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"IMPROVEMENTS IN OR RELATING TO COPPER/COPPER ALLOY ARTICLES WITH ATTRACTIVE AND DECORATIVE FINISH"

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 :-

This is an invention by BAIKUNJE ANANTHA SHENOI, Scientist, VANNIYUR KRISHNASWAMY VENKATESAN, Scientist, RAMASUBBU VENKATACHALAM, Junior Scientific Assistant, SRINIVASAN CHAKRAPANI, Junior Scientific Assistant and ARUMUGAM PALAMALAI, Junior Scientific Assistant, all are citizens of India and employed HANDADY VENKATAKRISHNA UDUPA, Director, all are citizens of India and employed in the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India.

1A

INDIAN PATENTS AND DESIGNS ACT 1911

PROVISIONAL SPECIFICATION

Section 4

IMPROVEMENTS IN OR RELATING TO DECORATIVE FINISH ON COPPER AND ITS ALLOYS

COUNCIL OF SCIENTIFIC & 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:

This is an invention by BAIKUNJE ANANTHA SHENOI, Scientist, VANNIYUR KRISHNASWAMY VENKATESAN, Scientist, RAMASUBBU VENKATACHALAM, Junior Scientific Assistant, SRINIVASAN CHAKRAPANI, Junior Scientific Assistant and ARUMUGAM PALAMALAI, Junior Scientific Assistant, all are citizens of India and employed in theCentral Electrochemical Research Institute, Karaikudi-3, India.

This invention relates to the improvements in or relating to obtaining decorative finish on copper and its alloys for decorative purposes such as fountain pen caps, table-ware, knife handles, door-handles.

Hitherto it has been proposed to obtain such finishes like colouring copper and its alloys by anodic treatments or by immersion techniques.

This is open to the objection that processes already existing cannot provide on copper and its alloys this new attractive and decorative finish.

The object of this invention is to develop a suitable process for imparting such decorative finish on copper and its alloys.

To these ends, the invention broadly consists in anodically treating copper and its alloys in orthophosphoric acid solutions already saturated with [illegible]

but an operating current density of 3-6 A/dm^2 is preferable. The temperature of the bath is varied from 50°-80°C. The percentage of addition agents is maintained in the range 2 to 15 by volume. The time for processing is in the order of 15 minutes to 45 minutes. The inter-electrode distance can be maintained between 5 cm and 20 cm.

The following typical examples are given to illustrate the invention:

EXAMPLE 1

The copper surface, before anodic treatment in the given electrolyte is mechanically polished, degreased and treated in an aqueous solution containing the following composition:

Phosphoric acid (sp.gr: 1.75-1.80):	1000 ml
Copper (as metal)	8-10 g/l
Isopropyl alcohol	3% by volume
Temperature:	50-55°C
Current density:	3 A/dm^2
Cathode material:	Copper or lead or stainless steel
Time:	15 minutes.

EXAMPLE 2

Phosphoric acid(sp.gr: 1.75-1.80):	1000 ml
Copper(as metal)	8-10 g/l
Triethanolamine:	3-10% by volume
Cathode material:	Copper, lead or stainless steel
Current density:	6 A/dm^2
Temperature	65-70°C
Time:	20 minutes

EXAMPLE 3

The brass surface is given the same pretreatment as in [illegible] treated anodically in -

Phosphoric acid(sp.gr: 1.75-1.80):	1000 ml
Copper(as metal)	8-12 g/l
Zinc(as metal)	20-25 g/l
Acetone	10% by volume
Current density:	6 A/dm^2
Cathode material:	Brass, lead or stainless steel
Temperature:	65-70°C
Time:	30 minutes.

The following are among the main advantages of the invention:

1. The surface pattern comprises bright crystal facets which impart superior finish.
2. It imparts resistance to tarnishing.
3. If necessary, a flash of bright nickel and chromium may be given to add extra finish on it.

Dated this 6 day of April, 1972.

PATENTS OFFICER,
Council of Scientific and Industrial Research.

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THE PATENTS ACT, 1970.

COMPLETE
SPECIFICATION

(SECTION 10)

"IMPROVEMENTS IN OR RELATING TO COPPER/COPPER ALLOY ARTICLES WITH ~~HERE~~ ATTRACTIVE AND DECORATIVE FINISH"

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 BAIKUNJE ANANTHA SHENOI, Scientist, VANNIYUR KRISHNASWAMY VENKATESAN, Scientist, RAMASUBBU VENKATACHALAM, Junior Scientific Assistant, SRINIVASAN CHAKRAPANI, Junior Scientific Assistant, and HANDADY VENKATAKRISHNA UDUPA, Director, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to the improvements in or relating to copper/copper alloy articles with attractive and decorative finish and has particular reference to obtaining decorative flaky finish on copper and its alloys for decorative purposes such as fountain pen caps, tableware, knife-handles, door-handles, hair pins.

Hitherto it has been proposed to obtain such finishes on copper and its alloys by anodic treatment or by immersion techniques under suitable solutions.

This is open to the objection that the process already in use cannot provide on copper and its alloys a decorative, flaky finish.

The object of this invention is to develop a suitable process for imparting attractive decorative flaky finish on copper and its alloys. In this finish, circular patterns are formed over the treated surface uniformly from the centre of the pattern radially in all directions.

To these ends, the invention broadly consists in anodically treating copper and/or its alloys in orthophosphoric acid containing copper phosphate and/or zinc phosphate and an organic

substance such as acetone, methyl ethyl ketone, n-butanol, isopropyl alcohol and triethanolamine at a current density of 3 A to 6A/dm^2 and with temperature of 55°C to 60°C. The concentration of copper phosphate and/or zinc phosphate are 8-10 g/l and 20-25 g/l calculated as copper(II) and zinc respectively. The copper phosphate alone and/or combination of zinc phosphate and copper phosphate are brought into the electrolyte by anodically dissolving copper or brass by passing a current of 1 to 2 A/litre for 20 hours.

To get a concentrated solution, the solution containing copper or its alloy introduced as above, is heated to a temperature between 150°C and 180°C for 1 to 1½ hours. By this way, the specific gravity of the solution is brought to within a range of 1.75 to 1.82. After cooling a suitable organic substance is added to it and specific gravity of the solution is adjusted to a value of 1.75. The organic substances used are aliphatic in nature with 3 to 8 carbon atoms in the chain and having any one of the groups such as alcoholic, ketonic, amino. These substances are chosen for (1) their complete miscibility with the electrolyte (2) their polar nature and (3) their stability during processing. Substances such as acetone, methyl ethyl ketone, n-butanol, isopropyl alcohol, and triethanolamine in the concentration of 5 to 15% by volume are found to be suitable for the above purpose.

The bath works best at any temperature between 50°C and 80°C. However, the preferred range is 55°C to 60°C. Though the bath can be operated with a wide range of current densities, i.e. 2 to 10 A/dm^2, the preferred range is 3 to 6 A/dm^2. The inter-electrode distance can be varied from 10 to 20 cms.

During operation, the current after an initial decrease (this decrease takes within 30-60 seconds) remains almost constant for a long time(15-20 minutes) and then slowly decreases

to a value of 0.1 A/dm^2. The time of frost formation depends on the metal content and free acid content of the bath. However, the finish is obtained within a period of 15 to 35 minutes. A flash of bright nickel or chromium if given adds to its appearance and improve its non-tarnishing quality.

The replenishment of the bath is effected by the addition of a fresh lot of phosphoric acid. This finish can be obtained on copper or its alloys irrespective of the nature of metal composition. Proper jigging of the anode and protection of the bath from contact with atmosphere improve the efficiency and life of the bath.

The following are among the main advantages of the invention:

1. The surface pattern comprises crystal facets which impart superior finish
2. It imparts to a limited extent resistance to tarnishing

The following typical examples are given to illustrate the invention:

EXAMPLE 1

Copper surface is mechanically polished, degreased with trichlorethylene or benzene and is treated anodically in a solution of composition given. Then the anode material after washing in water is dipped in orthophosphoric acid in water(1:1) and is followed by washing in tap water and distilled water.

Phosphoric acid:	1000 ml
Copper phosphate(calculated as copper)	8-10 g/l
Isopropyl alcohol	3% by volume
Specific gravity of the electrolyte after necessary additions	1.75-1.77
Current density	3 A/dm^2
Temperature	55°C
Time	15 minutes
Cathode material	Copper, lead or stainless steel

EXAMPLE 2

Similar pretreatment is given to the anode material as given in Example 1.

Phosphoric acid:	1000 ml
Copper phosphate (calculated as copper):	8-10 g/l
Acetone:	10% by volume
Specific gravity of the electrolyte after necessary additions:	1.75-1.8
Current density:	6 A/dm^2
Temperature:	60°C
Time:	30 minutes
Cathode material:	as given in Ex.1

EXAMPLE 3

Similar pretreatment is given to the anode material as given in Example 1. The anode is brass in this case.

Phosphoric acid:	1000 ml
Copper phosphate (calculated as copper)	8-10 g/l
Zmic phosphate (calculated as zinc)	20-25 g/l
Acetone:	10% by volume
Specific gravity of the electrolyte after necessary additions:	1.75-1.8
Current density:	6 A/dm^2
Temperature:	60°C
Time:	30 minutes
Cathode material:	as given in Ex.1

WE CLAIM

1. A process to obtain copper/copper alloy articles wi... attractive and decorative finish by anodically treating them in an electrolyte containing orthophosphoric acid and copper polyphosphate or a combination of copper polyphosphate and zinc polyphosphate with specific gravity range of 1.75-1.80 and with the use of any one of metal sheets such as lead, copper and stainless steel as cathode.

2. A process as ~~ex~~ claimed in claim 1 wherein the temperature of the electrolyte is maintained between 50°C and 80°C.

3. A process as claimed in Claim 1 wherein the electrolyte is saturated with copper polyphosphate when the finish is required on copper surface or with a combination of copper and zinc polyphosphates when the finish is required on brass surface and for a finish on copper, the concentration of copper polyphosphate

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being in the range of 8-12 g/l (as copper metal) and for brass the concentration of copper and zinc polyphosphates, in the concentration of 8-12 g/l and 12-25 g/l respectively (calculated as copper)

4. A process as claimed in claims 1 and 3 wherein any one of the organic substances such as acetone methylethyl ketone n-butanol, isopropyl alcohol, triethanolamine has been added to the electrolyte after the addition of the copper and/or zinc polyphosphate to facilitate the process but prior to the introduction of the anode material in the electrolyte for getting the finish.
5. A process as claimed in claims 1 to 4 wherein the anodic current density of $2A/dm^2$ to $10A/dm^2$ is maintained for getting the finish.
6. A process as claimed in claims 1 to 5 wherein the phosphates of copper and/or zinc are introduced in the electrolyte by anodically dissolving copper and/or brass at a current of 1 to 2 A/litre for 20 hours in ortho-phosphoric acid.

Dated this 6th day of August, 1973

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Council of Scientific & Industrial Research

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