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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 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 Chemical colouring of aluminium 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 iridescence 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/l each of potassium ferricyanide and ferrous chloride.
- (6) A grey iron like colour is obtained by treatment 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.

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The main drawbacks 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

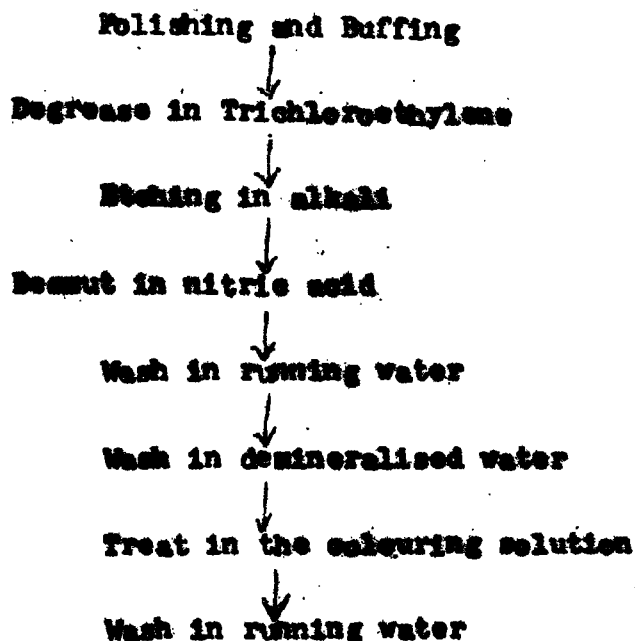
coating thickness of the order of 3to7 microns can be produced.

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 decorative and architectural applications on aluminium and its alloys 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 cheaply available ingredients.

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The flow sheet of the process is as follows:



The appearance of fineness produced according to the present invention is greatly dependant 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 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.

EXAMPLE I

25 (minimum 99% Al) Aluminium plates degreased with trichloroethylene, etched in an alkaline solution containing 50 g/l sodium hydroxide, rinsed and desmutted in 10% Nitric acid washed and then immersed in the following chemical colouring solution.

Ammonium Carbonate	20 g/l
Triethanol amine	1 ml/l
Zinc carbonate	0.4 g/l
	8.0 ± 0.5

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<u>Immersion Time</u>	<u>Colour</u>
5 Min	Light grey
15 Min	Medium grey

EXAMPLE II

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

Ammonium carbonate	15 g/l
Triethanolamine	0.5 ml/l
Manganese carbonate	0.5 g/l
pH	7.5 ± 0.5
Temp.	95 ± 2°C

<u>Immersion Time</u>	<u>Colour</u>
3 Min	Light yellow
10 Min	Medium yellow

EXAMPLE III

26 S 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 immersed in the following solution.

Ammonium carbonate	30 g/l
Triethanolamine	2 ml/l
Lead carbonate	0.1 g/l
pH	9.0 ± 0.5
Temp.	90 ± 2°C

<u>Immersion Time</u>	<u>Colour</u>
5 Min	Light yellow
10 Min	Medium yellow
15 Min	Dark yellow

EXAMPLE IV

26 S Aluminium alloys were degreased with trichloroethylene etched in an alkali solution containing 10g/l sodium carbonate

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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 treated in the following solution.

Ammonium carbonate	10 g/l
Monoethanolamine	1 ml/l
Nickel carbonate	0.5 g/l
pH	8.0 ± 0.5
Temp.	95 ± 2°C
<u>Immersion Time</u>	<u>Colour</u>
3 min	Light yellow
10 min	Golden yellow

EXAMPLE 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 Ferric chloride 175 ml/l hydrochloric acid washed and immersed in the following solution.

Ammonium carbonate	50 g/l
Diethanol amine	1 ml/l
Copper carbonate	0.2 g/l
pH	9 ± 0.5
Temp.	85 ± 2°C
<u>Immersion time</u>	<u>Colour</u>
5 min	Light grey
10 min	Medium grey

EXAMPLE VI

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

Ammonium carbonate	20 g/l
Triethanol amine	1 ml/l
Cadmium carbonate	0.2 g/l
pH	8.0 ± 0.5
Temp.	95 ± 2°C

3 min	Light grey
10 min	Dark brownish grey.

EXAMPLE VII

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

Ammonium carbonate	40 g/l
Triethanol amine	2 ml/l
Nickel carbonate	0.01 g/l
Copper carbonate	0.1 g/l
NaOH	.01 g/l
pH	9 ± 0.5
Temp.	97 ± 2°C
<u>Immersion time</u>	<u>Colour</u>
5 min	Light black
10 min	Medium black
20 min	Nearly jet black

EXAMPLE VIII

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

Ammonium carbonate	50 g/l
Monoethanolamine	2 ml/l
Ferrous carbonate	0.1 g/l
Copper carbonate	0.1 g/l
NaOH	0.1 g/l
pH	9.5 ± 0.5
Temp.	90 ± 2°C
<u>Immersion time</u>	<u>Colour</u>
5 Min	Light brownish grey
10 "	Medium brownish grey
15 "	Dark brownish grey
20 "	Jet black.

EXAMPLE IX

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

Ammonium Carbonate	25 g/l
Diethanolamine	1 ml/l
Zinc carbonate	0.1 g/l
Copper carbonate	0.1 g/l
NaOH	.01 g/l
pH	8.5 ± 0.5
Temp.	97 ± 2°C
<u>Immersion time</u>	<u>Colour</u>
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.

54/-
(I.M.S. NEMAK)
SCIENTIST (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

COMPLETE SPECIFICATION

(Section—10)

**" 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 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 Nationals and 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.
- 3) The chromate - phosphate process produces light bluish green with slight 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/l each of potassium ferricyanide and ferrous chloride.
- 6) A grey iron like colour is obtained by treatment 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 nitric acid.

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

- 1) 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.
- 2) 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.
- 3) the chromate-phosphate process produces attractive green shades of thickness ranging from 1-5 microns. But the range of colours is restricted to green only.
- 4) Both numbers 4 and 5 produces non adherent smutty black coating and are non uniform.
- 5) 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 aluminium and its alloys.

The main finding underlying the invention consists in the use of an improved aqueous solution comprising aluminium 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 amine having ^{carbon} atoms 1-6 in amounts of 0.5-5 ml/l, sodium hydroxide 0.01 to 0.1 g/l 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

order of 3 to 7 microns can be produced.

The main advantages of the present invention are:-

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

The invention accordingly provides an improved process for chemical colouring of aluminium and its alloys substrates comprising the steps of polishing and buffing, degreasing, alkaline etching, acid dipping and immersion in a chemical bath wherein the improvement consists in that an aqueous 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 ethanalamines having 1-6 carbon atoms 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.

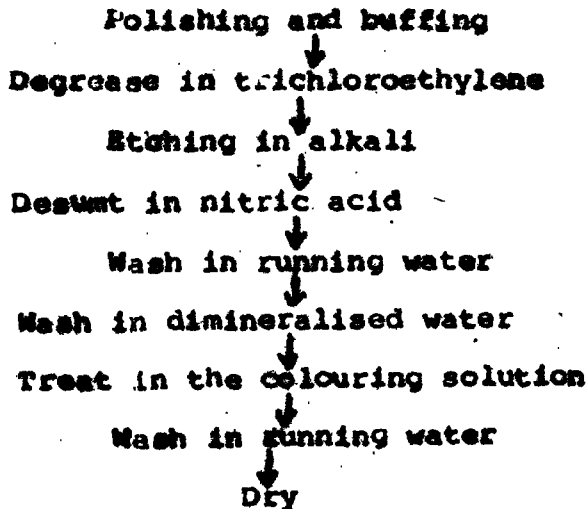
The carbonates of zinc, cadmium, manganese, lead, nickel, copper and iron produce coloured coating of thickness of the order of 3-7 microns and of colours ranging from grey to black and various shades of yellow can be obtained.

The new result flowing from the new finding is that various attractive shades ranging from grey to black and yellow to bronze and brown shades suitable for decorative and architectural applications on aluminium and its alloys 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 cheaply available ingredients.

The flow sheet of the process is as follows:



The appearance of finishes produced according to the present invention is greatly dependant 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 conventional 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.

Example - I

(Minimum 99% Al) Aluminium plates degreased with trichloroethylene, etched in an alkaline solution containing 30 g/l sodium hydroxide, rinsed and deacidified in 10% nitric acid washed and then immersed in the following chemical colouring solution.

1 5 0 1 6 4

Ammonium Carbonate	:	20 g/l
Triethanolamine	:	1 ml/l
Zinc carbonate	:	0.4 g/l
pH	:	8.0 \pm 0.5
Temperature	:	85 \pm 2°C

<u>Immersion time</u>	<u>Colour</u>
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 g/l
Triethanolamine	:	0.5 ml/l
Manganese carbonate	:	0.5 g/l
pH	:	7.5 \pm 0.5
Temperature	:	95 \pm 2°C

<u>Immersion time</u>	<u>Colour</u>
3 minutes	Light yellow
10 minutes	Medium yellow

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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

<u>Immersion time</u>	<u>Colour</u>
5 minutes	Light yellow
10 minutes	Medium yellow
20 minutes	Dark yellow

Example -4

Aluminium alloys were degreased with trichloroethylene etched in an alkali solution containing 10 g/l sodium carbonate, 20 g/l sodium carbonate, 20 g/l trisodium 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 g/l
pH	:	3.0 ± 0.5
Temperature	:	95 ± 2°C

<u>Immersion time</u>	<u>Colour</u>
3 minutes	Light yellow
10 minutes	Golden yellow

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Example 5

"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 ferric chloride 175 ml/l hydrochloric acid washed and immersed in the following solution:

Ammonium Carbonate	:	50 g/l
Diethanol amine	:	1 ml/l
Copper carbonate	:	0.2 g/l
pH	:	9 ± 0.5
Temperature	:	85 ± 2°C

Example 6

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

Ammonium	:	20 g/l
Triethanol amine	:	1 ml/l
Cadmium carbonate	:	0.2 g/l
pH	:	8.0 ± 0.5
Temperature	:	95 ± 2°C

<u>Time of immersion</u>	<u>Colour</u>
3 minutes	Light grey
10 minutes	Dark brownish grey

Example 7

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

Ammonium carbonate	:	40 g/l
Triethanol amine	:	2 ml/l
Nickel carbonate	:	0.1 g/l
Copper carbonate	:	0.1 g/l

1 5 0 1 6 4

NaOH	:	0.01 g/l
pH	:	9 ± 0.5
Temperature	:	97 ± 2°C
<u>Immersion time</u>		<u>Colour</u>
5 minutes		Light black
10 minutes		Medium black
20 minutes		Nearly jet black

Example 8

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

Ammonium Carbonate	:	50 g/l
Monoethanolamine	:	2 ml/l
Ferrous carbonate	:	0.1/g/l
Copper carbonate	:	0.1 g/l
NaOH	:	0.1 g/l
pH	:	9.5 ± 0.5
Temperature	:	90 ± 2°C
<u>Immersion time</u>		<u>Colour</u>
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 aluminium) alloys were degreased and pretreated as in example 7 and immersed in the following bath:

Ammonium carbonate	:	25 g/l
Diethanolamine	:	1 ml/l
Zinc carbonate	:	0.1 g/l
Copper carbonate	:	0.1 g/l
NaOH	:	0.01 g/l
pH	:	8.5 ± 0.5
Temperature	:	97 ± 2°C
<u>Immersion time</u>		<u>Colour</u>
5 min		Light greenish yellow
10 min		Medium greenish yellow

RE CLAIM:-

1. An improved process for chemical colouring of aluminium and its alloy substrates comprising the steps of polishing and buffing, degreasing, alkaline etching, acid dipping and immersing in a chemical bath wherein the improvement consists in that an aqueous solution containing 10-50 g/l of ammonium carbonate, 0.05 - 0.10 g/l of carbonates of zinc, cadmium, manganese, lead, nickel, copper and iron singly or in combination, 0.5 - 5 ml/l of ethanalamines having 1-6 carbon atoms 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.

2. The process as claimed in claim 1 wherein the chemical bath consists of 20 g/l of ammonium carbonate, 1 ml/l of triethanol amine, 0.4 g/l of zinc carbonate and the treatment is carried out at a pH of 8.0 to 8.5 and at a temperature of 85 to 87°C for 5 to 15 minutes.

3. An improved process for the chemical colouring of aluminium and alloy substrates substantially as herein described and illustrated in examples.

Dated this 1st day of October, 1979

24/-
(I. N. S. PAVAK)
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COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.