that the pulverulent-metal-containing base coating also forms the topcoating. In general such topcoating may be a second application, without variation, of the base coating. However, the undercoating may contain multi-valent metal differing from such metal of the topcoat. Also, although the topcoat is typically applied directly to the undercoating, such need not be the case. Thus, the chromium-containing bonding coating, disclosed as the topcoating in the 3,718,509 patent, can be an intermediate coating. The topcoating for such a composite, cured in accordance with the concepts of the present invention, can then contain both a pulverulent metal and a substance providing hexavalent chromium. The essential characteristic of the subsequent coating, according to this invention, is that, like the undercoating, it contains a hexavalent-chromium-providing substance and a reducing agent therefor.

When the topcoating is established, generally by application directly to the undercoating, such applied coating, prior to curing, can be removed in the same manner as freshly-applied undercoating, e.g., by rubbing with a damp cloth. The subsequent coating thus established is then subjected to elevated temperature curing conditions. These conditions are selected to initially transform the established topcoating to a dry and water-resistant coating, in the manner of the undercoating. Then, the curing conditions at elevated temperature are continued to orient the chromium of the subsequent coating towards a return to the higher valency state. Again selecting chromium as representative for determination of the appropriate cure conditions, the subsequent coating is subjected to an air temperature of 550°F. or more for a time of at least 10 minutes. Preferably, for greater efficiency, curing proceeds at an air temperature of 600°—700°F. for a cure time of 10 to 20 minutes. The resulting article can then be subjected to the same testing as hereinabove described for determining orientation of the valency state of the multivalent metal, i.e. the chromium, with any other such metal, in the subsequent coating.

The undercoated and topcoated substrates can be further topcoated typically with any suitable composition, e.g., a paint, primer, enamel, varnish or lacquer. Such compositions may contain pigment in a binder or can be unpigmented, as exemplified by cel-

lulose lacquers, rosin varnishes and oleo-resinous varnishes. The compositions can be solvent-reduced or may be water-reduced, e.g., latex or water-soluble resins, including modified or soluble alkyds, or they can have reactive solvents such as in the polyesters or polyurethanes.

Particularly when the metal substrate to be coated is a weldable metal substrate, additional composite coating systems may be contemplated. For example, after the topcoating composition is applied, a weldable primer is applied and then, following welding, the resulting metal assembly is further topcoated. Since weldable primers typically contain an electrically-conductive pigment, the topcoating may be an electrocoated primer.

The electrodeposition of film-forming materials is well known and can include simple electrocoating of a film-forming material in a bath which contains, for instance, one or more pigments, metallic particles, drying oils, dyes or extenders. Representative film-forming coating systems of this nature are set forth, for example, in US Patent Specifications 3,304,250 and 3,455,805. Also, substances of particular interest, for example in the automotive industry, are anodically-deposited film-forming materials, as exemplified by US Patent Specification 3,230,162. These composite coating systems can include an electrophoretically-deposited zinc paint, which may be deposited, for example, on the pre-paint-treated metal surface of a substrate treated according to the present invention. The deposited zinc paint provides an intermediate coating, for subsequent topcoating. In US Patent Specification 3,464,906 a zinc paint is disclosed which can be electrodeposited and which contains a water-soluble or dispersible resin in an aqueous medium, as a binder.

Before application of the pre-paint coating composition to a metal substrate, which is the preferred substrate for protection owing to the corrosion-protective nature of the undercoatings, although other substrates which can withstand the heat curing conditions are contemplated, it is generally advisable to remove foreign matter from the metal surface by thorough cleaning and degreasing. Degreasing can be accomplished with known agents, e.g. sodium metasilicate, caustic soda, carbon tetrachloride and trichlorethylene. Commercial alkaline cleaning compositions which combine washing and mild abrasive treatment, e.g., an aqueous trisodium phosphate-sodium hydroxide cleaning solution, may be employed. In addition to cleaning, the substrate can undergo etching, for example, with a strong inorganic acid etching agent.

The following is an illustrative embodiment and used test panels, which were all

cold-rolled, low carbon steel panels, measuring 4" x 8". These panels were prepared for coating by first scrubbing with a cleaning pad comprising porous synthetic fibres impregnated with an abrasive. Thereafter, the scrubbed panels were immersed in a bath of an alkaline cleaning solution containing 1—5 ounces per gallon of water of a mixture of 25 weight percent tripotassium phosphate and 75 weight percent potassium hydroxide. The bath of alkaline cleaning solution was maintained at a temperature of 150°—180°F. Following the cleaning, the panels were rinsed with warm water and dried.

A test composition was prepared from 200 ml dipropylene glycol, 4 ml of wetter (a non-ionic modified polyethoxy adduct having a viscosity of 180 centipoises at 25°C. and a density at 25°C. of 8.7 pounds per gallon), 350 grams of zinc flake (having a particle thickness of about 0.1—0.2 micron and a longest dimension of discrete particles of about 15 microns), 700 ml of deionized water, 50 grams of chromic acid and 2 grams of hydroxyethyl cellulose thickener. The thickener was a cream to white coloured powder having a specific gravity at 20°C. of 1.38—1.40 and an apparent density of 22—38 pounds/cu.ft., all particles passing through 80 U.S. mesh.

The panels were coated by dipping them into the coating composition and draining off excess composition. This draining was then immediately followed by baking. Some panels thus coated had a high coating weight of 1400 mg/ft², and others, by diluting the bath with distilled water before dipping, had a low coating weight of 700 mg/ft². Baking proceeded in a convection oven at an air temperature of about 450°F. for time of 10 minutes. Subsequently, some of the low coating weight panels were re-dipped in the water-diluted bath, so that they had a final two-coat weight of 1400 mg/ft². (Coating weights are determined by weighing the panel before coating and then reweighing the coated panel.) After the second coat, the two-coat panels were baked at an air temperature of 600°F. for 15 minutes.

Some of the coated panels were then subjected to testing for leachable hexavalent chromium. The test method involved was a standard iodimetric titration. First, a test panel was immersed in 100 ml of a 2% ammonium hydroxide solution for 15 minutes. The panel was removed and the solution titrated. (In this titration, the solution is acidified with concentrated hydrochloric acid to ensure that the pH of the sample is less than 7. A KI/starch ingredient is then added to the acidified sample. If the solution turns purple, the presence of leachable chromium is thus indicated. A purple sample can then be titrated with standard thiosulphate solu-

tion to the purple/white colour change. The titration measures the free iodine of the sample which is quantitatively associated with the hexavalent chromium.)

5 By this test, both a low coating weight panel (one coat) and a one-coat high coating weight panel, both cured at 450°F., showed no leachable chromium. However, a two-coat panel indicated a colour change and
10 thus the presence of leachable hexavalent chromium in the coating. Selected one-coat heavy coating weight panels, as well as two-coat panels, were then subjected to a corrosion resistance test by means of the
15 standard salt spray (fog) test for paint and varnishes as described in ASTM B-117-64. In this test, panels were placed in a chamber held at constant temperature where they were exposed to a fine spray (fog) of a 5%
20 salt solution for a period of time until red rust was first noted on the panel. By this test the two-coated panel was observed to proceed in the test more than 1,000 hours, i.e. more than four times longer than the
25 one-coat panel, although they had comparable coating weights.

WHAT WE CLAIM IS:—

30 1. A process of providing a substrate with a protective coating composite, wherein a portion of the coating composite comprises both an undercoating and a subsequent coating, each established from a heat-curable composition which before curing contains, in liquid medium, a hexa-
35 valent-chromium-providing substance and a reducing agent therefor, the hexavalent chromium being susceptible to valency reduction to a lower valence state during curing of the applied composition and being present in the composition at least partially in a higher valency state, which comprises:

40 (A) establishing the undercoating of the coating composite in a non-water-resistant condition;

45 (B) pre-curing the undercoating at elevated temperature to a dry and water-resistant coating, under precuring conditions selected to orient the undercoating towards

reduction of the chromium in the higher valency state;

(C) establishing the subsequent coating of the coating composite in a non-water-resistant condition; and

55 (D) curing the subsequent coating at elevated temperature under curing conditions to subject the subsequent coating firstly to the pre-curing conditions, thereby initially orienting the chromium of the subsequent coating towards reduction from the higher
60 valency state, and with the elevated temperature conditions, by continuation thereof, then orienting the chromium of the subsequent coating towards a return to the higher valency state chromium.

2. A process according to claim 1, wherein the substrate is a metal substrate and the undercoating is established on its surface.

3. A process according to claim 1 or 2, wherein the liquid medium of each heat-curable coating composition contains water.

4. A process according to any preceding claim, wherein the pre-cured undercoating is cooled prior to establishing the subsequent
75 coating of the composite.

5. A process according to claim 4, wherein the cooling includes quenching in or with a liquid medium containing water.

6. A process according to any preceding claim, wherein a water-based intermediate coating is established on the pre-cured undercoating and the subsequent coating is then established on the intermediate coating.

7. A process according to claim 1, substantially as herein described.

8. A coated substrate when produced by a process according to any preceding claim.

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(B) pre-curing the undercoating at elevated temperature to a dry and water-resistant coating, under precuring conditions selected to orient the undercoating towards

reduction of the chromium in the higher valency state; 50

(C) establishing the subsequent coating of the coating composite in a non-water-resistant condition; and

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60 valency state, and with the elevated temperature conditions, by continuation thereof, then orienting the chromium of the subsequent coating towards a return to the higher valency state chromium. 65

2. A process according to claim 1, wherein the substrate is a metal substrate and the undercoating is established on its surface.

3. A process according to claim 1 or 2, wherein the liquid medium of each heat-curable coating composition contains water. 70

4. A process according to any preceding claim, wherein the pre-cured undercoating is cooled prior to establishing the subsequent coating of the composite. 75

5. A process according to claim 4, wherein the cooling includes quenching in or with a liquid medium containing water.

6. A process according to any preceding claim, wherein a water-based intermediate coating is established on the pre-cured undercoating and the subsequent coating is then established on the intermediate coating. 80

7. A process according to claim 1, substantially as herein described. 85

8. A coated substrate when produced by a process according to any preceding claim.

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