

(19)



(11)

EP 2 712 331 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
16.11.2016 Bulletin 2016/46

(51) Int Cl.:
B05D 1/18 (2006.01) **B05D 7/14** (2006.01)
C23C 2/00 (2006.01) **C23C 22/00** (2006.01)

(21) Application number: **12716407.7**

(86) International application number:
PCT/EP2012/057334

(22) Date of filing: **23.04.2012**

(87) International publication number:
WO 2012/156176 (22.11.2012 Gazette 2012/47)

(54) A PROCESS OF ELECTROLYTIC GALVANIZING WITH AN ENHANCED ANTI-CORROSIVE PROTECTION

VERFAHREN ZUR ELEKTROLYTISCHEN VERZINKUNG MIT VERBESSERTEM
KORROSIONSSCHUTZ

PROCÉDÉ DE GALVANISATION ÉLECTROLYTIQUE PRÉSENTANT UNE PROTECTION
ANTICORROSION AMÉLIORÉE

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **19.05.2011 SI 201100179**

(43) Date of publication of application:
02.04.2014 Bulletin 2014/14

(73) Proprietor: **Kovinoplastika Loz Industrija
kovinskih in
plasticnih izdelkov d. d.
1386 Stari trg pri Lozu (SI)**

(72) Inventors:
• **TRUDEN, David**
1386 Stari trg pri Lozu (SI)
• **SIMIC, Kristina**
1319 Draga (SI)

(74) Representative: **Ivancic, Bojan**
Inventio d.o.o.
Dolenjska cesta 11
1000 Ljubljana (SI)

(56) References cited:
EP-A1- 1 199 376 EP-A1- 1 524 332
DE-A1- 10 309 908 GB-A- 2 211 762
US-A- 5 108 554

EP 2 712 331 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention refers to a process of electrolytic galvanizing, thick layer passivation and subsequent treatment in order to enhance anti-corrosive protection, wherein said process comprises a pretreatment and, respectively, cleaning of products to be protected against corrosion, galvanizing in an alkaline media and final treatment.

[0002] A process of electrolytic galvanizing of the aforementioned kind has been disclosed by the publication of a patent application No. EP 1 199 376 A1. In said document is disclosed a Zn coated steel material, a Zn coated steel sheet and a painted steel sheet that are excellent in corrosion resistance and can be applied to various purposes, such as for home electrical appliances and building materials, and a process for production thereof. In spite of the known process meets the requirements set by the users, it also comprises certain disadvantages as demonstrated particularly in a relative high power consumption and, as result, in use of relatively aggressive medium. In addition, the layer thickness of the anti-corrosive protection on products exceeds 20 μm and are thus useless in the environment with very demanding and up to extremely demanding climatic load.

[0003] It is the object of the present invention to create a process of electrolytic galvanizing with an enhanced anti-corrosive protection which remedies the drawbacks of the known solutions.

[0004] A process of electrolytic galvanizing with an enhanced anti-corrosive protection according to the invention comprises a pretreatment, wherein organic impurities, rust, dross and similar is removed from the surface of a product to be protected. Said pretreatment is carried out in alkaline solutions comprising sodium metasilicate, sodium hydroxide, sodium carbonate, and in acidic water solutions comprising sodium hydroxide and sodium carbonate. By means of said pretreatment the surface of a product to be protected is prepared for the next process step.

[0005] Further step of the process of electrolytic galvanizing with an enhanced anti-corrosive protection according to the invention comprises galvanization being carried out in an alkaline cyanide-free media. It is provided for according to the invention that the alkalinity of said cyanide-free media is as high as possible. Said alkaline cyanide-free media comprises silicic acid, sodium salt comprising sodium silicate, components of a water polymer solution comprising nitrogen, a solution of tritron trisodium salt and triazine, and a polymer solution comprising methanol and formaldehyde.

Between the steps of the pretreatment and galvanization processes of washing by means of a flow system, cascade system and spraying system, respectively, are carried out alternately after each operation.

[0006] Furthermore, the process of electrolytic galvanizing with an enhanced anti-corrosive protection according to the invention comprises a step of final treat-

ment, wherein a thick layer passivation based on chromium III compounds and cobalt compounds represents the primary layer on the zinc coating applied by means of galvanization to the product to be protected. Said product to be protected is treated in a working bath at the temperature in the range between about 19 °C and about 30 °C, preferably in the range between about 21 °C and about 28 °C. Said working bath comprises a pH value in the range between about 2,0 and about 3,0, preferably in the range between about 2,3 and about 2,7. Afterwards, said product is flushed by means of a pure water, preferably by means of demineralized and deionized water. The previous step is followed by sinking said product for the first time period into a polymer dispersion of silicate and polyurethane in water. It is provided for according to the invention, that the ratio between the silicate and the polyurethane in said polymer dispersion in water amounts to approximately 10 : 1. Said first time period lies in the range between 40 seconds and 80 seconds, preferably between 50 seconds and 70 seconds. Further, it is provided for according to the invention, that said polymer dispersion in water comprises a pH value in the range between about 8,0 and about 11,0, preferably in the range between about 8,5 and about 10,5.

[0007] In the continuation of the process, said product to be protected is removed for the second time period from said polymer dispersion of silicate and polyurethane in water. It is provided for according to the invention that said second time period lies in the range of about 10 seconds.

[0008] The removal of said product from said polymer dispersion of silicate and polyurethane in water is followed by a re-immersion for the third time of period of said product to be protected into said polymer dispersion of silicate and polyurethane in water. Said third time period lies in the range between 15 seconds and 50 seconds, preferably between 20 seconds and 40 seconds.

[0009] It appeared as preferred according to the present invention that said polymer dispersion of silicate and polyurethane in water must be continuously stirred during the process.

The above disclosed process step is followed by draining and/or removing of the surplus of said polymer dispersion in water off the product to be protected being followed by drying. The drying is carried out during the fourth time period by means of a hot air in closed or partially closed drying chambers in the temperature range between about 50 °C and about 90 °C, preferably in the temperature range between about 60 °C and about 80 °C. According to the invention, it is provided for that said fourth time period ranges between 6 minutes and 15 minutes, preferably between 8 minutes and 12 minutes.

[0010] The above disclosed process of electrolytic galvanizing with an enhanced anti-corrosive protection according to the invention is carried out entirely at relatively low temperatures, thus having significant advantages over the present solutions. Thus, the process of low-temperature thick layer passivation features substantial en-

ergy savings since it is carried out at the room temperature. In addition, less aggressive media having smaller content of Zn^{2+} and Fe^{2+} ions is used during the process, resulting in waste waters comprising no nano particles.

[0011] By means of the disclosed process according to the invention, the anti-corrosion protection increases on products intended for building hardware and other sectors where high anti-corrosion protection on zinc coating is required. The layer of the anti-corrosion protection is equally distributed over the entire surface of the product to be protected. By means of the process according to the invention, an outstanding anti-corrosion protection is obtained where the thickness of an average layer of the anti-corrosion protection lies in the thickness range of 10 μm without reducing the anti-corrosion protection of products being used in extreme climate conditions.

Claims

1. A process of electrolytic galvanizing, thick layer passivation and subsequent treatment in order to enhance anti-corrosive protection, wherein said process comprises a pretreatment and cleaning of products to be protected against corrosion, respectively, galvanizing in an alkaline media and final treatment, **characterized in that** a final treatment, in which a thick layer passivation based on chromium III compounds and cobalt compounds represents the primary layer on the zinc coating applied by means of galvanization to a product to be protected, comprises
 - a) treating the product to be protected in a working bath;
 - b) flushing the product to be protected by means of a pure water, preferably by means of demineralized and deionized water;
 - c) sinking the product to be protected for the first time period into a polymer dispersion of silicate and polyurethane in water, said polymer dispersion of silicate and polyurethane in water must be continuously stirred;
 - d) removing the product to be protected for the second time period from said polymer dispersion of silicate and polyurethane in water;
 - e) re-immersion the product to be protected for the third time period into said polymer dispersion of silicate and polyurethane in water, said polymer dispersion of silicate and polyurethane in water must be continuously stirred;
 - f) draining and/or removing of the surplus of said polymer dispersion of silicate and polyurethane in water off the product to be protected;
 - g) drying the product to be protected during the fourth time period by means of a hot air.
2. Process according to claim 1, **characterized in that** the temperature of a working bath lies in the range

between about 19 °C and about 30 °C, preferably in the range between about 21 °C and about 28 °C.

3. Process according to claim 1, **characterized in that** a pH value of the working bath lies in the range between about 2,0 and about 3,0, preferably in the range between about 2,3 and about 2,7.
4. Process according to claim 1, **characterized in that** ratio between the silicate and the polyurethane in said polymer dispersion in water amounts to approximately 10 : 1.
5. Process according to any of the preceding claims, **characterized in that** said polymer dispersion in water comprises a pH value in the range between about 8,0 and about 11,0, preferably in the range between about 8,5 and about 10,5.
6. Process according to any of the preceding claims, **characterized in that** said first time period lies in the range between 40 seconds and 80 seconds, preferably between 50 seconds and 70 seconds.
7. Process according to any of the preceding claims, **characterized in that** said second time period lies in the range of about 10 seconds.
8. Process according to any of the preceding claims, **characterized in that** said third time period lies in the range between 15 seconds and 50 seconds, preferably between 20 seconds and 40 seconds.
9. Process according to any of the preceding claims, **characterized in that** temperature of said hot drying air lies in the range between about 50 °C and about 90 °C, preferably in the range between about 60 °C and about 80 °C.
10. Process according to any of the preceding claims, **characterized in that** said forth time period ranges between 6 minutes and 15 minutes, preferably between 8 minutes and 12 minutes.

Patentansprüche

1. Verfahren zur elektrolytischen Verzinkung, Dickschichtpassivierung und Nachbehandlung zur Verbesserung des Korrosionsschutzes, wobei das Verfahren jeweils eine Vorbehandlung und Reinigung der Produkte, die vor Korrosion geschützt werden sollen, eine Verzinkung in einem alkalischen Medium und eine Endbehandlung umfasst, **dadurch gekennzeichnet, dass** die Endbehandlung, bei welcher eine Dickschichtpassivierung basierend auf Chrom-(III)-Verbindungen und Cobalt-Verbindungen die Primärschicht auf der Zinkbeschichtung bil-

det, die durch Galvanisierung auf dem zu schützenden Produkt aufgebracht worden ist, umfasst:

- a) Behandeln des zu schützenden Produkts in einem Bearbeitungsbad,
 - b) Spülen des zu schützenden Produkts mithilfe von Reinwasser, vorzugsweise mittels demineralisiertem und entionisiertem Wasser,
 - c) Eintauchen des zu schützenden Produkts für eine erste Zeitspanne in eine Polymerdispersion aus Silikat und Polyurethan in Wasser, wobei die Polymerdispersion aus Silikat und Polyurethan in Wasser kontinuierlich gerührt werden muss,
 - d) Entnehmen des zu schützenden Produkts für eine zweite Zeitspanne aus der Polymerdispersion aus Silikat und Polyurethan in Wasser,
 - e) Wiedereintauchen des zu schützenden Produkts für eine dritte Zeitspanne in die Polymerdispersion aus Silikat und Polyurethan in Wasser, wobei die Polymerdispersion aus Silikat und Polyurethan in Wasser kontinuierlich gerührt werden muss,
 - f) Abgießen und/oder Entfernen des Überschusses der Polymerdispersion aus Silikat und Polyurethan in Wasser von dem zu schützenden Produkt,
 - g) Trocknen des zu schützenden Produkts während einer vierten Zeitspanne mittels Heißluft.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Temperatur eines Bearbeitungsbad in einem Bereich zwischen etwa 19 °C und etwa 30 °C, vorzugsweise in einem Bereich zwischen etwa 21 °C und etwa 28 °C, liegt.
 3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** ein pH - Wert des Bearbeitungsbad in einem Bereich zwischen etwa 2,0 und etwa 3,0, vorzugsweise in einem Bereich zwischen etwa 2,3 und etwa 2,7, liegt.
 4. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** das Verhältnis zwischen Silikat und Polyurethan in der Polymerdispersion in Wasser näherungsweise 10:1 beträgt.
 5. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Polymerdispersion in Wasser einen pH - Wert aufweist, der in einem Bereich zwischen etwa 8,0 und etwa 11,0, vorzugsweise in einem Bereich zwischen etwa 8,5 und etwa 10,5, liegt.
 6. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die erste Zeitspanne in einem Bereich zwischen 40 Sekunden und 80 Sekunden, vorzugsweise zwischen 50 Sekunden

und 70 Sekunden, liegt.

7. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die zweite Zeitspanne in einem Bereich von etwa 10 Sekunden liegt.
8. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die dritte Zeitspanne in einem Bereich zwischen 15 Sekunden und 50 Sekunden, vorzugsweise zwischen 20 Sekunden und 40 Sekunden, liegt.
9. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Temperatur der Heißluft zur Trocknung in einem Bereich zwischen etwa 50 °C und etwa 90 °C, vorzugsweise in einem Bereich zwischen etwa 60 °C und etwa 80 °C, liegt.
10. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die vierte Zeitspanne zwischen 6 Minuten und 15 Minuten, vorzugsweise zwischen 8 Minuten und 12 Minuten, beträgt.

Revendications

1. Procédé de galvanisation électrolytique, de passivation en couche épaisse et de traitement ultérieur de façon à améliorer une protection anti-corrosion, ledit procédé comprenant un prétraitement et un nettoyage de produits à protéger contre la corrosion, respectivement, de galvanisation dans un milieu alcalin et de traitement final, **caractérisé par le fait qu'un** traitement final, dans lequel une passivation en couche épaisse à base de composés du chrome III et de composés du cobalt représente la couche primaire sur le revêtement de zinc appliqué au moyen d'une galvanisation à un produit à protéger, comprend:
 - a) traiter le produit à protéger dans un bain de traitement;
 - b) rincer le produit à protéger au moyen d'une eau pure, de préférence au moyen d'eau déminéralisée et désionisée;
 - c) plonger le produit à protéger pendant une première période de temps dans une dispersion de polymère de silicate et de polyuréthane dans l'eau, ladite dispersion de polymère de silicate et de polyuréthane dans l'eau devant être agitée en continu;
 - d) retirer le produit à protéger pendant une deuxième période de temps à partir de ladite dispersion de polymère de silicate et de polyuréthane dans l'eau;
 - e) re-plonger le produit à protéger pendant une

- troisième période de temps dans ladite dispersion de polymère de silicate et de polyuréthane dans l'eau, ladite dispersion de polymère de silicate et de polyuréthane dans l'eau devant être agitée en continu; 5
- f) drainer et/ou retirer l'excédent de ladite dispersion de polymère de silicate et de polyuréthane dans l'eau à partir du produit à protéger; 10
- g) sécher le produit à protéger pendant une quatrième période de temps au moyen d'air chaud. 10
2. Procédé selon la revendication 1, **caractérisé par le fait que** la température d'un bain de traitement se situe dans la plage entre environ 19°C et environ 30°C, de préférence dans la plage entre environ 21°C et environ 28°C. 15
3. Procédé selon la revendication 1, **caractérisé par le fait qu'**une valeur de pH du bain de traitement se situe dans la plage entre environ 2,0 et environ 3,0, de préférence dans la plage entre environ 2,3 et environ 2,7. 20
4. Procédé selon la revendication 1, **caractérisé par le fait que** le rapport entre le silicate et le polyuréthane dans ladite dispersion de polymère dans l'eau s'élève à approximativement 10:1. 25
5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé par le fait que** ladite dispersion de polymère dans l'eau comprend une valeur de pH se situant dans la plage entre environ 8,0 et environ 11,0, de préférence dans la plage entre environ 8,5 et environ 10,5. 30
6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé par le fait que** ladite première période de temps se situe dans la plage entre 40 secondes et 80 secondes, de préférence entre 50 secondes et 70 secondes. 35
7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé par le fait que** ladite deuxième période de temps se situe dans la plage d'environ 10 secondes. 40
8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé par le fait que** ladite troisième période de temps se situe dans la plage entre 15 secondes et 50 secondes, de préférence entre 20 secondes et 40 secondes. 45
9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé par le fait que** la température dudit air de séchage chaud se situe dans la plage entre environ 50°C et environ 90°C, de préférence dans la plage entre environ 60°C et environ 80°C. 50
10. Procédé selon l'une quelconque des revendications précédentes, **caractérisé par le fait que** ladite quatrième période de temps se situe dans la plage entre 6 minutes et 15 minutes, de préférence entre 8 minutes et 12 minutes. 55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1199376 A1 [0002]