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(54) Process for the preparation of corrosion resistant zinc and zinc-nickel plated linear or complex shaped parts

(57) A process for the preparation of corrosion resistant two layer plating of zinc and zinc-nickel for linear or complex shaped parts is described. Such layers possess a very homogeneous thickness distribution and corrosion protection with the advantage of not using high concentrations of strong complexing agents (e.g. amines or ammonia). Furthermore, the layers have good ductility.

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Description

[0001] The present invention relates to a process for the preparation of corrosion resistant zinc and zinc nickel deposits on linear or complex shaped parts, usually made of steel. The deposition according to the present invention consists of a two step deposition, wherein a layer of zinc from an alkaline zinc bath and a layer of zinc nickel alloy deposited from an acid bath is deposited.

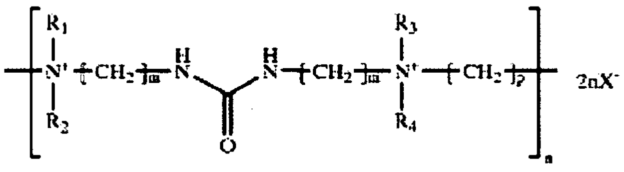
[0002] Such coated substrates possess a similar corrosion protection and similar thickness distribution as zinc nickel coated parts deposited from an alkaline zinc nickel electrolyte with the advantage of not using high concentrations of amines or ammonia as strong complexing agents and not forming cyanide while at the same time providing reasonable post-forming capability.

[0003] A lot of components in a diversity of applications are plated for protection from corrosion. In order to provide the required corrosion protection, zinc or zinc alloy coatings are plated onto these components to the desired thickness. Often a passivating conversion coating is applied on top of the zinc or zinc alloy coating, typically by immersion of the substrate into an acidic solution containing trivalent chromium salts. For even further improvement, such passivated parts are often immersed in sealer solutions and dried.

[0004] Substrates to be plated either have a linear shape (like window frames) or complex shapes (like lock housings). These kind of parts are preferably plated from an alkaline electrolyte as the current efficiency in the high current density area (on the end of linear parts or at the edges of complex shaped parts) is reduced by using special polymeric inhibitors. Due to this fact the deposited coating exhibits a very homogeneous thickness distribution over the entire component surface and also provides excellent corrosion protection.

[0005] As corrosion is very aggressive when the component is used in a humid environment the corrosion protection requirement for window frames and automotive components is steadily increasing. For this reason zinc-nickel coatings become more and more interesting to the industry and alkaline electrolytes were developed. Such bath usually contain zinc ions, nickel ions and poly(alkyleneimines) obtained from ethyleneimine, 1,2-propyleneimine, 1,2-butyleneimine and 1,1-dimethylethyleneimine. The poly(alkyleneimines) may have molecular weights of from about 100 to about 100,000.

[0006] US 6,652,728 discloses a zinc and zinc alloy bath which contains zinc ions, hydroxide ions, optionally nickel ions and a polymer having the following formula:



Wherein m has a value of 2 or 3, n has a value of at least 2; R_1, R_2, R_3, which may be the same or different, each independently denote methyl, ethyl or hydroxyethyl; p has a value in the range from 3 to 12; and X^- denotes chloride, bromide and/or iodide.

[0007] Such bath is suitable for depositing alkaline zinc deposits.

[0008] The best corrosion protection is realized when the zinc-nickel coating contains a gamma-phase zinc-nickel alloy. This is realized with a nickel content of an average of 15 %. However, this coating is significantly less ductile than pure zinc coatings.

[0009] There is a disadvantage of using alkaline zinc-nickel electrolytes, because all such electrolytes used in the plating industry today contain require high amounts of strong amine complexing agents for success plating. In the plating industry a lot of rinse water has to be waste water treated and with complexing agents in the water it is very difficult to realize the limit values for metals. For this reason high investments have to be made by the plating industry to treat the waste water. EP 1 369 505 A2 teaches to evaporate a part of the process bath until phase separation occurs and separate the organic from the aqueous phase. However, this procedure is both energy and time consuming. Another disadvantage when using alkaline baths is the formation of cyanide by an anodic oxidation. This can only be avoided by other important investments like membranes to prevent anodic oxidation of amine complexing agents to cyanide as for example described in WO 00/06807 and WO 01/96631).

[0010] It is the object underlying the present invention to provide a plating process for coating of linear and complex shaped parts, which satisfies the stringent requirements for corrosion protection and post-forming capability and at the same time does not apply high concentrations of amines or ammonia as complexing agent in the electrolytes used. Furthermore, it is the aim to obtain a deposit with homogeneous surface distribution also for workpieces having a complex shape.

[0011] This object is achieved by a process for the preparation of corrosion resistant two layer system of zinc and zinc-nickel onto substrates comprising the steps of:

(i) plating of a zinc coating from an alkaline electrolyte providing very homogeneous thickness distribution and resistance against corrosion of the coating with good ductility,

(ii) plating a layer of a zinc nickel alloy from an acidic zinc nickel plating bath having a high corrosion protection, particularly against red rust,

(iii) optionally, providing a Cr(VI)-free passivating conversion coating for the zinc nickel surface,

(iv) optionally, applying a sealer.

[0012] Thus, according to the present invention a process is provided wherein the homogeneous coating thickness and ductility is provided by a pure zinc layer also providing corrosion protection and the very high corrosion protection particularly regarding red rust is provided by a subsequent zinc-nickel, which is deposited from an acid electrolyte and which does not contain high concentrations of amines or ammonia.

[0013] In one embodiment, the pure zinc layer is deposited on the metal substrate and the zinc nickel layer is deposited on the zinc layer:

[0014] Such process for the preparation of corrosion resistant substrate comprises the steps of

(i) providing a metal substrate

(ii) plating a layer of zinc from an alkaline electrolyte thereon,

(iii) plating a layer of zinc-nickel from an acid electrolyte.

[0015] In a second embodiment the zinc nickel layer is deposited on the metal substrate and the zinc deposited on the zinc nickel layer.

[0016] Such process for the preparation of corrosion resistant substrate comprises the steps of

(i) providing a metal substrate

(ii) plating a layer of zinc-nickel from an acid electrolyte thereon,

(iii) plating a layer of zinc from an alkaline electrolyte.

[0017] The thickness of the zinc layer typically is between 1 - 12 μm, preferably between 2 - 8 μm, and more preferably 4-6 μm.

[0018] The thickness of the zinc nickel layer typically is between 1 - 12 μm, preferably between 2 - 8 μm, and more preferably 4-6 μm.

[0019] The alkaline zinc electrolyte preferably has the following composition:

5 - 20 g/l Zn ions from a souble zinc source, e.g. ZnO

80 - 250 g/l hydroxide like NaOH

0.1 - 5 g/l Polymer (as described in Example 2.1 of US 6,652,728).

[0020] Brightening additives are used depending on the demand of the optical aspect. Such brightening agents are well known in the art and for example described in US 6,652,728.

[0021] A suitable process for preparing such an alkaline zinc electrolyte is described, for example in European patent application EP 1 114 206.

[0022] Acid zinc nickel electrolytes are known in the art and for example described in US 4,699,696. Such acid zinc-nickel electrolytes solutions contain zinc ions and nickel ions, and an additive agent of a class selected from the group consisting of (a) aromatic sulfonic acids, (b) aromatic sulfonamides, sulfonimides and mixed carboxamides/sulfonamides, (c) acetylene alcohols.

[0023] Solutions for passivating zinc and zinc alloy surfaces are known and for example described in EP 1 484 432.

Such solutions typically contain a water soluble Cr(III)-salt in a concentration of 0.5-80 g/l, preferably 1-40 g/l, more preferably 1-10 g/l. The pH of such solution is 0.8 - 4.0 and the temperature 10-80°C. Furthermore, the passivate solution can contain additional metals such as cobalt, nickel, zinc, iron, zircon, titanium, aluminium, silver, copper, pigments. Optional additional components contain silicates, nitrates, phosphates, fluorides and polymer resins. For treatment the zinc and zinc nickel plated surface is immersed in the passivation solution, rinsed and thereafter optionally treated at elevated temperatures of 100 to 250°C for 10 to 300 minutes.

[0024] According to the following examples coatings are obtained by electroplating in zinc and an acid zinc-nickel electrolytes. Thickness distribution was tested according to the following test procedure:

Comparative Example 1 - Deposition of a pure zinc layer from an alkaline zinc plating bath

[0025] 250 ml of an alkaline zinc electrolyte, which contains zinc ions in an amount of 10 g/l, 120 g/l NaOH, 0.5 g/l polymeric inhibitor according to Example 2.1 of US 6,652,728 and a brightening additive, the composition of which is described in US 6,652,728, is filled into a Hull cell.

[0026] Zinc is used as anode material. The cathode steel panel will be deposited for 15 minutes at 1 A. The temperature is 28°C. The panel is rinsed and dried. The thickness distribution is measured at 2 positions on the panel: 3 cm of the lower edge and 2.5 cm of the right and left edge of the panel at high (app. 2.8 A/dm^2) and low current density (app 0.5 A/dm^2). The thickness of the coating is measured four times at the two positions to avoid measuring mistakes. The thickness distribution is the ratio of the measured layer thicknesses between the two positions (thickness distribution = thickness at high current density : thickness at low current density).

Comparative Example 2 - Deposition of a zinc nickel layer from a commercially available alkaline zinc nickel plating bath

[0027] The same test was performed with a zinc nickel layer obtained from an alkaline zinc nickel electrolyte Reflectalloy® ZNA (commercially available from Atotech Deutschland GmbH and described in US 5,417,840) with 1 A for 15 minutes plating at a temperature of 28°C in the Hull cell.

Comparative Example 3 - Deposition of a zinc nickel layer from a commercially available acidic zinc nickel plating bath

[0028] The same test was performed with a zinc nickel layer obtained from an acid zinc nickel electrolyte The composition of the bath acidic zinc nickel plating bath was as follows:

$ZnCl_2$	0.3 M/l
$NiCl_2$	0.5 M/l
KCl	2.7 M/l
H_3BO_3	0.3 M/l
aromatic sulfonamide	1.1 g/l
acetylenic alcohol	0.02 g/l
sodium acetate	0.7 M/l
alkylene oxide polymer	1.1 g/l
sulfosuccinate-alkyl diester	1.1 g/l

[0029] Plating is with 1 A for 15 minutes plating at a temperature of 35°C in the Hull cell.

Example according to the present invention:

[0030] The same test was performed with a surface containing two layers, a first layer of pure zinc plated from the alkaline zinc plating bath described in Comparative Example 1 (time: 7.5 minutes, 1 A, temperature: 28°C). Thereafter a second layer of zinc nickel from the acidic zinc nickel plating bath as described in Comparative Example 3 is plated (time: 7.5 minutes, 1A, temperature: 35°C).

[0031] The coating thicknesses and the thickness distribution of all coatings is shown in Table 1.

Table 1: Thickness distribution for different plated layers

	hcd	lcd	hcd : lcd
Comp. Example 1	4.1 micron	2.8 micron	1.5
Comp. Example 2	5.5 micron	1.8 micron	3
Comp. Example 3	8.1 micron	2.2 micron	3.7
Example 4 (invention)	6.1 micron	2.6 micron	2.4

[0032] The plated thickness for the same plating time and current clearly shows that higher thicknesses and better thickness distributions - represented by the high current density (hcd) to low current density (lcd) thickness ration - can be achieved with the two layer sequence of the present invention according to Example 4 compared to the alkaline zinc nickel process Reflectalloy ZNA (Comparative Example 2). 20% higher thickness is obtained in the low current density regime.

[0033] Ductility of deposits according to the Comparative Example 2 and Example 4 was evaluated by hardness measurements.

Comparative Example 2:	600 Vicker's Hardness at 50 mN
Example 4:	525 Vicker's Hardness at 50 mN

[0034] Hardness is lower for deposits from acidic zinc nickel baths (Example 4) compared to zinc nickel deposits from alkaline baths (Comparative Example 2). Consequently the inelastic deformation work is higher for the acidic alloy process of the process according to the present invention and such deposit has superior post-forming capability.

[0035] The grain size in the zinc nickel layer also influences the ductility of the coating. With increasing grain size the ductility of the coating is increasing. A good compromise between grain size and current density is observed at a value of 2 A/dm^2.

[0036] Corrosion protection of the coatings obtained according to Example 4 was evaluated in DIN 50021 neutral salt spray exposure and found >240 h to first appearance of white corrosion and >1000 h to substrate corrosion.

[0037] The formation of gamma-phase ZnNi from the acid zinc nickel obtained by Example 4 was confirmed by XRD. Such phase exhibits very good corrosion resistance. The deposit shows a homogeneous alloy composition over a wide range of current density. The gamma phase zinc-nickel layer is consistently obtained even on complex shaped parts, as confirmed by X-ray diffraction.

Claims

1. A process for the preparation of a corrosion resistant substrate comprising the steps of

(i) providing a metal substrate
(ii) plating a layer of zinc from an alkaline electrolyte thereon,
(iii) plating a layer of zinc-nickel from an acid electrolyte.

2. A process for the preparation of a corrosion resistant substrate comprising the steps of

(i) providing a metal substrate
(ii) plating a layer of zinc-nickel from an acid electrolyte thereon,
(iii) plating a layer of zinc from an alkaline electrolyte.

3. The process according to any of the foregoing claims wherein the metal substrate is a steel substrate.

4. The process according to any of the foregoing claims wherein the layer of zinc-nickel or zinc layer is additionally treated with a Cr(VI)-free passivating conversion coating.

5. The process according to any of the foregoing claims wherein the substrate is finally treated with a sealer.

6. The process according to any of the foregoing claims wherein the zinc coating is deposited from an alkaline zinc electrolyte containing a polymeric inhibitor in a concentration of 0.2 - 2 g/l.

7. The process according to any of the foregoing claims wherein the plating is operated for 5-50 minutes at 0.5 - 5 A/dm^2 and a temperature of 18-35°C.

8. The process according to any of the foregoing claims wherein the zinc layer has a thickness of 1-12 μm, preferably 2-8 μm, more preferably 4-6 μm.

9. The process according to any of the foregoing claims wherein the acid zinc-nickel electrolyte comprises zinc in an amount of 10 - 60 g/l - and nickel in an amount of 10 - 50 g/l.

10. The process according to any of the foregoing claims wherein the plating is operated for 5-50 minutes at 0.5 - 5 A/dm^2 and a temperature of 18-35°C.

11. The process according to any of the foregoing claims wherein the passivate comprises 1 to 5 g/l Cr(III) ions.

12. The process according to any of the foregoing claims wherein the sealer comprises oxygenated silicon compounds, organo-silicon compounds, polymer dispersions made from acrylic resins, polyurethane resins, or polyethylene resins or mixtures thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 08 07 5132

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
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Y		4-6,11,12
D,Y	US 6 652 728 B1 (SONNTAG BIRGIT [DE] ET AL) 25 November 2003 (2003-11-25) * abstract * * column 1, lines 9-11,24-35,62-67 * * column 2, lines 1-6,31-42,53-57 * * column 7, lines 29-42 * * examples 13,15,16,18 *	1,3-12
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A	* column 1, line 63 - column 2, line 3 *	1

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CLASSIFICATION OF THE APPLICATION (IPC)

INV.
C25D5/12
C23C28/00

TECHNICAL FIELDS SEARCHED (IPC)

C25D
C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	3 July 2008	Zech-Agarwal, Nicole

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 08 07 5132

DOCUMENTS CONSIDERED TO BE RELEVANT

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	3 July 2008	Zech-Agarwal, Nicole

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 07 5132

03-07-2008

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