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(54) **PROCEDE D'APPLICATION D'UN ENDUIT DE CONVERSION SUR DES SURFACES DE ZINC OU D'ALLIAGES DE ZINC**

(54) **FORMATION OF CONVERSION COATINGS ON SURFACES OF ZINC OR ZINC ALLOYS**

(57) In a process of forming conversion coatings on surfaces of zinc and zinc alloys, in which the surfaces are contacted in a first stage with a solution which contains at least two different polyvalent metal ions and also contains such an amount of complexing agent that the polyvalent metal ions are kept in solution, and which has a pH value of at least 11, and the surfaces are treated in a succeeding stage with a post rinsing solution, a succeeding stage comprises a treatment with a post rinsing solution which contains aluminum, zirconium and fluoride and has been adjusted to a pH value not in excess of five. According to desirable features of the process the total concentration of Al + Zr + F is adjusted to a value between 0.1 and 8.0 g/l, preferably between 0.2 and 5.0 g/l, and the Al : Zr : F mole ratio is adjusted to (0.15 to 8.0) : 1 : (5 to 52) or to (0.15 to 0.67) : 1 : (5 to 7). The treatment is suitably carried out for 1 to 120 seconds preferably 1 to 30 seconds, and at a temperature of 20 to 80 °C, preferably 20 to 50 °C. The process can desirably be used for a pretreatment before a succeeding painting, film laminating or adhesive coating operation.

ABSTRACT

In a process of forming conversion coatings on surfaces of zinc and zinc alloys, in which the surfaces are contacted in a first stage with a solution which contains at least two different polyvalent metal ions and also contains such an amount of complexing agent that the polyvalent metal ions are kept in solution, and which has a pH value of at least 11, and the surfaces are treated in a succeeding stage with a post rinsing solution, a succeeding stage comprises a treatment with a post rinsing solution which contains aluminum, zirconium and fluoride and has been adjusted to a pH value not in excess of five.

According to desirable features of the process the total concentration of Al + Zr + F is adjusted to a value between 0.1 and 8.0 g/l, preferably between 0.2 and 5.0 g/l, and the Al : Zr : F mole ratio is adjusted to (0.15 to 8.0) : 1 : (5 to 52) or to (0.15 to 0.67) : 1 : (5 to 7).

The treatment is suitably carried out for 1 to 120 seconds preferably 1 to 30 seconds, and at a temperature of 20 to 80 °C, preferably 20 to 50 °C. The process can desirably be used for a pretreatment before a succeeding painting, film laminating or adhesive coating operation.

This invention relates to a process of forming conversion coatings on surfaces of zinc and zinc alloys, comprising a first stage of contacting the surfaces with a solution containing at least two different polyvalent metal ions and complexing agent in such an amount that the polyvalent metal ions are kept in solution, and a pH value of at least 11, and a following stage of rinsing the surfaces with a post rinsing solution, wherein the post rinsing contains aluminum, zirconium, and fluoride having a Al : Zr : F molar ratio of (0.15 to 8) : 1 : (5 to 52) and a pH value not in excess of 5.

Such a process of forming a conversion layer is known from DE-C-1 521 854 published on 15 July 1971 particularly as a pretreatment before a painting or film laminating operation.

The layer is formed on the surface of zinc or zinc alloy by a treatment with aqueous alkaline solutions, which contain so-called non-alkali metal ions consisting of ions of one or more of the metals silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, iron, and nickel. It has been emphasized that particularly suitable solutions contain non-alkali metal ions consisting of ions of iron or of cobalt together with another of the stated metals. The solutions also contain organic complexing agents in an amount which is sufficient to keep the non-alkali metal ions in solution. The conversion coatings formed by means of said ions will increase the resistance to corrosion and will improve the adhesion of subsequently applied organic coatings.

The resistance to corrosion and the bond strength will be further improved if the surfaces on which the conversion layer has been formed are post-rinsed with an acid solution which contains hexavalent chromium and optionally contains also trivalent chromium.

Whereas that known process produces good results as regards the resistance to corrosion and the bond strength, the use of trivalent chromium ions and particularly of hexavalent chromium ions in the passivating post rinse solution is most undesirable because hexavalent chromium is toxic and requires a special disposal.

It is an object of the invention to provide for the formation of conversion coatings on surfaces of zinc or zinc alloys a process by which the disadvantages of the known process are avoided and, in particular, the environment is not polluted or is only very slightly polluted and which produces at least equally good results as regards the resistance to corrosion and the adhesion of paint.

That object is accomplished in that the process of the kind described first hereinbefore is carried out in such a manner in accordance with the invention that the solution used for post rinsing contains aluminum, zirconium, and fluoride and has been adjusted to a pH value not in excess of 5 .

The process in accordance with the invention can be used to treat all surfaces which contain zinc or zinc alloys, such as materials of massive zinc or massive zinc alloys, but also to treat surfaces which have been plated with zinc or zinc alloys electrolytically, by deposition from the gas phase or by hot dip coating. Elements which can be alloyed with zinc include particularly aluminum, silicon, lead, iron, nickel, cobalt and manganese. Sheet materials may be plated with zinc or with a zinc alloy on one side or on both sides.

If the surface of zinc or zinc alloy is only slightly greased or soiled, there may be no need for a preceding cleaning and degreasing of the surface. In said cases, surfactants may be added in the first stage so that the cleaning and degreasing are effected with the treating solution used also to form the conversion coating. That embodiment affords mainly the advantage that the entire pretreatment of the surface can be carried out in fewer stages because the separate cleaning and the associated rinsing with water are omitted.

The alkaline solution used in the first stage may be applied, e.g., by spraying, dipping or flooding.

It has been found that alkaline solutions which contain iron(III) ions and additionally contain cobalt ions and/or nickel ions and/or chromium (III) ions and/or aluminum ions in a total content between 0.3 and 3 g/l, preferably between 0.4 and 1.2 g/l, are particularly suitable. The polyvalent metal ions may be used as salts of inorganic acids, such as nitric acid, or as salts of organic acids, such as formic acid and particularly also of acetic acid. It is also possible to use salts of such organic acids which also serve as complexing agents. Amphoteric metals, such as aluminum, may be dissolved in the form of the hydroxy complex even without an additional anion or complexing agent.

Due to the pickling attack during the treatment in the first stage, additional polyvalent cations, which are present in the surface to be treated and are not contained in the freshly prepared bath solution, may enter the treating solution from the surface of zinc or zinc alloy. On surfaces plated with zinc by hot dipping such cations consist of e.g. zinc, aluminium and lead. The total concentration of such cations may increase up to a few grams per liter and in general this will not disturb the formation of the conversion coating.

Suitable complexing agents include particularly organic chelating agents of various kinds, for instance, dicarboxylic acids (malonic acid, fumaric acid etc.); amino acids (e.g., glycine); hydroxycarboxylic acids (e.g., citric acid, gluconic acid, lactic acid); 1,3-diketones (e.g., acetylacetone); aliphatic polyalcohols (e.g., sobitol, 1,2-ethanediol); aromatic carboxylic acids (e.g., salicylic acid, phthalic acid); aminocarboxylic acid (e.g., ethylenediamine-tetraacetic acid). Other complexing agents, such as methanephosphonic acid diethanolamide, may also be used. The amount of the complexing agent contained in the solution must be sufficient for a complex binding of all polyvalent metal ions which are present. For this reason the content of complexing agent must be increased too when the content of polyvalent metal ions in the solution increases. Because increasing amounts of certain complexing agents, which are inherently acidic, may decrease the alkalinity of the solution, it is preferred to use complexing agents in the form of neutral salts, particularly of the alkali metal salts. It has been found that no advantage will be afforded by the use of complexing agents in a surplus.

Particularly desirable results will be produced by the use of complexing agents consisting of salts of gluconic acid, particularly of hexahydroxyheptanoic acid. The solution should contain complexing agents in an amount between 0.05 and 10 g/l, in most cases between 1.5 and 5.5 g/l (based on the sodium salt of hexahydroxyheptanoic acid)

The aqueous solution must have a pH value of at least 11. Best results will be produced with pH values in the range from 12.2 to 13.3. The pH value may be adjusted, e.g., by triethanolamine, alkali hydroxides, alkali carbonates, alkali phosphates, alkali polyphosphates, alkali pyrophosphates, alkali borates, alkali silicates or mixtures thereof. But the use of alkali hydroxides, particularly sodium hydroxide, is most desirable.

The temperature of the solution used in the first stage may generally lie between 20 and 90°C. The preferred temperature range is about 45 to 65°C.

The treating time is generally about 2 to 60 seconds, as a rule, and preferably 5 to 30 seconds. It will depend, inter alia, on the application technology that is employed. For instance, the treating time will be shorter in a spraying process than in a dipping process under conditions which are equal in other respects.

In general, solutions having a lower metal ion concentration must be used at higher temperatures and for longer treating times than solutions having a higher metal ion concentration.

When a conversion coating has been formed, any surplus treating solution should be removed as completely as possible from the surface of zinc or zinc alloy. That may be effected, e.g., by dripping, squeegeeing, blasting or rinsing with water or with an aqueous solution, which may have been acidified, e.g., by an inorganic of organic acid (hydrofluoric acid, boric acid, nitric acid, formic acid, acetic acid, etc.).

The post rinse solution may be applied, e.g., by dipping, flooding, spraying or roller coating.

In a preferred embodiment of the invention the solution employed for the aftertreatment contains aluminum, zirconium and fluoride in a total concentration of Al + Zr + F between 0.1 and 8 g/l preferably between 0.2 and 5 g/l. The Al : Zr : F mole ratios should desirably be adjusted to (0.15 to 8) : 1 : (5 to 52), particularly to (0.15 to 2.0) : 1 : (5 to 16). In a particularly preferred embodiment of the process the

Al : Zr : F ratio in the post rinsing solution is (0.15 to 0.67) : 1 : (5 to 7). According to a further preferred feature of the invention the pH value should be adjusted to 2 to 5.

The post rinsing solutions used in the process in accordance with the invention contain, inter alia, acid aluminum fluoride zirconates and in case of a surplus of aluminum additionally contain other salts of aluminum, such as fluorides, tetrafluoroborates, nitrates. They may be produced, e.g., in that zirconium metal or zirconium carbonate is initially dissolved in aqueous hydrofluoric acid to form complex fluorozirconium acid. Aluminum metal or aluminum hydroxide or an aluminum salt, such as the nitrate, fluoride, tetrafluoborate, formate, acetate, is then added, preferably in dissolved form, and is optionally dissolved. A possible slight cloudiness of the solution will not adversely affect its effectiveness. Whereas the preparation is preferably effected on the described route, the solutions may alternatively be prepared in a different manner.

The pH value of the solution is preferably adjusted with cations of volatile bases. These include particularly ammonium, ethanolammonium and di- and triethanolammonium. The adjustment particularly to relatively high pH value in the stated pH range and to relatively high concentrations in the range stated for the total concentration of Al + Zr + F may result in a cloudiness of the solution but this will not adversely affect the effectiveness of the process.

According to a further desirable feature of the invention the surfaces provided with a conversion coating are rinsed with an aqueous solution which additionally contains at least one of the anions benzoate, caprylate, ethyl hexoate, salicyate, preferably in a total concentration of 0.05 to 0.5 g/l. This will further increase the bare corrosion protection. The anions may be introduced by means of the corresponding acids or their salts.

According to a further desirable feature of the invention the post rinsing solution is applied for between about 1 and 120 seconds, particularly for between 1 and 30 seconds. The solution may be applied at a temperature between 20°C and about 80°C. Temperatures between 20 and 50 °C are preferred.

Deionized water or low-salt water is preferably used to prepare the post rinsing bath. Water having a high salt content is less suitable for the preparation of the bath.

After the passivating aftertreatment the surface may be dried, e.g., on the air or in an oven and optionally may be rinsed before with deionized water. According to a preferred embodiment of the invention the surface which has been subjected to the passivating aftertreatment is subjected to an accelerated drying, e.g., with hot air or by infrared radiation.

The process in accordance with the invention serves primarily to pretreat surfaces of zinc or zinc alloys before they are painted, laminated with a film or coated with an adhesive. It will improve the adhesion of the organic films on the metallic substrate and will also improve their resistance to a formation of blisters under corrosive action and will inhibit subsurface corrosion proceeding from defects in the film.

The process in accordance with the invention will be explained more in detail and by way of example with reference to the following example.

Example

To form a conversion coating on cleaned and degreased sheets of hot galvanized steel they were dipped for 30 seconds into a solution which was at a temperature of 55°C and had the following composition:

Co^{2+}	0.3 g/l
Fe^{3+}	0.2 g/l
NO_3^-	1.3 g/l
sodium salt of hexahydroxyheptanoic acid	2.2 g/l
NaOH	27.4 g/l

Thereafter the sheets were rinsed with

water and were then subjected to a passivating after-treatment. To that end the sheets were dipped into the post rinse solution for 5 seconds and were subsequently squeegeed for a removal of surplus solution. After a drying at 75°C in an oven operated with circulating air for 0.5 minute the pretreated sheets were painted with an epoxy primer and an acrylate top coat. The total coating had a thickness of about 25 µm.

The treated sheets were subsequently subjected to the following tests:

The adhesion of paint was determined by the T-Bend Test, in which the sheets were bent through 180° and the various radii of curvature (Tn) were stated as amounting to n times the sheet metal thickness (n==, 1,2 ...). The test result is stated as the percentage of the flaked-off paint surface area in the total curved surface area.

In other treated sheets, scratches extending as far as to the metal substrate were made by means of a metal needle and the sheets were formed with a cut edge by plate shears. Thereafter the sheets were subjected to the salt spray test in accordance with DIN 50021 SS for 1008 hours. The test result was stated as the extent in mm of the migration under the paint from the crack or the cut edge.

To prepare the post rinsing solution to be employed, 1,6 g/l and 20 g/l respectively of an aqueous concentrate, which contained

0.855% by weight Al and 8.62% by weight Zr and 10.7% by weight F, was diluted with deionized water to yield post rinsing solution A and post rinsing solution B. Both solutions were adjusted with ammonia to a pH value of about 3.6.

For comparison, a post rinsing solution C was employed, which contained Cr(VI) and Cr(III) and had a pH value of about 3.3.

The post rinsing solutions had the following compositions:

Post rinsing solution A:

Al	0.014 g/l
Zr	0.14 g/l
F	0.17 g/l
NH_4	0.016 g/l

Post rinsing solution B:

Al	0.17 g/l
Zr	1.72 g/l
F	2.14 g/l
NH_4	0.40 g/l

Post rinsing solution C:

Cr^{6+}	2.0 g/l
Cr^{3+}	0.8 g/l
F	0.2 g/l
Zn	0.3 g/l

The test results are stated in the following Tables.

Table 1: Paint adhesion in T-Bend Test

Post rinsing Solution	Flaked off surface area (%) in case of radius of curvature Tn			
	T1	T2	T3	T4
A (invention)	100	55	15	5
B (invention)	100	65	25	5
C (comparison)	100	80	30	5

Table 2: Resistance to corrosion in salt spray test

Post rinsing solution	migration under paint (mm) after 1008 h	
	at the scratch	at the edge
A (invention)	<1 to 1	8 to 9
B (invention)	0 to 1	7
C (comparison)	1 to 3	9 to 10

A comparison of the tabulated data reveals that the data obtained with the process in accordance with the invention are just as good or better than those of the also tested comparison process in which an post rinsing solution was used that contained Cr(VI) and Cr(III).

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process of forming conversion coatings on surfaces of zinc and zinc alloys, comprising a first stage of contacting the surfaces with a solution containing at least two different polyvalent metal ions and complexing agent in such an amount that the polyvalent metal ions are kept in solution, and a pH value of at least 11, and a following stage of rinsing the surfaces with a post rinsing solution, wherein the post rinsing solution contains aluminum, zirconium, and fluoride having a Al : Zr : F molar ratio of (0.15 to 8) : 1 : (5 to 52) and a pH value not in excess of 5.

2. A process according to claim 1, wherein the post rinsing solution contains aluminum, zirconium and fluoride in a total concentration of Al + Zr + F between 0.1 and 8 g/l.

3. A process according to claim 2, wherein the total concentration of Al + Zr + F is between 0.2 and 5 g/l.

4. A process according to any one of claims 1 to 3, wherein the post rinsing solution has a Al : Zr : F molar ratio of (0.15 to 0.67) : 1 : (5 to 7).

5. A process according to any one of claim 1 to 4, wherein the pH value of the post rinsing solution has been adjusted to 2 to 5.

6. A process according to any one of claims 1 to 5, wherein the pH value of the post rinsing solution has been adjusted with cations of volatile bases.

7. A process according to claim 6, wherein said volatiles bases are selected from the group of consisting of ammonium, ethanolammonium and di- or triethanolammonium.

8. A process according to any one of claims 1 to 7, wherein the post rinsing solution additionally contains at least one of the anions benzoate, caprylate, ethyl hexoate, salicylate, in a total concentration of 0.05 to 0.5 g/l.

9. A process according to any one of claims 1 to 8, wherein the rinsing with the post rinsing solution takes 1 to 120 seconds.

10. A process according to any one of claims 1 to 9, wherein the post rinsing solution has a temperature of 20 to 80°C.

11. A process according to any one of claims 1 to 10, wherein the surface is dried after the post rinsing with the post-rinsing solution.

12. A process according to any one of claims 1 to 11, wherein the rinsing with the post rinsing solution takes 1 to 30 seconds.

13. A process according to any one of claims 1 to 12, wherein the post rinsing solution has a temperature of 20 to 50°C.

14. The use of the process according to any one of claims 1 to 13 as a pretreatment before a painting, film-laminating or adhesive coating operation.