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" PROCESS FOR DIRECT NICKEL CHROMIUM PLATING OF SUBSTRATES OF ALUNINOUM AND ITS ALLOTS FOR SOLAR COLLECTOR APPLICATIONS " _

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

153303

This invention relates to "Improvement in or relating to Direct Nickel Plating on Aluminium and its alloys and Black chromium plating there" for solar collectors.

Hitherto it has been propose to use methods such as zincating, Anodising or to give Bronze strike prior to plating on aluminium surface.

It is difficult to have an adherent plating on aluminium without the above mentioned operations involving many steps.

The object of the present invention is to obviate these difficulties by plating Nickel directly on to Aluminium surface and to plate black chromium thereon.

To these ends the present invention consists in degreasing Aluminium surface with organic solvent, alkaline cleaning, Acid etching, Nickel plating and finally black chromium plating with intermediate washing and rinsing after each step.

Aluminium and its alloys in the form of sheet, tape, strip, wire, foil or tube are used in the present invention for direct plating of Nickel and black chromium plating thereon.

The aluminium surface is polished by mechanical means and degreesed with trichloroethylene or with perchloroethylene. The degreesed surface is alkali cleaned in 5 - 10% W/v Sodium hydroxide containing conventional wetting agents for 30 seconds to 2 minutes at $25 - 40^{\circ}$ C. After alkali cleaning the

aluminium surface is washed and etched in an acid etching bath consisting of 20 - 35% v/v hydrochloric acid (35 - 38% concentration) 1 - 5% V/V hydrofluoric acid (40% concentration) 0 - 2% W/V thicures and conventional wetting agents for 15 seconds to 2 minutes at $25 - 40^{\circ}$ C.

The etched aluminium surface is washed with tap water, rinsed in deionised water and plated with nickel either from a bath comprising of Nickel sulphate 150 - 200 g/1, Nickel fluoborate 60 - 90 g/1, Nickel chloride 1 - 5 g/1, Boric acid 20 - 35 g/1 with pH 1.9 to 2.3 at $45 - 60^{\circ}\text{C}$ using a current density of $5 - 20 \text{ A/dm}^2$ to the required thickness or from a Nickel sulphamate bath.

The Nickel plated aluminium surface is washed and rinsed with distilled water, optionally heat treated at 350° to 450°C and finally black chrome plated in the following bath comprising of chromic acid 400 - 450 g/l, sodium hydroxide 50 - 60 g/l, fluosilicic acid 0.5 - 1.0 g/l, sucrose 2-3 g/l and sodium nitrate 0 - 3 g/l at 21° - 35°C using a current density of 15 - 30 A/dm² Either 8% Sn. 92% Lead alloy or mild steel is used as anode material. The black chrome plated Aluminium surface is jet black and suitable as solar collectors. The thermal emittance (et) and solar absorption (s) of the above black chromium plating are reported to be 0.95 and 0.08 - 0.2 respectively.

The following are the examples to illustrate the invention are not to limit the scope of the invention.

EXAMPLE I

Commercial grade 25 aluminium sheet of size 10 cm x 24 cm is mechanically polished, degreased with trichloro ethylene, alkali cleaned in 10% addium hydroxide containing 0.1 cc/litre Teepol as wetting agent at 30°C for 1 minute. washed in tap water, etched in 30 v/v hydrochloric acid (35-38%) containing 5% v/v hydrofluoric acid (39-40%) 0.5 g/l thiourse and 0.2 g/l sodium lauryl sulphate. After stching, the specimen is washed in tap water, rinsed with distilled water and nickel plated in a modified fluoborate bath containing Nickel sulphate 200 g/l, Nickel 'fluoborate 66 g/litre, Nickel chloride 1 /gl and boric acid 20 g/l. The pH of the bath was maintained at 2 and the temperature of the bath was 55°C. Nickel was plated at 10 A/dm2 current density to get 6 micron thick deposit. After nickel plating, the plate was washed, rinsed and black chromium plated in a bath containing 400 g/1 chromic acid. 60 g/1 sodium hydroxide 1 o/1 fluosilicic scid. 2 o/1 sucross and 2 o/1 sodium Nitrate. The bath was operated at 30°C. A current density of 23 A/dm2 was employed for plating for 5 minutes. The chromium deposit obtained was jut black and was very adherent.

EXAMPLE II

515WP Aluminium alloy extruded tube was taken and precleaning operations were done as in example 1 and nickel plated in the modified nickel fluoborate bath, containing Nickel fluoborate 83 g/l, Nickel sulphate 170 g/l, Nickel chloride 1 gm/l and Boric acid 33 g/l. The pH of the bath was maintained at 2 and the speciment was Nickel plated to give 6 micron at 45° C at current density of 20 A/dm². The

nickel plated specimen was washed rinsed with distilled water, dried and heat treated at 400°C for 3 minutes and air cooled. The specimen was black chrome plated using the bath mentioned in the example 1 for 5 minutes at 25 C using a current density of 20 A/dm². The black chromium plating obtained was very adherent and it was matt black in appearance.

EXAMPLE III

Commercial grade 2S-aluminium strip was degreased and precleaned as in example I and Nickel plated from the modified sulphamate bath containing Nickel sulphamate 210 g/l Nickel chloride 5 g/l, Nickel sulphate 41 g/l and Boric acid 25 g/l. The pH of the bath was maintained at 4 and the bath was operated at 55°C at 15 A/dm² current density to get 6 micron thick nickel deposit. The nickel plated strip was washed and rinsed in distilled water and black chromium plated in a bath containing chroimum tri-oxide 300 g/l Nitric acid 2ml/l, Fluosilicic acid 0.5 g/l (calculated as 100% acid) at 20°C using a current density of 25 A/dm² for 3 minutes to get a matti black finish. The plating was very adherent and was tested by 180° bent test.

EXAMPLE IV

265 aluminium alloy sheet was degreased and precleaned

and Nickel plated as in example 1 and Black chromium plated in a solution containing 250 g/l chromic acid 20 g/l ammonium sulphamate 15 g/l Boric acid at a pH of 1.5 at 15 A/dm^2 at 25° C using a lead tin alloy anode (Pb 90% + Sm 10%) for 5 minutes. The deposit was very adherent and jet black in appearance. Following are the main advantages of the invention:

- 1. The method of direct plating on aluminium avoids the intermediate steps such as zincating, bronze strike, anoidising, hence making the process more simple, quick and economical.
- 2. The black chrome plated aluminium in different forms obtained by this process finds application as solar collectors and it is reported that the black chrome surface on Nickel is highly suitable for solar collectors.
- All the materials needed for this process are indigenously available.

Dated this 2nd day of November 1979

Sd/-

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COMPLETE SPECIFICATION

(Section-10)

PROCESS FOR DIRECT NICKEL AND CHROMIUM PLATING OF SUBSTRATES OF ALUMINIUM AND ITS ALLOYS FOR SOLAR COLLECTOR APPLICATIONS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—

This is an invention by Balkunje Anantha Shenoi, Scientist; Venkataraman Balasubramanian, Scientist and Nathi Upendra Nayak, Junior Scientific Assistant, all of them are employed in Central Electrochemical Research Institute, Karaikudi-6, Tamil Nadu and are Indian nationals.

This invention relates to a process for direct nickel and chromium plating of substrates of aluminium and its elloys for solar collector applications.

Hitherto it has been proposed to use methods such as zincating, anodising or to give bronze strike prior to plating on aluminium substrate surface.

It is difficult to have an adherent plating film formed on aluminium withouth the above mentioned operations, involving a plurality of steps. The object of the present invention is to obviate these difficulties by plating nickel directly on the aluminium substrate surfaces, and to plate black chromium thereon. To these ends the present invention consists in degressing aluminium surface with organic solvent, alkaline cleaning, acid stohing, nickel plating and finally black chromium plating with intermediate washing and rinsing after each step.

This invention thus relates to a process for black chromium plating nickel plated aluminium surface for use as solar collecturs. Nickel plating of aluminium and its alloys are made by direct nickel plating without using conventional methods such as zincating, bronze strike, tin strikes and the like. Black chromium plating on nickel plated surface is made using tetra chromate baths described in the invention to get a matt black surface which can be used as solar collectors.

Aluminium and its alloys substrates in the form of sheet, taps, strip, wire, foil or tube are used in the present inven-

tion for direct plating of nickel and black chromium plating thereon.

Accordingly this invention provides a process for direct nickel and chromium plating of substrates of aluminium and its alloys for solar collector applications comprising Polishing, degreasing and alkali cleaning the substrate which is characterised in that the substrate is further subjected to acid etching, nickel plating in an electrolytic bath consisting of:

- a) mickel sulphate ... 50-200 g/l
- b) mickel sulphamate ... 0 -300 g/l
- e) mickel fluoborate ... 0 90 g/l
- d) nickel chloride, and ... 1 6 g/1
- m) boric soid ... 25- 40 q/1

and them black chromium plating in an electrolytic bath consisting of:

- a) chromic acid ... 400-450 g/l
- b) Sodium hydroxide ... 50-60 g/l
- o) Sucrose, and ... 2- 3 g/1
- d) modium nitrate ... 0- 3 g/l

in the presence of a catalyst such as fluoboric acid, fluosilicic acid or seleneous acid in an amount of 0.5 to 1.5 g/l

The aluminium surface is polished by mechanical, chemical or electrochemical means and degreesed with trichloroethylene of perchioroethylene. The degreesed surface is alkali cleaned in 5-10 % w/w sedium hydroxide containing conventional wetting agents for 30 sec to 2 min at 25-40°C. After alkali cleaning the aluminium surface is washed and etched in an acid stohing bath consisting of 20-35% v/v hydrochloric acid (35-38% concentration), 1-5% v/v hydrofluoric acid (40% concentration), 0-2% u/v thioures and conventional wetting agents for 15 seconds to 2 minutes at 25-40°C. The stohed aluminium surface is washed with tap water rinsed in deionized water and plated with nickel either from a bath comprising nickel sulphate 150-200 g/l, nickel

fluoborate 60-90 g/l, nickel chloride 1-5 g/l, boric acid 20-35 g/l with pH 1.9 to 2.3 at $40-60^{\circ}$ C using a current density of 5-20 A/dm² at the required thickness or from sulphamate bath consisting of nickel sulphamate 200-300 g/l, nickel sulphate 50-100 g/l, nickel chloride 1-5 g/l, boric acid 30-40 g/l with pH 3.5 to 4 at $50-60^{\circ}$ C using a current density of 10-25 A/dm².

The nickal plated aluminium surface is washed and rinsed with distilled water and finally black chrome plated in the following electrolyte comprising of chromic acid 400-500 g/l, sodium hydroxide 30-60 g/l, catalyst such as fluoboric acid, fluosilicic acid or seleneous acid in the range of 0.5 to 1.5 g/l. Sodium nitrate in the range of 2-3 g/l, and sucrose 2.3 g/l are optionally added to the bath. The bath is operated at 20-35°C using current density of 15-30 A/dm² using lead-tin alloy anode (92% lead and 8% tin). The black chrome plated eluminium surface was jet black and suitable for solar collectors. The thermal emittance (\$\mathbb{E}\$) and solar absorption () of the black chromium plating are reported to be 0.08-02 and 0.95 respectively. The desirable value of \$\mathcal{L}\$ is \$\mathcal{T}\$ 0.95 and \$\mathcal{E}\$\mathcal{L}\$ 0.1.

The following examples further illustrate the invention and do not to limit the scope of the invention.

Example 1

was mechanically polished, degreased with trichloroethylene, alkali cleaned in 10 % sodium hydroxids containing 0.1 cc/1 teepol as wetting agent at 30°C for 1 minute, washed in tap water, etched in 20° v/v hydrochloric acid (35-38%), containing 5% v/v hydrofluoric acid (39-40%) 0.5 g/l thiourea and 0.2 g/l sodium lauryl sulphate. After etching, the specimen is washed in tap water, rinsed with distilled water and nickel plated in a modified fluoborate bath containing nickel sulphate 200 g/l nickel fluoborate 66 g/l, nickel chloride 1 g/l and boric acid 20 g/l. The pH of the bath was maintained at 2 and the temperat-

ure of the bath was 55° C. Nickel was plated at 10 A/dm^2 current density to get 6 micron thick deposit. After nickel plating, the plate was washed, rinsed and black chromium plated in a bath containing 400 g/l chromic acid, 60 g/l sodium hydroxide, 1 g/l fluosilicic acid, 2 g/l sucrose and 2 g/l sodium nitrate. The bath was operated at 30° C. A current density of 23 A/dm^2 was employed for plating for 5 minutes. The chromium deposit obtained was jet black and was very adherent.

Example 2

1 SWP aluminium alloy extruded tube was taken and precleaning operations done as in example 1 and nickel plated in the modified nickel fluoborate bath containing nickel fluoborate 83 g/l, nickel sulphate 170 g/l, nickel chloride 1 g/l, and boric acid 33 g/l. The pH of the bath was maintained at 2 and the specimen was nickel plated to give 6 micron at 45°C at current density of 20 amp/chm². The nickel plated specimen was washed rinsed with distilled water and dried. The specimen was black chrome plated using the bath mentioned in the example 1 with seleneuous acid 1 g/l in lieu of feluosilicic acid as catalyst for 5 minutes at 25°C using a current density of 20 A/dm². The black chromium plating obtained was very adherent and it was matt black in appearance.

Example 3

Commercial grade 25-aluminium strip was degreased and precleaned as in example 1 and nickel plated from the modified sulphamate bath containing nickel sulphamate 210 g/l, nickel chloride 5 g/l, nickel sulphate 41 g/l and boric acid 25 g/l. The pH of the bath was maintained at 4 and the bath was operated at 55°C at 15 A/dm² current density to get 6 micron thick nickel deposit. The nickel plated strip was washed, rinsed in distilled water and black chromium plated in bath containing chromium tri oxide 300 g/l, nitric acid 2 ml/l (sp. gr 1.4) fluoboric

acid 0.5 g/l (calculated as 100% acid) at 20° C using a current density of 25 A/dm² for 3 minutes to get a mett black finish. The plating was very adherent and was tested by 180° bend test.

Example 4

26 S aluminium alloy stat was degreased and precleaned and nickel plated as in example 1 and black chromium plated in a solution containing 250 g/l chromic acid, 20 g/l ammonium sulphamate, 15 g/l boric acid at a pH of 1.5 at 15 A/dm² at 25° C using a lead tin alloy anode 2% Pb > 8% Sn) for 5 minutes. The deposit was very adherent and jet black in appearance.

The other objections of the invention are:

- to develop a method for direct plating on aluminium surfaces to avoid the intermediate steps such as zincating bronze strike, ano-dizing, hence making the process more simple, quick and economical.
- 2. to black chrome plating the aluminium surfaces in different representation of forms obtained by this process which find application as solar collectors as the black chrome surface on nickel is highly suitable for solar collectors.
- to develop a process for which all the materials needed for this process are indigenously available.

We claim:

1. Process for direct nickel and chromium plating of substrates of aluminium and its alloys for solar collector applicatiions comprising polishing, degreasing and alkali cleaning the
substrate, characterised in that the subtrated is further
subjected to acid etching and then to nickel plating in an electrolytic bath consisting of :

a)	nickel sulphate	• • •	50-260 g/1
b)	nickel sulphamate	• • •	0-300 g/l
c)	nickel fluoborate	•, • •	0- 90 g/l
d)	nickel chloride, and	•••	1- 6 g/l
•)	boric acid	• • •	25- 40 g/l.

and then black chromium plating in an electrolytic bath consisting of:

a)	chromic acid	• • •	400-450 g/
b)	sodium hydroxide	•••	50 - 60 g/
c)	sucrose, and	•••	2- 3 g/
d)	sodium nitrate	•••	0- 3 p/

in the presence of a catalyst such as fluoboric acid, fluosilicic acid or seleneous acid in an amount of 0.5 to 1.5 g/l $_{*}$

- 2. Process as claimed in claim 1 wherein the etching solution used for acid etching the substrate consists of 25-35% of 35-38% Conc. hydrochloric acid, 1-5% v/v of 40% conc. hydrochloric acid, 0-2% u/v of thiourse and 0.2% u/v of wetting agents such as sodium lauryl and the etching operation is carried out at $30-35^{\circ}C$ for 45 seconds to 2 minutes.
- 3. Process as claimed in claim 1 wherein the nickel plating bath used consists of 150 200 g/l of nickel sulphate, 60 -90 g/l of nickel fluoborate, 1-5 g/l of nickel chloride and 20-35 g/l of boric acid and the electrolysis is carried out at a pH of 1.9 to 2.3 at a temperature of 40° - 60° C using a current

density of $5-20 \text{ A/dm}^2$.

- 4. Process as claimed in claim 1 wherein the nickel plating bath consists of 200-300 g/l of nickel sulphamate, 50-100 g/l of nickel sulphate, 1-6 g/l of nickel chloride and 30-40 g/l of boric acid and the electrolysis is carried out a pH of 3.5 to 4 at 50° - 60° C in the current density range of 10-25 A/dm².
- 5. Process as claimed in any of preceding claims wherein a current density of $15-30 \text{ A/dm}^2$ is used at a temperature of $20-35^{\circ}$ C with a lead-tin alloy (Pb 92% and Sn 8%) as the anode material.
- 6. Process for direct nickel and chromium plating of substrates of aluminium and its alloys for solar collectors application substantially as herein described and illustrated

Dated this 11th day of November 1980.

Sd/-

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