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" AN IMPROVED PROCESS FOR CHEMICAL COLOURING
OF ALUMINIUM AND ITS
ALLOYS SUBSTRATES "

COUNCIL OF SCIENTIFIC AND 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.

This is an invention by Welkunje 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 Chemical colouring of aluminiums and its alloys.

Hitherto it has been proposed to chemically colour aluminium and its alloys to various shades in the following ways:

- (1) The modified Bauer Vogel Process produces light to dark grey coatings depending on alloys
- (2) The chromating process produces colours ranging from iridescent yellow to brown coatings from chromate fluoride baths.
- (3) The chromate phosphate process produces light bluish green with slight iridenscence on copper free alloys, and an olive green colour on copper containing alloys.
- (4) Black colours can be obtained by immersing the metal in a solution containing potassium permanganate, copper nitrate and nitric acid at temperatures of 80 - 100°C for 20-30 minutes.
- (5) A blue bronzing solution contains 5g/1 each of potassium ferricyanide and ferrous chloride.
- (6) A grey iron like colour is obtained by treatement with a solution containing 25 g/l potassium sulphide and 1 g/l vanadium sulphate at 80°- 90°C.
- (7) A reddish brown colour is obtained from a solution containing potassium permanganate, cadmium nitrate, ferrous chloride and

and nitric acid.

The main draw backs associated with the hitherto known . process are that:-

- 1) the MBV process produces iridescent shades and they are not so attractive as to meet the architectural applications. Moreover the coating is very thin of the order of 1 2 microns.
- 2) the chromating process produces iridescent yellow colours of film thickness 0.1-1/u and they are not all attractive as to stand themselves for architectural applications.
- 3) the chromate-phosphate process produces attractive green shades of thickness ranging from 1-5 /u But the rang of colours is restricted to green only.
- 4) Bath numbers 4 & 5 produces non-adherent smutty black coating and are non-uniform.
- 5) Baths given in 6&7 produces very thin coatings of the order of 0.5 to 1/u and are usually iridescent and non-uniform.

The main object of the present invention is to obviate these disadvantages by using a more versatile process for producing various colours suitable for architerctural applications on aluminium and its alloys.

The main finding underlying the invention consists in chemically treating aluminium and its alloys in an aqueous solution comprising Ammonium carbonate, 10-50 g/l carbonates of Zinc, Cadmium, Manganese, Lead, Nickel, Copper and Iron singly or in combination 0.05-0.1 g/l. Ethanol amines having carbon atoms 1-6 in amounts of 0.5-5 ml/l, sodium hydroxide 0.01-0.1 g/l. at a pH of 7-10 at a temperature of 80 -100°C for a period of 3-20 minutes wherein coating thickness of the order of 3to7 microns can be produced.

The new result flowing from the new finding is that various attractive shades ranging from grey to black and yellow to bronze and brown shades suitable for decrative and architectural applications on aluminium and its alloys can be produced.

The named feature of the present invention is that various shades on aluminium and its alloys can be produced in short durations from the baths containing cheaply available ingredients.

1 50 16 4. The flow sheet of the process is as follows:

Polishing and Buffing

Degreese in Trichlemethylene

Desire in alkali

Descript in nitric acid

Wash in running water

Treat in the colouring solution

Wash in running water

me appearance of finances produced according to the present invention is greatly dependent on the intial surface of the metal being treated. The coloured films accountely reproduce the surface condition of the underlying metal. Thus, antirely different effects result from the same colouring treatment depending on whether the metal has been pretreated by acid dipping, shot blasting scratch brushing, etc.

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

BIANKE I

25 (minimum 99% Al) Aluminium plates degreeded with trichloreethylene, etched in an alkaline solution containing 50 solution hydroxide, rinsed and desaudged in 10% Mitric said washed and then immersed in the fellowing chemical colouring solution.

Ammonium Carbonate Triethanol amine Tine carbonate 20 s/1 1 m1/1 800 mg 025 - 0.4 s/1 8.0 ± 0.5

Innersian Time

Colour

5 Min

Light grey

15 Min

Medium grey

PERMIT II

35 Aluminium (contain 1.25 Mm, rest Al) punels were degreesed with acetone etched in an acid solution contain hydrofineric acid 55 Mitrie meid 15%, washed and immersed in the following bath.

Ammonium carbonate	15 8/1
Triethenolumine	0.5 =1/1
Nanganose carbonate	0.5 8/1
pil	7.5 ± 0.5
Temp.	95 ± 2°C

Inversion Time	Colour

3 Min Light yellow 10 Min Medium yellow

PERMIT III

26 S aluminium (4.25% Cu, rest Al) plates were degreesed with trichloroethylene and etched in a solution containing Ferric chloride 100 g/l, Hydrochloric said 150 ml/l washed and immersed in the following solution.

Associum carbonate	30 s/l
Triethmolemine	2 =1/1
Lead carbonate	0.1 6/1
ing.	9.0 ± 0.5
Tesp.	90 ± 2°0
Innersion Ties	C are
	Light yellow
5 Min	Medium yellow
10 Min	Dark yellow

REALE IV

15 Min

26 S Aliminium alloys were degreesed with trichloroethylone etched in an alkali solution containing 10g/l sedium carbons / 50/640 20 g/l trisodium phosphate at 50 C for 2 to 3 min. and chemically polished to produce a nearly mirror bright finish washed and trea-Wed in the following solution,

Ammonium carbonate	10 g/l
Mencethenol amine	1 ml/l
Nickel carbonate	0.5 g/l
Hq	8.0 ± 0.5
Temp.	95 ± 2°C
Imersion Time	Colour
3 min	Light yellow
10 min	Golden yellow

TIMMLE V

Hindalium plates (containing 4.0 - 4.9% Mg, 0.5 - 1.0% Si 0.1% copper) were degreased, etched in 5% Sodium hydroxide solution washed etched in a solution containing 50 g/l Perric chleride 175 ml/l hydrochloric acid washed and immersed in the following solution.

Ammonium carbonate	50 g/l
Diethanol amine	1 m3/1
Copper carbonate	0.2 8/1
ρĦ	9 ± 0.5
Temp.	85 ± 2°C
Immersion time	Colour
5 man	Light grey
10 min	Kedi vm grey

EXAMPLE VI

Super purity aluminium panels were degreased alkaline etched in 2% sodium hydroxide solution, washed dipped in 10% Witric acid washed electropolished and immersed in the fellowing bath.

Ammonium carbonate	20 g/l
Triethmel amine	1 ml/1
Cadmium carbonate	0.2 8/1
	8.0 ± 0.5.
15	95 ± 2 ⁰ 6
	

3 min

10 min

Light grey

Dark brownish grey.

EXAMPLE VIII

Commercial purity aluminium alloys were degreased stated in 25 g/l Ammonium bi fluoride, 15% Witric acid, washed and immersed in the fellowing bath.

Ammonium carbonate	40 g/1
Triethanol amine	2 =1/1
Wickel carbonate	0.01 8/1
Copper carbonate	0.1 g/l
WeOH	.01 g/ l
yil	9 ± 0.5
Temp.	97 ± 2°C
Innersion time	Colour
5 min	Light black
10 min	Medium black
20 min	Nearly jet black

BYMPIR VIII

28 aluminium alloys were degreesed and pretrected as per Example VII, washed and immersed in the following bath.

Ammonium carbonate	50 g/l
Monoethanolmine	2 =1/1
Ferrous carbonate	0.1 g/l
Copper carbonate	0.1 g/l
Kaoh	0.1 4/1
#E	9.5 ± 0.5
Temp.	90 ± 2°C
Intersica time	Colour
5 Min	Light brownish grey
10 *	Medium brownish gray
15 *	Dark breonish grey
17 "	Jet black.

EXAMPLE IX

61S Aluminium (1.0% mg, 0.6% Si, 0.25% Cu, 0.25 Cr rest Aluminium) alloys were degreesed and pretreated as in Example VII and immersed in the following bath.

Ammonium Carbonate	25 9/1
Diethenolemine	1. m1/1
Zinc carbonate	. 0.1 g/1
Copper carbonate	0.1 g/1
NaOH	.01 g/1
рң	8.5 ± 0.5
remp.	97 ± 2°C
Immersion time	Colour
5 min.	light greenish yellow
10 min.	Medium greenish yellow
20 min.	Dark greenish yellow.

The main advantages of the present invention are:

- 1. The chemicals involved in this process are cheap and hence more economical.
- 2. A wide range of shades are obtained on aluminium and its alloys.

Dated this 30th day of September, 1978.

(I.M.S.MAMAK)

SCIENTIST (PRIMITS)

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

1 50164 THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section-10)

* AM IMPROVED PROCESS FOR CHEMICAL COLOURING
OF ALUMINIUM AND ITS ALLOYS SUBSTRATES *

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
Rafi Marg, New Delhi - 110001, India, an Indian
registered body incorporated under the Registration
of Societies (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, SUBBIAH JOHN, Senior Scientific Assistant and
ANGUSAMY PERUMAL, Junior Technical Assistant, all are
Indian Nationalsand employed in the Central Electrochemical
Research Institute, Karaikudi - 623006, Tamil Nadu.

This invention relates to an improved process for chemical colouring of aluminium and its alloys substrates.

Hitherto a number of process have been proposed to chemically colour aluminium and its alloys substrates to various shades. These are mainly:-

- 1) The modified Bauer Vogel process produce light to dark grey coatings depending on alloys.
- 2) The chromating process produces colours ranging from iridescent yellow to brown coatings from chromate-fluoride baths.
- The chromate phosphate process produces light
 bluish green with flight irridescence on copper free
 alloys and an olive green colour on copper containing
 alloys.
- 4) Black colours can be obtained by immersing the metal in a solution containing potassium permanganate, copper nitrate and nitric acid at temperatures of 80-100°C for 20-30 minutes.
- 5) A blue bronzing solution contains 5g/1 each of potassium ferricyanide and ferrous chloride.
- 6) A grey iron like colour is obtained by treatment with a solution containing 25 g/1 petassium sulphide and 1 g/1 vanadium sulphate at 80-90°C.

7) A reddsh bram colour is obtained from a solution containing potassium permanganage, cadmium nitrate, ferrous chloride and nitric acid.

The main drawbacks associated with the hitherto known process are that:

- the modified Bauer Vogel process produces iridescent shades and they are not so attractive as to meet the architectural applications. Moreover the coating is very thin of the order of 1-2 microns.
- the chromating process produces iridescent yellow colours of film thickness 0.1 - 1 micron and they are not all attractive as to stand themselves for architectural applications.
- the chromate-phosphate; rocess produces attractive green shades of thickness ranging from 1-5 microns. But the range of colours is restricted to green only.
- Both numbers 4 and 5 produces non adherent smutty black coating and are non uniform.
- Baths given in 6 and 7 produces very thin coatings of the order of 0.5 to 1 micron and are usually iridescent and non uniform.

The main object of the present invention is to obviate these dis-advantages by using an improved process for producing desired colours suitable for architectural applications on aluminium and its alloys.

The main finding underlying the invention consists in the use of an improved aqueous solution comprising alluminium and its alloys.

The main finding underlying the invention consists in the use of an improved dequeous solution comprising emeaning carbonate 10-50 g/1, carbonates of zinc cadmium, mangeness, lead, nickel, copper and iron singly or in combination 0.05-O.1 g/1, ethanol amine having/atoms 1-6 in amounts of 0.5-5 ml/1, sodium hydroxide 0.01 to 0.1 g/1 at a PH of 7-10 for immersion of the metal at a temperature of 80-100°C for a period of 3-20 minutes wherein coating thickness of the

eader of 3 to 7 micross can be produced.

The main advantages of the present invention aresThe chemicals involved in this process are cheep
and hence more economical and a wide range of shades are
abtained on aluminium and its alloys.

The invention accordingly provides an improved process for chemical colouring of aluminium and its allows substrates comprising the steps of polishing and buffing, degreesing, alkaline etching, acid dipping and immersion in a chemical bath wherein the improvement consists in that an aquacus solution containing 10-50 g/l of ammonium carbonate, 0.05 - 0.1 g/l of carbonates of zinc, cadmium, manganese, lead, nickel, copper and iron singly or in combination, 0.5 to 5 ml/l of ethanolamines having 1-6 darken etcoms and 0.1 g/l of sodium hydroxide is used as the chemical bath and the treatment is carried out at a pH of 7-10 and at a temperature between 80-100°C for a period of 3-20 minutes, followed by washing and drying the coloured substrates obtained.

The carbonates of zinc, cadmium, manganese, lead, nickel, copper and iron produce coloured coating of thickness of the order of 3-7 microns and of colours ranging from error to black and various shades of yellow can be obtained.

The new result flowing from the new finding is that various attractive shades ranging from grey to black and yellow to bromes and brown shades suitable for depositive and architectural applications on aluminium and its allegs can be produced.

The novel feature of the present invention is that

various shades on aluminium and its alloys can be produced in short durations from the baths containing cheeply available iCngradients.

The flow sheet of the process is as follows:

Polishing and buffing
Degreese in trichloroethylene
Etching in alkali
Desumt in nitric acid
Wash in running water
Wash in dimineralised water
Treat in the colouring solution
Wash in running water

The appearance of finishes produced according to the present invention is greatly dependent on the initial surface of the metal being treated. The coloured films accurately reproduce the surface condition of the underlying metal. Thus, entirely different effects result from the same colouring treatment depending on whether the metal has been pretreated by commentional steps like acid dipping, shot blasting and scratch brushing.

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

Syample - I

(Minimum 99% Al) Aluminium plates degreesed with trichloroethylene, etched in an alkaline solution containing 50 g/1 sodium hydroxide, rinsed and definded in 16% nitric acid washed and then immersed in the following chemical colouring solution.

Ammonium Carbonate : 20 g/1 Triethanelamine 2 1 ml/1Minc carbonate 2 $0.4 \, \text{g/l}$ pH \$ 8.0 <u>+</u> 0.5 l'emperature 85 <u>+</u> 2°C

immersion time Colour 5 minutes Light grey 10 minutes Medium grey

Example -2

Aluminium (containing 1.2% Mn, rest Al) panels were degreased with acetone etched in an acid solution containing hydro fluric acid 5% Nitric acid 15% wased and immersed in the following bath.

> Ammonium carbonate : 15 q/1 Triethanolamine * $0.5 \, \text{ml/l}$ $0.5 \, \text{g/l}$ Manganese carbonate : : 7.5 <u>+</u> 0.5 рH ; 95 ± 2°C Temperature Colour Immersion time Light yellow 3 minutes

Medium yellow 10 minutes

1 50164 Example -3

Aluminium (4.25% Cu, rest Al) plates were degreased with trichloroethylene and etched in a solution containing ferric chloride 100 g/l Hydrochloric acid 150 ml/l washed and immered in the following solution:

Ammonium carbonate		30 g/l
Triethanolamine	:	2 ml/l
Lead carbonate	:	0.1 g/l
pH		9.0 ± 0.5
Temperature	*	90 ± 2°C

Immersion time	Colour
5 minutes	Light yellow
10 minutes	Medium yellow
20 minutes	Dark yellow

Brample -4

Aluminium alloys were degreased with trichleroethylene etched in an alkali solution containing 10 g/l sedium carbonate, 20 g/l sodium carbonate, 20 g/l trimodium phosphate at 50°C for 2 to 3 minutes and chemically polished to produce a nearly mirror bright finish washed and treated in the following solution.

Ammonium carbonate	•	10 g/l
Monoethanelamine	:	1 ml/l
Nickel carbonate	:	8+0-± 0.5 E/1
pël	1	3.0 ± 0.5
Temperature	1	95 ± 2°C
Immersion time		Colour
3 minutes		Light yellow

3 minutes Light yellow to minutes

Branche &

"Mindalium" plates (containing 4.0 - 4.9% Mg. 0.5-2.0% Md. 0.1% copper) were degreesed, stched in 5% sodium hydroxide solution washed etched in a solution containing 50 g/1 ferric chloride 175 ml/1 hydrochlorid acid washed and immerced in the following solution:

Ammonium Carbonate	2	50 g/1
Diethenol amine	*	1 ml/1
Copper carbonate	\$,	0.2 9/1
рH	•	9 + 0.5
Temperature		85 <u>+</u> 2 ^Q C

Example 6

Super purity aluminium panels were degreesed alkaline etched in 2% sodium hydroxide solution, washed dipped in 10% nitric acid weshed electropolished and immersed in the following baths.

Amedialum	3	20 9/1
Triethanol amine		1 ml/1
Cadmium carbonate	2.	0.2 g/1
W	:	8.0 <u>+</u> 0.5
Semperature	2	95 ± 2 ⁰ C
Time of impossion		Colons
3 minutes		Light grey
10 minutes	•	Dark brownish gray

Example 7

Commercial purity aluminium alloys were degreesed etched in 25 g/l ammonium bifluoride, 15% nitric acid, washed a immersed in the following bath.

Ammonium carbonate	2	40 g/1
Triethanol emine	i	2 ml/l
Mickel carbonate		0.1 9/1
Connec carbonate	:	0.1 0/1

NaOH		0.01 g/1
рН		9 + 0.5
Temperature	*	97 <u>+</u> 2 ⁰ C
Immersion time		Colour
5 minutes		Light black
10 minutes		Medium black
20 minutes		Nearly jet black

Example

Aluminium alloys were degreased and pretreated as per example 7 washed and immersed in the following bath.

Ammonium Carbonate	50 g/1
Monoethanolamine	2 ml/1
Feerous carbonate	0.1/g/1
Copper carbonate	0.1 9/1
NaOH .	0.1 g/1
рН	9.5 + 0.6
Temperature	90 <u>+</u> 2 ⁰ C
Immersion time	Colour
5 minutes	Light brownish grey
10 minutes	Medium brownish grey
15 minutes	Dark brownish grey
20 minutes	Jet black

Example 9

Aluminium (1.0% mg, 0.6% Si, 0.25% Cu, 0.25 Cr rest sluminium) alloys were degreesed and pretreated as in example 3 and immersed in the following bath:

Ammonium carbonate		25 g/1
Diethanolamine		1 ml/1
Zinc carbonate		0.1 g/l
Copper carbonate	1 .	0.1 g/l
NaOH		0.01 g/1
		8.5 ± 2.5 97 ± 2°C
pH Temperature Immersion time		Colour's Light greenish yellow
5 min sion time		Medium greenish vallos

BE CAMPE:-

- aluminium and its alloy substrates comprising the steps of polishing and buffing, degreesing, alkaline etching, acid displing and immersing in a chemical bath wherein the improvement consists in that an equeous solution containing 10-50 g/l of ammonium carbonate, 0.05 0.10 g/l of carbonates of size, codmium, mangamene, lead, nickel, copper and issue singly or in combination, 0.5 5 ml/l of otherolamines having 1-6 caubon atoms and 0.1 g/l of soldium hydroxide is used as the chemical bath and the treatment is carried out at a pH of 7-10 and at a temperature between 80-100°C for a pessed of 3-20 minutes, followed by washing and drying the explaured substrates obtained.
- 2. The process as claimed in claim 1 wherein the chemical both sensists of 20 g/1 of amenium customete, 1 ml/1 of tylephonel amine, 0.4 g/1 of Mine ensbenete and the taustment is engried out at a pH of 8.0 to 8.5 and at a taugum tupe of 85 to 87°C for 5 to 15 minutes.
- 3. An improved process for the chandeal columning of aluminium and alloy substrates substantially as herein described and illustrated in examples.

Dated this fact day of Orighes, 1979

(I.M.S. MANN)

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