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(21) International Application Number: PCT/EP97/07148 (22) International Filing Date: 12 December 1997 (12.12.97) (71) Applicant (for all designated States except US): WM. CANNING LTD. [GB/GB]; 133 Great Hampton Street, Birmingham B18 6AS (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): PYE, Maurice, William [GB/GB]; Wm. Canning Ltd., 133 Great Hampton Street, Birmingham B18 6AS (GB). (74) Agent: BLEUKX, Luc; Hydro AS, Avenue Marcel Thiry 83, B-1200 Brussel (BE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR COATING ALUMINIUM PRODUCTS WITH ZINC (57) Abstract A method of producing a zinc coated aluminium product by electroplating zinc from a bath containing soluble zinc and an alkali metal hydroxide and an effective amount of an amine without an aldehyde function.		

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Method for coating aluminium products with zinc

The invention relates to a method of producing a zinc coated aluminium product by electroplating zinc from a bath containing soluble zinc and an alkali metal hydroxide and an effective amount of an amine.

- 5 By zinc respectively aluminium is meant zinc or zinc alloys respectively aluminium or aluminium alloys.

Traditional electroplating has been described in ASTM method B253-73, 1973, and Surface Technology, 12 (1981) 141-155. "A study of the effect of Pre-treatment Procedures on the Plating of Aluminium Alloys". According to this known technique
10 aluminium is pre-treated prior to electroplating in a solution containing soluble tin or more normally zinc and an alkali metal hydroxide (usually sodium). A method according to the preamble is known from EP-A-0 263 592.

According to this publication an aluminium product is submersed in a bath containing the above mentioned elements and using aldehyde lustering agents. In this way the
15 pre-treatment and electroplating is accomplished in the same bath, the pre-treatment taking place before application of the current. This pre-treatment is in fact a chemical deposition of zinc on the aluminium product.

The problems encountered with this known process is that the residence time without current is at least 5 seconds and preferably between 15-90 seconds. A satisfactory
20 deposit quality can be only be obtained by using relatively low current densities, i.e. the current per surface area to be coated and is therefore limited to an inconveniently low deposition rate. In EP-A-0 263 592, the maximum plating rate is not claimed explicitly but appears to correspond to a current density of 5 A/dm² which would correspond to about 0,6 µm/ minute at a typical current efficiency of 50%, which is
25 typical for this type of process.

Therefore where high deposition rates are desirable, for example for plating continuous substrates, this cannot be achieved by raising the current density or

temperature of the solution without obtaining an unsatisfactory deposit quality, i.e. a very coarse and grainy or dull dendritic deposit.

It is an object of the invention to provide a process according to the preamble of the claim, which is suitable for high speed electroplating.

- 5 The objective is reached by using an amine without aldehyde function. Preferably the electroplating is performed in a bath at a temperature of at least 20°C, with a cathodic current density of at least 5A/dm² so as to achieve an adherent smooth zinc deposit at a rate of at least 1µm per minute.

- 10 Preferably a polymeric amine is used for example poly ethylene imine having a molecular weight at greater than 500, most preferably greater than 800.

It has been found that additives with quaternary amine functionality are more effective than others and enable higher current densities and / or higher zinc concentrations to be used. This enables higher rates of deposition to be obtained. Polymeric amines with multiple quaternary functionality are particularly effective.

- 15 Below a temperature of 20°C the process will become slower. As the temperature increases the maximum potential deposition rate increases, making the process more attractive. However increasing the temperature above defined values may lead to a deterioration of some of the compounds in the bath, especially the amines. Below a current density of 5 A/dm² the deposition is considered to be too slow to achieve
20 convenient coating rates for high speed continuous plating. It has been found that the quantity of the deposit (particularly brightness) can be improved by raising the current density e.g. to 15 A/dm² even when there is no corresponding increase in deposition rate, or in some cases even a slight reduction in rate.

- 25 The deposition rate is preferably at least 1µm per minute corresponding to approximately 3,5 g/m² per 30 seconds. Zinc deposit rates are dependent on a number of parameters, such as concentration of soluble zinc in the plating bath, current density, temperature, agitation, depletion of the solution, nature of the additives

etc. All these parameters must be maintained on such a level that the deposition rate is maintained above 1µm per minute in order to have the required speed of deposit for continuous processing lines and consistent with acceptable appearance.

5 A number of alkali metal hydroxides may be used according to the invention, but preferred are sodium and/ or potassium hydroxides. It was found that with these hydroxides excellent results could be obtained with respect to surface finishing while maintaining a high deposit speed. Moreover these hydroxides are readily available commodities at reasonable market prices.

10 Tests revealed that the zinc concentration, especially the concentration of soluble zinc has an important influence on the zinc deposition rate on the surface to be coated. It was found that doubling the zinc concentration may result in a more than double the coating thickness while maintaining the coating time and current density at the same level. For continuous deposition the concentration of soluble zinc in the plating bath should preferably be at least 15 g / l, more preferably 20 g / l and even higher
15 concentrations above 25 g / l or 30 g / l may be used.

The aluminium surface should be free of harmful amounts of oil, grease, etc. and of thick oxide / hydroxide or similar films on introduction into the plating solution. They can be removed by known cleaners accelerated by agitation, spray etc. Cleaners containing alkali hydroxides e.g. sodium hydroxide are preferred as those can dissolve
20 oxides etc. Silicates are usually avoided as they reduce attack on the oxides / hydroxides etc. It is not necessary to pre-treat in a zinc-containing solution, as disclosed in the cited prior art.

Silicates tend to passivate aluminium, even after rinsing, thereby reducing adhesion of the subsequent electrodeposit or even the effect of conventional "zincate"
25 pre-treatments, according to the prior art.

It is not necessary to include a period of immersion without applied cathodic current in a zinc containing solution, as per the prior art cited above. This step increases the

costs and length of the plating machine and is particularly disadvantageous on a continuous plating machine.

The invention will now further be elucidated by means of the following examples in which a number of processes according to the invention are described and compared with processes according to the prior art.

In the examples that follow the term "satisfactory deposit quality" means a zinc deposit that :

- is metallurgically sound and free from significant dendrites
- exhibits no loss of adhesion to the substrate when examined by the cross hatch (1 mm squares) and adhesive tape tests.

EXAMPLE A

Comparative experiment. In order to compare the invention with the prior art Example 1 of EP-A-0 263 592 has been repeated. This was done in the following way.

A bath was prepared containing :

15	ZnO	15 g/L
	NaOH	130 g/L

15 ml / l, heliotropine was added, resulting in a saturated solution , with solid heliotropine on the surface. After removal of the excess heliotropine, a plating test was done sending the following conditions :

20	Temperature :	25°C
	Standard Hull Cell containing	267 ml of solution
	Current :	2 amps
	Time :	10 minutes
	Cathode:	Aluminium

25 Deposit characteristics at primary current densities of :

Above 10 A / dm ²	Very coarse, grainy deposit. Unsatisfactory
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3 to 10 A / dm ²	Grey deposit, gradually becoming less coarse at lower current densities. Unsatisfactory.
Below 3 A / dm ²	Semi-bright, fine grained deposit. Satisfactory.

Maximum plating rate for satisfactory deposit quality : 0.4 microns / min.

5 **EXAMPLE 1**

Example A was repeated, but heliotropine replaced with polyethylene imine G35 (BASF) 6 g/l.

Deposit characteristics at primary current densities of :

	Above 1.3 A/dm ² :	Semi-bright deposit. Satisfactory.
10	Below 1.3 A/dm ² :	Bright deposit. Satisfactory.

Maximum plating rate for satisfactory deposit quality : 0.8 microns / min.

EXAMPLE 2

Example 2 was repeated but with current 5 amps and temperature 45°C.

Deposit characteristics at primary current densities of :

	Above 2 A/dm ² :	Semi-bright deposit. Satisfactory.
15	Below 2 A/dm ² :	Bright deposit. Satisfactory.

Maximum plating rate for satisfactory deposit quality : 1.1 microns / min.

EXAMPLE B

Comparative experiment : A bath was prepared containing :

	ZnO	36 g / L
20	NaOH	160 g / L

Saturated with heliotropine.

The plating conditions of Example A was maintained but with a current of 5 amps and a temperature of 45°C.

Deposit characteristics at primary current densities of :

- | | | |
|---|-----------------------------|--------------------------------------|
| 5 | Above 2 A/dm ² : | Very coarse. Unsatisfactory deposit. |
| | Below 2 A/dm ² : | Satisfactory dull deposit. |

Maximum plating rate for satisfactory deposit quality: 0.55 microns / min.

EXAMPLE 3

- Example B was repeated, but heliotropine replaced with polyethylene imine G35 (BASF) 6 g / l .

Deposit characteristics at primary current densities of :

- | | |
|------------------------------|------------------------------------|
| Above 15 A/dm ² : | Coarse. Unsatisfactory deposit. |
| 15 - 17 A/dm ² : | Semi-bright. Satisfactory deposit. |
| Below 7 A/dm ² : | Bright. Satisfactory deposit. |

- 15 Maximum plating rate for satisfactory deposit quality : 1.8 Microns / min.

EXAMPLE 4

The example 3 was repeated, but with the G35 replaced with poly quaternary amino additives.

- 20 The alternative polyquaternary amino additives (to replace the G35) were prepared in all cases by reflecting the stated starting materials for 4 hours unless otherwise stated.

3 ml / l of the reaction product was added to the basic electrolyte in each case.

N, N, N¹, N¹ - Tetra methyl -

1 - 6 - hexanediamine	9.56 g	(5 1/2 hrs)
1,2-bis (2-chloroethoxy) ethane	7.93 g	
Water	18 00 g	

Deposit characteristics at primary current densities of :

5	Above 15 A/dm ² :	Unsatisfactory coarse deposit.
	15 - 1 A/dm ² :	Dull, but satisfactory deposit.
	Below 1 A/dm ² :	Bright. Satisfactory deposit.

Maximum plating rate for satisfactory deposit quality : 3.1 microns / min.

EXAMPLE 5

10 Example 4 was repeated, but with the following reaction product additive:

N,N' - Bis {3 - (amino dimethyl) propyl } urea	11.54 g	
1,6 dibromohexane	12.36 g	
Water	24 g	(4 hrs)

Deposit characteristics at primary current densities of :

15	Above 15 A/dm ² :	Semi-bright. Satisfactory.
	Below 10 A/dm ² :	Bright. Satisfactory.

Maximum plating rate for satisfactory deposit quality : 1.7 microns / min.

EXAMPLE 6

Example 4 was repeated, but with the following reaction product additive:

20	N,N,N', N' tetramethyl - 1,6-diamine hexane	15 g	
	1,4-dichlorobutane	11.1 g	
	Water	26.1 g	(5 1/2 hrs)

Deposit characteristics at primary current densities of:

	Above 25 A/dm ² :	Coarse. Unsatisfactory.
25	25 - 7 A/dm ² :	Dull. Satisfactory.
	Below 7 A/dm ² :	Semi-bright. Satisfactory.

Maximum plating rate for satisfactory deposit quality : 3.4 microns / min.

EXAMPLE 7

Example 4 was repeated, but with the G35 replaced :

5	N,N' - bis {3 - (dimethylamino) propyl } urea	15 g
	1,4-dichlorobutane	8.28 g
	Water	23.3 g

Deposit characteristics at primary current densities of :

Above 2 A/dm² : Bright. Satisfactory deposit.

Below 2 A/dm² : Dull, unsatisfactory.

10 Maximum plating rate for satisfactory deposit quality: 1.7 microns / min.

EXAMPLE 8

Example 4 was repeated, but with the following reaction product additive:

15	N,N' - bis {3 - dimethylamino) propyl} urea	15.07 g
	bis (2-chloroethyl) ether	9.36 g
	Water	24.5 g

Deposit characteristics at primary current densities of:

Above 1 A/dm² : Semi-bright. Satisfactory.

Below 1 A/dm²: Dull, unsatisfactory.

Maximum plating rate for satisfactory deposit quality : 2.3 microns / min.

EXAMPLE 9

As per example 6, but with additional sodium metasilicate to give an SiO_2 -concentration of 2 g/L .

An improvement in brightness at current densities over 15 ASD was observed.

- 5 Maximum plating rate for satisfactory deposit quality: 1.8 microns / min.

10 It is clear that polyamino compounds allow higher plating rates at satisfactory quality than heliotropine. They also generally have a wider range of current density consistent with satisfactory quality than heliotropine. It is also well known that benzaldehyde derivatives, such as heliotropine tend to chemical instability, particularly at higher sodium hydroxide concentrations and higher temperatures, when they undergo the "Cannizzaro reaction". This is important, as higher hydroxide concentrations and/or higher temperatures tend to raise the maximum deposition rate consistent with satisfactory deposit quality.

15 It is also seen to be the case that polyquaternary amines are more "active" than additives which are uncharged, or have only a low density of quaternary groups, for example the G35 polyethylene imine which is thought to have a low density of quaternary functionality compared to the polymers of examples 4 - 9, which are thought to have a much higher positive charge density.

20 In all cases, additions of the polymeric amines at rates comparable to, or less than those used for the heliotropine applied in EP-A-0 263 592 provide for increases in the maximum plating rate achievable for the same base electrolyte.

Using the polymeric quaternary amines, deposition rates can be further enhanced by increasing concentration of both alkali metal hydroxide and zinc in solution.

25 Additions of soluble silicates to the electrolyte have a small but significant effect in improving brightness in combination with other additives under conditions of increased current density.

Actual rates of deposition for satisfactory quality for a given electrolyte at a fixed temperature are critically dependent upon agitation, more specifically, the rate of mass transfer at the cathode.

5 All of the examples given are performed under essentially stagnant conditions, the only agitation being that generated by the electrolysis itself. In practice, forced agitation would almost always be employed for the plating of continuous strip, or where high deposition rates are required. However, the rates achieved under such stagnant conditions provide a reliable indication of the relative performances achievable under "forced" conditions.

10 It has been found that even higher deposition rates can be achieved when suitable electrolyte circulation or agitation is provided so that solution is replenished at the cathode, thereby optimising conditions for maximum mass transfer at the cathode.

15 Furthermore, it has been well demonstrated in the examples given above that direct electroplating of zinc onto aluminium, without the need for an intermediate "zincate" treatment is feasible and capable of producing deposits of excellent adhesion and quality.

Claims

1. A method of producing a zinc coated aluminium product by electroplating zinc from a bath containing soluble zinc and an alkali metal hydroxide and an effective amount of an amine without an aldehyde function.
- 5 2. A method according to claim 1, characterised in that the cathodic current density is at least 5 A/dm².
3. A method according to claim 1, characterised in that the cathodic current density is at least 10 A/dm².
- 10 4. A method according to claim 1, characterised in that the cathodic current density is at least 15 A/dm².
5. A method according to any one of the claims 1 - 4, characterised in that the zinc deposit rate is at least 1 µm per minute.
6. A method according to any one of the claims 1- 5, characterised in that the amine is polymeric.
- 15 7. A method according to claim 6, characterised in that the amine is polyethylene imine.
8. A method according to any of the claims 6 or 7, characterised in that the amine has a molecular weight greater than 500.
9. A method according to any of the claims 6 or 7, characterised in that the amine has a molecular weight greater than 800.
- 20 10. A method according to any of the preceding claims, characterised in that the alkali metal hydroxide is sodium and/or potassium hydroxide.

11. A method according to any of the preceding claims, characterised in that the concentration of soluble zinc is greater than 15 g/l.
12. A method according to any of the preceding claims, characterised in that the concentration of soluble zinc is greater than 20 g/l.
- 5 13. A method according to any of the preceding claims, characterised in that the concentration of soluble zinc is greater than 25 g/l.
14. A method according to any of the preceding claims, characterised in that the concentration of soluble zinc is greater than 30 g/l.
- 10 15. A method according to any preceding claims, characterised in that the amine molecule bears at least three positive charges, derived from quaternary amine functionality.
16. A method according to any preceding claims, characterised in that the amine molecule bears at least eight positive charges, derived from quaternary amine functionality.
- 15 17. A method according to any one of the preceding claims, characterised in that the aluminium is introduced into the plating bath without a significant period of immersion without applied cathodic current.
18. A method according to any one of the preceding claims, characterised in that the electroplating is preceded by treatment of the aluminium product in a chemical bath which is substantially zinc-free.
- 20 19. A method according to any of the preceding claims, characterised in that electroplating takes place in a bath containing an effective amount of a soluble silicate.

- 5 20. A method according to any of the preceding claims, characterised in that the electroplating bath additionally contains an effective amount of a soluble form of one or more of the metals selected from the group of Fe, Co, Ni and Mn effective to codeposit sufficient alloying metal to improve the resistance to corrosion and / or passivation and / or tolerance to high temperatures of the deposit.
21. A method according to any one of the preceding claims, characterised in that the electroplating step is followed by passivation.
22. A method according to claim 21, characterised in that the passivation is done by means of soluble chromium.
- 10 23. A method according to claim 22, characterised in that the chromium is primarily present in trivalent form.
24. A method according to any one of the preceding claims, characterised in that the temperature of the bath is at least 35° C.
- 15 25. A method according to any one of the preceding claims, characterised in that the temperature of the bath is at least 40° C.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C25D3/22 C25D3/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9711 Derwent Publications Ltd., London, GB; Class E13, AN 97-117477 XP002077339 & RU 2 063 482 C (SEM M RES PRODN ENTERP) , 10 July 1996 see abstract	1,10-14
A	FR 2 289 637 A (POPESCU FRANCINE) 28 May 1976 see the whole document	1,2,6-16
A	US 5 417 840 A (BLOCK DALE G ET AL) 23 May 1995 see example 11	1,6-10, 20,24,25
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	US 3 993 548 A (CREUTZ HANS GERHARD ET AL) 23 November 1976 see example 2 ---	1,6-14, 19
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Information on patent family members

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