GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 150405 dated 28th December 1979
Application and Provisional Specification No. 966/Del/78 dated 30th Dec. 1978.
Acceptance of the complete specification advertised on 25th September 1982.

Index at acceptance— 7004 [LVIII(5)]

International Classification— C 23 b 9/02

"IMPROVED PROCESS FOR THE SEALING OF ANODISED ALUMINIUM AND ITS ALLOY SUBSTRATES".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, 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

150403

This is an invention by Balkunje Anantha Shenoi, Scientist Subbiah John, Senior Technical Assistant and Angusamy Perumal, Senior Laboratory Assistant, all are Indian Nationals and employed in the Central Electrochemical Research Institute, Karaikudi-623006 Tamil Nadu, India

This invention relates to improvements in or relating to the development of sealing solution for anodised aluminium and its alloys.

Hitherto it has been proposed to seal the oxide films on aluminium and its alloys by the following methods:

(1) In decorative anodising where a colourless transparent anodic film is formed e.g. over a polished surface, the coatings are sealed in hot water or steam.

(2) Dichromate sealing is used for sealing sulphuric acid anodic coatings for improved corrosion resistance.

(3) Sodium silicate (water glass) sealing is also used.

(4) Sealing is also carried out in metallic salt solutions of nickel, cobalt and lead in low concentrations. They hydrolize in the pores to form the respective hydroxides.

(5) Electrolytic sealing methods e.g sodium phosphate solutions are also available for sealing.

The main draw back of the hitherto known sealing processes are:

(1) The hot water sealing process causes the formation of sealing bloom. This sealing bloom is an unwanted side effect of sealing in the form of a thin powdery layer which forms on the surface and is usually invisible until the surface is dried and rubbed with the finger when a white mark appears, like a chalk mark.

(2) Dichromate sealing is frequently used for non decorative purposes. It gives the coating a yellow colour and is therefore often unsuitable for decorative applications.

(3) Sodium silicate sealing is less important than water, dichromate or nickel/cobalt acetate sealing for anodic oxide films and is used in-frequently.

(4) Sealing in salt solutions for e.g in Nickel/Cobalt acetate is carried out at higher temperatures of 90°C - 100°C. Sealing carried in this bath is also left with a bloom on anodised aluminium. When sealing is carried out at a lower temperatures of 60 - 80°C, sealing is imperfect and the bloom formation takes places.

(5) Electrolytic sealing is rarely used and is still of theoretical interest.

The main object of the present invention is to obviate the above disadvantages by the use of a modified metal salt solution sealing process for anodised aluminium at compratively lower temperatures.

The main finding underlying the present invention consists in sealing the anodised aluminium in aqueous solutions of either nickel sulphate or Pot. (or Na) dichromate or Ni/Co acetate which contain small quantities of addition agents such as ethonolamines, metal fluorides, aliphatic amines and aliphatic thioamides. These solutions with any one of the above mentioned addition agents are operated at the temperature range of 65 - 80°C.

The new result flowing from the new finding is that perfect sealing is achieved from the solutions as indicated in the examples at a comparatively lower operating temperature.

The present invention consists of a process for sealing of anodised aluminium and its alloys which comprises the steps of polishing and buffing, degreasing, alkaline cleaning, desmutting, anodising and sealing at a temperature of 65 - 75°C for a period of 10 to 25 minutes at a pH of 6 - 8 in an aqueous solution containing

I. Nickel acetate 5 - 15 g/l + Cobalt acetate 1 - 2 g/l ; or

II. Nickel sulphate 10 - 20 g/l; or III. Sodium or Potassium dichromate 10 - 20 g/l; with any one of the addition agents

namely Ethylene diamine or Triethanolamine in amounts of 1 - 10 ml/l or thiourea or EDTA or Nickel fluoride in amounts of 1 - 5 gm/l wherein the incorporation of the addition agents enables sealing at a substantially lower temperature and eliminates the formation of sealing bloom.

The following two tests were carried out to ascertain whether sealing is perfect or not.

Dye stain test: This test is commonly employed to know whether sealing has been performed or omitted.

Kape test: This test is commonly employed to know the degree of sealing.

The following numerical system of rating is given for the samples tested according to the kape test.

Rating	Visual Appearance after test.	Degree of Bloom.
5	Little or no change	None
4	Very light Bluish tinge	Very light
3	Light Bluish tinge	Light
2	Bluish grey	Moderate
1	Grey or white	Heavy

A rating of 3 or higher after treatment is considered acceptable whereas 2 or lower is cause for rejection.

The following typical examples are given to illustrate how the invention is carried out in actual practice but not to limit the scope of this invention.

EXAMPLE - 1

2S aluminium (miniumum 99% Al) plates were polished, degreased and alkaline cleaned in 10% sodium hydroxide and washed in water. This was followed by acid dipping in 10% nitric acid for desmutting. Then the specimens were washed in tap water and rinsed in distilled water and anodising carried out in 10% V/V sulphuric acid at 20 ± 2°C for 30 min. at 12 Asf. After anodising, the specimens were washed and sealing carried out under the following conditions:

15J403

Nickel acetate	5 g/l
Cobalt acetate	1 g/l
pH	6.0 ± 0.5
Temp.	@ 70 ± 2°C
Time	10 min.

After sealing the panels were washed and tested for sealing efficiency by the Dye stain test and Kapo test. Both tests indicated poor sealing. The sealed panel is ~~xxxxxxxxxxx~~ covered with a bloom or chalk.

Another set of anodised panels were sealed in the following bath.

Nickel acetate	5 g/l
Cobalt acetate	2 g/l
Ethylene Diamine	to pH 7.5 ± 0.5
Temp.	70 ± 2°C
Time	10 min.

Good sealing was obtained according to the dye stain and kapo test. The surface is free from sealing blooms.

Still another set of anodised panels were sealed under the following conditions:

Nickel acetate	10 g/l
Cobalt acetate	1 g/l
Triethanol amine	to pH 7.5 ± 0.5

Best sealing was obtained according to the dye stain and kapo test. The surface is free sealing blooms.

Another set of anodised panels were sealed under the following conditions.

Nickel acetate	7 g/l
Cobalt acetate	1 g/l
Thiourea	2 g/l
pH	6 - 7
Temp.	70 ± 2°C

Good sealing was obtained according to the dyestain and kapo test. The surface is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions:

Nickel acetate	5 g/l
Cobalt acetate	1 g/l
EDTA	3 g/l
pH	6 - 7
Temp.	70 ± 2°C

Good sealing was obtained according to the dyestain and kape test. The surface is free from sealing blooms.

In the following table the rating (according to kape test) upon the effect of the different addition agents is given:

	Solution	Addn. Agent	Rating (according to kape test)
1.	Nickel acetate + Cobalt acetate (60 - 80°C)	Ethylene diamine	5
2.	-do-	Triethonol Amine	5
3.	-do-	Thiourea	4
4.	-do-	Nickel fluoride	4
5.	-do-	EDTA	5
6.	-do-	nil	2

EXAMPLE 2 II

3S aluminium plates (containing 1.2% Mn, rest aluminium) were cleaned and anodised as in Example 1 and sealed under the following conditions:

Nickel sulphate	10 g/l
Temp.	70 ± 2°C
pH	5 - 6
Time	10 min.

The anodised plates were poorly sealed according to the dyestain and kape tests. The sealed panel is covered with a bloom of chalk.

Another set of anodised panels were sealed under the following conditions:

Nickel sulphate	15 g/l
Ethylene diamine	to pH 7.5 ± 0.5
Temp.	70 ± 2°C
Time	10 min.

Good sealing was obtained according to Dyestain and kape tests. The sealed panel is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions.

Nickel sulphate	10 g/l
Triethanolamine	to pH 7.5 ± 0.5
Temp.	70 ± 2°C
Time	10 min.

Good sealing was obtained according to the Dyestain and kape test. The sealed panel is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions:

Nickel sulphate	20 g/l
EDTA	5 g/l
pH	6 - 7
Temp.	70 ± 2°C
Time	10 min.

Good sealing was obtained according to the Dye stain and kepe test.

Another set of anodised panels were sealed under the following conditions:

Nickel sulphate	10 g/l
Thiourea	4 g/l
pH	6 -7
Temp.	70 ± 2°C
Time	10 min.

Good sealing was obtained according to the Dye stain and kape Test. The sealed panel is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions:

Nickel sulphate	10 g/l
Nickel fluoride	2 g/l
pH	6 - 7
Time	10 min.

Good sealing was obtained according to the dye stain and kape test. The sealed panel is free from sealing blooms and chalks.

In the following table, the rating (according to the kape test) upon the effect of the different addition agents is given.

	Solution	Addition Agent	Rating (According to kape test)
1.	Nickel sulphate (60 - 80°C)	Ethylene diamine	5
2.	-do-	Triethonolamine	5
3.	-do-	EDTA	5
4.	-do-	Thiourea	4
5.	-do-	Nickel Fluoride	4
6.	-do-	nil	2

EXAMPLE III

26S aluminium plates (containing 4.85% Cu, 0.5 Mg 0.75 Mn and rest Al) were cleaned and anodised as in Example I and sealed under the following conditions:

Sodium dichromate	15 g/l
Temp.	70 ± 2°C
Time	10 min.
pH	7 ± 0.5

The anodised plates were poorly sealed according to the Dye stain and kape test. The sealed panel is covered with bloom and chalk.

Another set of anodised panels were sealed in a modified solution under the following conditions:

Sodium dichromate	15 g/l
Ethylene diamine	5 ml/l
pH	7.5 ± 0.3
Temp.	70 ± 2°C
Time	10 min

Good sealing was obtained according to Dye stain and kape tests. The sealed panel is free from sealing bloom and chalk.

Another set of anodised panels were sealed in the modified solution under the following conditions:

Sodium dichromate	20 g/l
Triethanolamine	to pH 7.5 ± 0.5
Temp.	70 ± 2°C
Time	10 min.

Good sealing was obtained according to the Dye stain and kapo tests. The sealed panel is free from sealing bloom and chalk.

Another set of anodised panels were sealed under the following conditions:

Potassium dichromate	25 g/l
EDTA	5 g/l
pH	6 - 7
Temperature	65 ± 2°C
Time	15 min.

Good sealing was obtained according to the Dye stain and kapo test. The sealed panel is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions:

Potassium dichromate	10 g/l
Thiourea	2 g/l
pH	6 - 7
Temp.	75 ± 2°C

A good sealing was obtained by dye stain test and kapo s test. The sealed panel is free from sealing blooms.

In the following table, the rating (according to kapo test) upon the effect of the different addition agents is given.

Solution	Addition Agent	Rating (Accord. to kapo test)
1. Sodium Dichromate (60 - 80°C)	Ethylene diamine	5
2. -do-	Triethanolamine	5
3. Potassium Dichromate	EDTA	5
4. -do-	Thiourea	4
5. -do-	nil	2.

150403

The following are the main advantages of this invention

(1) Sealing can be carried out at substantially lower temperature.

(2) The additions made to the sealing bath eliminates the formation of sealing blooms

(3) The chemicals used in this invention are indigeneously available

(4) Since the sealing operation is carried out between 65° and 80°C there is ~~an~~ considerable energy gain in this process.

Dated This 30th day of Dec. 1978

S. Kumar,
Agent Patents Offices
Council of Scientific
& Industrial Research
[illegible], CSIR Complex,
[illegible], Library Road,
Pusa, New Delhi 110012

150403

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

"IMPROVED PROCESS FOR THE SEALING OF ANODISED ALUMINIUM AND ITS ALLOY SUBSTRATES".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registred 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 :—

150403

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist; SUBBIAH JOHN, Senior Technical Assistant and ANGUSAMY PERUMAL, Senior Laboratory Assistant, all are Indian Nationals and employed in the Central Electrochemical Research Institute, Karaikudi 623 006, Tamilnadu, India.

This invention relates to an improved process for the sealing of anodised aluminium and its alloy substrates by using a modified sealing solution containing addition agents.

Hitherto it has been proposed to seal the oxide films on aluminium and its alloy substrates by the following methods:

1) In decorative anodising where a colourless transparent anodic film is formed e.g. over a polished surface, the coating are sealed in hot water or steam
2) Dichromate sealing is used for sealing sulphuric acid anodic coatings for improved corrosion resistance
3) Sodium silicate (water glass) sealing is also used
4) Sealing is also carried out in metallic salt solutions of nickel, cobalt and lead in low concentrations. They hydrolize in the pores to from the respective hydroxide.
5) Electrolytic sealing methods e.g. sodium phosphate solution-s are also available for sealing.

The main draw back of the hitherto known sealing process are:

1) The hot water sealing process causes the formation of sealing bloom. This sealing bloom is an unwanted side effect of sealing in the form of a thin powdery layer which forms on the surface and is usually invisible until the surface is dried and rubbed with the finger when a white mark appears like a chalk mark.

2) Dichromate sealing is frequently used for non decorative purposes. It gives the coating a yellow colour and is therefore

often unsuitable for decorative applications.

3) Sodium silicate sealing is less important than water, dichromate or nickel/cobalt acetate sealing for anodic oxide films and is used infrequently.

4) Sealing in salt solutions for e.g. in nickel/cobalt acetate is carried out at higher temperatures of 90°C - 100°C. Sealing carried in this bath is also left with a bloom on anodised aluminium. When sealing is carried out at a lower temperature of 60-80°C sealing is imperfect and the bloom formation takes place.

5) Electrolytic sealing is rarely used and is still of theoretical interest.

The main object of the present invention is to obtiate the above disadvantages by the use of a modified metal salt solution in the improved process for sealing anodised aluminium substrates at comparatively lower temperatures.

The other main objects of this invention are that:

1) the sealing can be carried out at substantially lower temperature
2) the additions made to the sealing bath eliminates the formation of sealing blooms
3) the chemicals used in this invention are indigenously available
4) since the sealing operation is carried out between 65°C and 80°C there is considerable energy gain in this process.

The main finding underlying the present invention consists in sealing the anodised aluminium substrates using an aqueous solutions of either nickel sulphate or K (or Na) dichromate or Ni/Co acetate which contain small quantities of addition agents such as ethonolamines, Sn metal fluorides, aliphatic

amines and aliphatic thioamides. These solutions with any one of the above mentioned addition agents are operated at the temperature range of 65-80°C.

The new result flowing from the improved process of this invention is that perfect sealing is achieved from the use of modified solutions at a comparatively lower operating temperatures.

The invention thus provides an improved process for sealing of anodised aluminium and its alloy substrate comprising the steps of treating the anodised substrate in an aqueous bath of cobalt and/or nickel salts or an alkali metal dichromate salt wherein the improvement comprises in incorporating in the aqueous bath one or more of the addition agents namely triethanolamine, thiourea, ethylene diamine tetra acetic acid or nickel fluoride.

The present invention consists of a process for sealing of anodised aluminium and its alloy which comprises the steps of polishing and buffing, degreasing, alkaline cleaning, desmutting, anodising and sealing at a temperature of 65-75°C for a period of 10-25 minutes at a pH of 6-8 in an aqueous solution containing :

i) Nickel acetate 5-15 g/l + cobalt acetate 1-2 g/l

ii) Nickel sulphate 10-20 g/l or

iii) Sodium or potassium dichromate 10-20 g/l with any one of the addition agents namely ethylene diamine or triethanolamine in amounts of 1-10 ml/l or thiourea or EDTA or nickel fluoride in amounts of 1-5 gm/l wherein the incorporation of the addition agents enables sealing at a substantially lower temperature and eliminates the formation of sealing bloom.

The following two tests were carried out to ascertain whether sealing is perfect or not.

Dye Stain test: This test is commonly employed to know whether sealing has been performed or ommitted.

Kape test : This test is commonly employed to know the degree of sealing.

The following numerical system of rating is given for the samples tested according to the kape test.

Rating	Visual appearance after test	Degree of Bloom
5	Little or no change	None
4	Very light bluish tinge	Very light
3	Light bluish tinge	Light
2	Bluish grey	Moderate
1	Grey or white	Heavy

A rating of 3 or higher after treatment is considered acceptable whereas 2 or lower is cause for rejection.

The following typical examples further illustrate how the invention is carried out in actual practice but not to limit the scope of this invention.

EXAMPLE 1

2S aluminium (minimum 99% Al) plates were polished, degreased and alkaline cleaned in 10% sodium hydroxide and washed in water. This was followed by acid dipping in 10% nitric acid for desmutting. Then the specimens were washed in tap water and rinsed in distilled water and anodising carried out in 10% V/V sulphuric acid at 2 ± 2°C for 30 minutes at 12 Asf. After anodising, the specimens were washed and sealing carried out under the following conditions:

Nickel acetate	: 2 g/l
Cobalt acetate	: 1 g/l
pH	: 6.0 ± 0.5
Temperature	: 70 ± 2°C
Time	: 10 minutes

After sealing the panels were washed and tested for sealing efficiency by the Dye stain test and Kape test. Both tests indicated poor sealing. The sealing panel is covered with a bloom or chalk.

Another set of anodised panels were sealed in the following bath :

Nickel acetate	: 5 g/l
Cobalt acetate	: 2 g/l
Ethylene diamine to pH	: 7.5 ± 0.5
Temperature	: 70 ± 2°C
Time	: 10 minutes

Good sealing was obtained according to the dye stain and Kape test. The surface is free from sealing blooms.

Still another set of anodised panels were sealed under the following conditions:

Nickel acetate	: 10 g/l
Cobalt acetate	: 1 g/l
Triethanol amine to pH	: 7.5 ± 0.5

Best sealing was obtained according to the dye stain and Kape test. The surface is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions :

Nickel acetate	: 7 g/l
Cobalt acetate	: 1 g/l
Thiourea	: 2 g/l
pH	: 6-7
Temperature	: 70 ± 2°C

Good sealing was obtained according to the dyestain and Kape test. The surface is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions.

Nickel acetate	: 5 g/l
Cobalt acetate	: 1 g/l
EDTA	: 3 g/l
pH	: 6-7
Temperature	: 70 ± 2°C

Good sealing was obtained according to the Dyestain and Kape test. The surface is free from sealing blooms.

In the following table the rating (according to Kape test upon the effect of the different addition agents is given.

Solution	Addition agent	Rating(According to Kape test
1. Nickel acetate + cobalt acetate (60-80°C)	Ethylene diamine	5
2. -do-	Triethanol amine	5
3. -do-	Thiourea	4
4. -do-	Nickel fluoride	4
5. -do-	EDTA	5
6. -do-	Nil	2

Example 2

3S aluminium plates (containing 1.2% Mn, rest aluminium) were cleaned and anodised as in Example 1 and sealed under the following conditions.

Nickel sulphate	: 10 g/l
Temperature	: 70 ± 2°C
pH	: 5-6
Time	: 10 min

The anodised plates were poorly sealed according to the Dyestain and Kape tests. The sealed panel is covered with a bloom of chalk.

Another set of anodised panels were sealed under the following conditions :

Nickle sulphate	: 15 g/l
Ethylene diamine to pH	: 7.5 ± 0.5
Temperature	: 70 ± 2°C
Time	: 10 minutes

Good sealing was obtained according to the Dyestain and Kape test. The sealed panel is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions:

Nickel sulphate	: 10 g/l
Nickel fluoride	: 2 g/l
pH	: 6-7
Time	: 10 min.

Good sealing was obtained according to the dye stain and kape test. The sealed panel is free from sealing blooms and chalks.

In the following table, the rating (according to the Kape test) upon the effect of the different addition agents is given.

Solution	Addition agent	Rating (according to Kape test)
1. Nickel sulphate (60-80°C)	Ethylene diamine	5
2. -do-	Triethonolamine	5
3. -do-	EDTA	5
4. -do-	Thiourea	4
5. -do-	Nickel fluoride	4
6. -do-	Nil	2

26 S aluminium plates (containing 4.25% Cu, 0.5 Mg, 0.75 Mn and rest Al) were cleaned and anodised as in example 1 and sealed under the following conditions:

Sodium dichromate	: 15 g/l
Temperature	: 70 ± 2°C
Time	: 10 minutes
pH	: 7 ± 0.5

The anodised plates were poorly sealed according to the Dye stain and Kape test. The sealed panel is covered with bloom and chalk.

Another set of anodised panels were sealed in a modified solution under the following conditions:

Sodium dichromate	: 15 g/l
Ethylene diamine	: 5 ml/l
pH	: 7.5 ± 0.5
Temperature	: 70 ± 2°C
Time	: 10 minutes.

Good sealing was obtained according to Dye stain and Kape test. The sealed panel is free from sealing bloom and chalk.

Another set of anodised panels were sealed in the modified solution under the following conditions:

Sodium dichromates	: 20 g/l
Triethanolamine to pH	: 7.5 ± 0.5
Temperature	: 70 ± 2°C
Time	: 10 minutes

Good sealing was obtained according to the Dye stain and Kape test. The sealed panel is free from sealing bloom and chalk.

Another set of anodised panels were sealed under the following centiend conditions:

Potassium dichromate	: 25 g/l
EDTA	: 5 g/l
pH	: 6-7
Temperature	: 65 ± 2° C
Time	: 15 minutes.

150403

Good sealing was obtained according to Dye Stain and Kape test. The sealed panel is free from sealing blooms.

Another set of anodised panels were sealed under the following conditions:

Potassium dichromate	: 10 g/l
Thiourea	: 2 g/l
pH	: 6-7
Temperature	: 75 $\pm$ 2°C

A good sealing was obtained by Dye stain and kape test. The sealed panel is free from sealing blooms.

In the following table, the rating (according to Kape test.) upon the effect of the different addition agents is given.

Solution		Addition Agent	Rating According to Kape test
1.	Sodium dichromate (60 - 80°C)	Ethylene diamine	5
2.	-do-	Triethonolamine	5
3.	Potassium dichromate	EDTA	5
4.	-do-	Thiourea	4
5.	-do-	Nil	2

150403

WE CLAIM :

1. Improved process for the sealing of anodised aluminium and its alloy substrates comprising the steps of treating the anodised substrate in an aqueous bath of cobalt and/or nickel, salts or alkali metal dichromate salts, wherein the improvement comprises in incorporating in the aqueous bath one or more of addition agents namely triethanolamine, thiourea, ethylene diamine-tetra-acetic acid or nickel fluoride.

2. Process as claimed in claim 1 wherein the aqueous bath contains 1-10 ml/l of triethanolamine as the addition salt.

3. Process as claimed in claim 1 wherein the aqueous bath contains 1-5 g/l of thiourea, ethylenediamine tetra acetic acid or nickel fluoride as the addition agent.

4. Process as claimed in any of the preceding claims wherein the treatment in the aqueous bath is carried out at a temperature range of 65-75°C for a period of 10-25 minutes and at a pH of 6-8.

5. Process as claimed in claims 1,2 and 3 wherein the aqueous bath consists of 5-15 g/l of nickel acetate, 1-2 g/l of cobalt acetate and 1-10ml/l of the addition agent.

6. Process as claimed in claims 1,2 & 3 wherein the aqueous bath consists of 10-20 g/l of sodium or potassium dichromate and the addition salt.

7. Process as claimed in claims 1,2 and 3 wherein the aqueous bath consists of 10-20 g/l of nickel sulphate and the addition salt.

8. Improved process for sealing of anodised aluminium and its alloy substrates substantially as herein described and illustrated in the examples.

Dated this 28th day of December, 1979.

(I.M.S.MAMIK)
SCIENTIST (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.