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(54) **Process for rinsing phosphate conversion coatings with compositions containing an S-triazine compound.**

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Description

The present invention relates to the pretreatment of a ferrous or galvanized metal surface prior to the application of a subsequently applied coating.

5 In the metal pretreatment process, it is known to employ a phosphating conversion coating which is usually followed by a final rinsing or sealing step. The rinsing composition usually comprises chromic acid. While effective in the rinsing step, chromic acid is, nonetheless, undesirable because of its toxicity and the attendant problems of disposal.

Hence, considerable work has been done in finding a replacement for chromic acid in the final rinsing
10 step. The present invention provides a process for the pretreatment of ferrous or galvanized metal surfaces prior to the application of a subsequently applied coating in which the rinsing composition is essentially free of chromic acid.

US-A-3,706,604 discloses an improved process for coating metal wherein a phosphate or oxalate conversion coating composition is applied to an aluminium, zinc or ferrous metal surface to form a
15 substantially dry, uniform phosphate or oxalate conversion coating, a portion of which is water-soluble. An organic containing reducing and/or esterifying fixing or immobilizing coating composition containing hexavalent chromium is then applied which reacts out the water soluble portion of the conversion coating to produce water-insoluble phosphate or oxalates and form a substantially dry, uniform composite coating. This process is said to eliminate the need for rinsing procedures.

20 US-A-2,976,193 discloses inter alia a process for producing a substantially colorless chemically bonded coating on an aluminum article, which comprises treating said article with an aqueous acid aluminum conversion coating bath, said bath comprising a halogen-containing anion, an anion including a member of the group consisting of hexavalent chromium, molybdenum, tungsten and ferricyanide, a cation of the group consisting of zinc, cadmium, mercury, vanadium, chromium, manganese, iron, cobalt, nickel and copper
25 forming a colored conversion coating on said article, and contacting said colored conversion coating with a color discharging agent which is an aqueous solution of a soluble agent of the group consisting of a soluble thiocyanate, a soluble cyanate, thiourea, urea, cyanuric acid, thiocyanuric acid, soluble sulfur-containing compounds, soluble phosphorus-containing compounds, soluble ferrocyanides, soluble divalent and trivalent chromium compounds, hydroquinone, quinhydrone and hydrazines, and forming a substantially colorless
30 conversion coating of high corrosion resistance, the pH of said solution being about 1.5 to about 3.5 the amount of said agent in said solution being about 1 to about 5 grams per liter of solution.

The present invention provides a process for rinsing a phosphate conversion coating applied to a ferrous metal or galvanized steel prior to the application of a subsequently applied coating comprising
35 applying to the phosphate conversion coating an aqueous chromic acid free composition having a pH of 3.4 to 6.0 at a temperature of 30 °C to 80 °C, said composition comprising at least 0.01 percent by weight based on the total weight of the composition of an S-triazine compound having at least one hydroxyl group on a carbon atom of the triazine ring.

The S-triazine compound or a modification thereof which is useful herein, is one that enolizes in a manner that renders the aqueous composition containing the same acidic. While not desiring to be bound to
40 any particular theory, it is believed that the enolized form of the S-triazine compound is reactable with the metal surface. The enol form of the preferred S-triazine compound is commonly referred to as cyanuric acid. In accordance with this invention, the S-triazine compound or a modification thereof useful herein is characterized as having at least one hydroxyl group on a carbon atom of the triazine ring.

The useful S-triazine compound must be compatible with an aqueous medium, i.e., it is mixable to
45 produce an aqueous composition that can be applied to a substrate to produce a corrosion resistant surface that can adhere to a subsequently applied coating. Typically, it may have a solubility of at least about 0.01 gram per 100 grams of water at 25 °C. The aqueous composition can be prepared by mixing the S-triazine compound with an aqueous medium, preferably at a temperature of about 30 °C to 80 °C and more preferably about 40 °C to 80 °C. By an aqueous medium is meant water or water in combination with an
50 adjuvant that can enhance the solubility of the S-triazine compound. The aqueous composition may also contain an additive such as a pH buffer, phosphate, borate, potassium salt or the like or a mixture thereof.

Accordingly, the aqueous pretreating composition has a pH of about 3.4 to 6 and preferably about 4.0 to 5.0. The composition may contain 0.01 to 0.2 percent by weight and preferably 0.05 to 0.15 percent by
55 weight of the S-triazine compound based on the total weight of the composition. While higher amounts of the S-triazine compound can be employed in the aqueous composition, it does not appear that there is an improvement in performance with such a composition. However, under certain circumstances, the higher concentration in the form of a concentrate may be desirable, for reasons such as ease of handling.

The aqueous composition of the S-triazine compound is applied under conditions that produce a corrosion-resistant barrier which is receptive to a subsequent coating process such as a conventional coating or electrocoating. The temperature of the aqueous composition at which a substrate is treated therewith is from 30 °C to 80 °C and preferably 40 °C to 60 °C. The pH of the treating composition during application is 3.4 to 6 and preferably 4 to 5.0.

In the process of this invention, the aqueous composition of the S-triazine compound is employed in treating a ferrous metal, such as cold rolled steel, or galvanized steel, comprising a phosphate conversion coating: a zinc phosphate conversion coating is preferred herein. The aqueous composition containing the S-triazine compound is applied to the phosphate conversion coating by spraying, immersion or any other convenient means. After the aqueous composition has been applied, the metal is usually rinsed with deionized water and then coated with a surface coating, usually after it has been dried.

In a typical pretreatment process, the metal to be treated is cleaned by a physical or chemical means and water rinsed in order to remove surface contamination such as grease or dirt. The metal surface is then brought into contact with a phosphate conversion coating composition, rinsed with water and then rinsed with the composition of this invention. After the application of the aqueous solution of the S-triazine compound with rinsing and drying, the ferrous metal or galvanized steel surface can be coated by any convenient means. It has been found that the pretreatment process of the metal with the aqueous composition of the S-triazine compound imparts to the coated substrate improved adhesion and corrosion resistance properties.

The invention is further illustrated by the following non-limiting examples.

Example 1

Hot dipped galvanized steel panels were phosphated with CHEMFOS 710 zinc nickel manganese phosphating solution (from Chemfil Corporation) at an average coating weight of 2.91g/m² (270 mg/ft²). The panels were then rinsed with water to remove residual phosphating chemicals and then immersed for 30 seconds in an aqueous solution of cyanuric acid at 48.9 °C (120 °F). Two concentrations of the cyanuric acid solutions were employed: 0.1 and 0.2 percent cyanuric acid in city water. The measured pH's were 4.0 and 3.4, respectively. The panels were dried with a compressed air jet and primed the same day with ED315OW electrodeposition primer (from PPG Industries, Inc., herein "PPG") at about 240 volts giving about 30 to 40µm (1.2 to 1.6 mils) dry film thickness. The panels were subsequently top coated with HUBC 90270 white basecoat (from PPG) at about 22.5µm (.9 mils) and then with URC 1000 clearcoat (from PPG) at about 47.5µm (1.9 mils). The panels were then prepared for testing by scribing and abrading with steel shot according to the "CHRYSLER" chipping scab test procedure, as follows.

1. 10.2cmx30.5cm (4" x 12") test panels were coated as described above.
2. The top half of the panel was scribed with a 12 cm (4.7") "X" scribe. A strip of pull tape was firmly applied to one side of the "X" and removed in a rapid vertical motion. Repeat of this procedure was conducted with the other side of the "X".
3. The air pressure of the gravelometer (from the Q-Panel Company) was adjusted to 205 kPa (30 psi).
4. The air valve of the gravelometer was shut off and 200 ml (32 oz.) of steel shot was collected.
5. A test panel was placed in the panel holder with the coated side facing the gravel projecting mechanism of the gravelometer. This lid of the test chamber was then closed.
6. The air valve was opened to let the pressure stabilize. Two hundred milliliters (200 ml) (32 oz.) of shot was poured into the hopper. The air was turned off when all of the shot had been spent.
- 7) The panel was placed in 5 percent salt solution (pH of about 6.6 to 7.1) for a minimum of 15 minutes.
- 8) The panel was removed and allowed to recover at lab conditions for 1 hour and 15 minutes and then placed in humidity cabinet for 22.5 hours.

An "accelerated" test was conducted as follows:

- a) The humidity cabinet was set at 85 percent relative humidity and 60 °C (140 °F).
- b) A cycle program as outlined in steps 7 to 8 was run over a period of four days.
- c) Thereafter (on the fifth day), the panel was removed from the humidity cabinet and within 30 minutes, steps 3 to 8, as set forth above, were followed.
- d) At the conclusion of a five-week cycle of steps a - c (after step 6), the panels were washed with sponge and water (a mild detergent could be used). Excess water was removed and the panel(s) were allowed to recover for 30 minutes.
- e) The target areas was covered with pull tape and removed as outlined in step 2.
- f) The percent paint loss in the target area was estimated.

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CONTROL: Control panels were also prepared with CHEMSEAL 20 chrome rinse (from Chemfil Corporation) and with a deionized water rinse for comparison purposes. Triplicate panels were prepared for each system and subjected to the same CHRYSLER chipping scale test as described above. The total test period was 10 weeks. The panels were evaluated according to the amount of paint removed by taping with #898 3M SCOTCH tape after the test period. The results of the tests are reported in Table I hereinbelow.

TABLE I

RESULTS	PAINT ADHESION LOSS
.1% aqueous composition of cyanuric acid rinse	4%
.2% aqueous composition cyanuric acid rinse	4%
CHEMSEAL 20 chrome rinse	10%
Deionized water rinse	24%

EXAMPLE 2

Cold rolled steel (CRS) and hot dipped galvanized (HDG) panels were phosphated with CHEMFOS 86 zinc nickel phosphate (from Chemfil Corporation) at about 2.48 g/m² (230 mg/ft²). After rinsing with water, the panels were immersed for 30 seconds in a .1 percent solution of cyanuric acid in water at 48.9 °C (120 °F), pH at 4.1.

Controls for comparison were made with CHEMSEAL 20 chrome rinse and with deionized water. The series were rinsed with deionized water, dried with a compressed air jet, and primed with UNI-PRIME electrocoat (from PPG) at 240 volts for 30μm (1.2 mils) thickness on cold rolled steel. The panels were top coated with HUBC 90270 white basecoat at 25.4μm (1.0 mils) and URC 1000 clearcoat at 40μm (1.6 mils). Triplicate panels were prepared and tested according to the CHRYSLER chipping scab test described in Example 1. The results of the test are reported in Table II hereinbelow.

TABLE II

RESULTS	PAINT ADHESION LOSS ON:	
	HDG ¹	CRS ²
.1% aqueous composition of cyanuric acid rinse	6%	17%
CHEMSEAL 20 Rinse	.5%	24%
Deionized Water Rinse	12%	24%

(1) Hot dipped galvanized steel.

(2) Cold rolled steel.

EXAMPLE 3

Heavy gauge hot rolled steel panels were pretreated with CHEMFOS 86 zinc nickel phosphate coating at about 2.58 g/m² (240 mg/ft²), rinsed with water, and immersed for 30 seconds in .1 percent aqueous composition of cyanuric acid at 48.9 °C (120 °F). The panels were then rinsed again with water, dried with compressed air, and then painted with a single coat of ED 4201 black electrocoat primer (from PPG) at about 20μm (.8 mils) dry thickness.

Control panels were prepared with CHEMSEAL 20 chrome and with deionized water rinses. Triplicate panels were prepared for each system and tested in essentially the same manner as described in the CHRYSLER scab test cabinet for eight weeks. The results of the test are reported in Table III hereinbelow.

TABLE III

RESULTS	SCRIBE CREEPAGE FACE CORROSION (ASTM D610-85)*
.1% Cyanuric Acid Rinse	6.35mm ($\frac{1}{4}$ inch) 7
CHEMSEAL 20 Rinse	7.94mm (5/16 ") 6
Deionized Water Rinse	12.7mm ($\frac{1}{2}$ + ") 7

*The numerical rating for this aspect of the test is based on a scale of 0 to 10, with 10 indicating no failure and 0 indicating the total failure from rusting accompanying blistering which is not initially evidenced by visible rust.

Claims

1. A process for rinsing a phosphate conversion coating applied to a ferrous metal or galvanized steel prior to the application of a subsequently applied coating, comprising applying to the phosphate conversion coating an aqueous chromic acid free composition having a pH of 3.4 to 6.0 at a temperature of 30 ° C to 80 ° C, said composition comprising at least 0.01 percent by weight based on the total weight of the composition of an S-triazine compound having at least one hydroxyl group on a carbon atom of the triazine ring.
2. The process of claim 1 in which the S-triazine compound is cyanuric acid.
3. The process as claimed in claim 1 or 2 characterised in that the pH is 4 to 5.0.
4. The process as claimed in any of claims 1 to 3 characterized in that the S-triazine compound is present in an amount of .05 to .15 percent based on total weight of the aqueous composition.
5. The process as claimed in any of claims 1 to 4 in which the phosphate conversion coating is a zinc phosphate conversion coating.
6. The process as claimed in any of claims 1 to 5 characterised in an additional step of applying a surface coating to the metal substrate which has been previously contacted with the aqueous composition of the S-triazine compound.
7. The process as claimed in claim 6 in which the surface coating is applied by electrodeposition.

Patentansprüche

1. Verfahren zum Waschen von mit einer umgewandelten Phosphatierungsbeschichtung versehenen Eisenmetall oder galvanisiertem Stahl vor dem Aufbringen einer anschließend aufgetragenen Beschichtung durch Aufbringen einer wäßrigen chromsäurefreien Zusammensetzung mit einem pH von 3,4 bis 6,0 bei einer Temperatur von 30 ° C bis 80 ° C auf die umgewandelte Phosphatierungsbeschichtung, wobei die Zusammensetzung mindestens 0,01 Gew.-%, bezogen auf Gesamtgewicht der Zusammensetzung, einer S-Triazinverbindung mit mindestens einer Hydroxylgruppe an einem Kohlenstoffatomen des Triazinringes enthält.
2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß die S-Triazinverbindung Cyanursäure ist.
3. Verfahren nach Anspruch 1 oder 2,
dadurch gekennzeichnet,
daß der pH Wert 4 bis 5,0 ist.
4. Verfahren nach einem der vorstehenden Ansprüche 1-3,
dadurch gekennzeichnet,

daß die S-Triazinverbindung in einer Menge von 0,05 bis 0,15 %, bezogen auf Gesamtgewicht der wäßrigen Zusammensetzung, vorhanden ist.

- 5 5. Verfahren nach einem der vorstehenden Ansprüche 1-4,
dadurch gekennzeichnet,
daß die umgewandelte Phosphatierungsbeschichtung eine umgewandelte Zinkphosphatbeschichtung ist.
- 10 6. Verfahren nach einem der vorstehenden Ansprüche 1-5,
gekennzeichnet durch
den zusätzlichen Schritt des Aufbringens einer Oberflächenbeschichtung auf den Metallträger, der zuvor mit der wäßrigen Zusammensetzung der S-Triazinverbindung in Berührung gebracht wurde.
- 15 7. Verfahren nach Anspruch 6,
dadurch gekennzeichnet,
daß die Oberflächenbeschichtung durch Elektrotauchlackierung aufgebracht wird.

Revendications

- 20 1. Procédé de rinçage d'un revêtement de conversion au phosphate appliqué à un métal ferreux ou à un acier galvanisé avant l'application d'un revêtement appliqué ultérieurement, comprenant l'application au revêtement de conversion au phosphate d'une composition aqueuse exempte d'acide chromique ayant un pH de 3,4 à 6,0, à une température de 30 ° C à 80 ° C; ladite composition comprenant au moins 0,01 pourcent en poids par rapport au poids total de la composition d'un composé de S-triazine ayant au
25 moins un groupe hydroxyle sur un atome de carbone du cycle triazine.
2. Procédé selon la revendication 1, dans lequel le composé S-triazine est l'acide cyanurique.
3. Procédé selon la revendication 1 ou 2 caractérisé en ce que le pH est de 4 à 5,0.
- 30 4. Procédé selon l'une quelconque des revendications 1 à 3 caractérisé en ce que le composé S-triazine est présent en une quantité de 0,05 à 0,15 pourcent par rapport au poids total de la composition aqueuse.
- 35 5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le revêtement de conversion au phosphate est un revêtement de conversion au phosphate de zinc.
6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en une étape supplémentaire d'application d'un revêtement superficiel au substrat de métal que l'on a au préalable mis en contact
40 avec la composition aqueuse du composé S-triazine.
7. Procédé selon la revendication 6, dans lequel on applique le revêtement superficiel par électrodéposition.

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