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" AN ELECTROCHEMICAL PROCESS FOR PREPARATION OF LITHOGRAPHIC PRINTING TRIMETALLIC PLATES".

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

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India, Indian National.

This invention relates to improved lithographic printing of trimetallic plates and methods of producing such plates.

Hitherto it has been proposed to use aluminium plates processed by chemical or electrochemical graining with the subsequent anodic treatment for the formation of thin oxide film over the surface to make them suitable for printing work employing dichromated colloids of albumin, gum, polyvinyl alcohol, glue, casein and shellac. Zinc plates are also being used in the place of aluminium. The main principle is that the aluminium or zinc plates bearing a hardened photoresist acts as the ink-receiving image areas while the clean metal surface functions as an ink-repeller.

The other type of printing plates are the bimetallic and trimetallic. In a bimetal plate system, one of the two metals acts as support as well as non-printing area for the system and the other metal acts as printing area for the system. For instance, in systems of copper-aluminium and copper-stainless steel, copper acts as printing area of the system and aluminium and stainless steel as non-printing area as well as supporting metal for the system. In the case of trimetal system, for example, chromium-copper-mild steel, chromium acts as non-printing area, copper the printing area and mild steel the supporting base metal.

The main drawbacks of the hitherto known process are given below:

The difficulties encountered with the first method are that the grains are susceptible to friction during printing and hence the impressions obtained with them are low in comparison with the bimetallic and trimetallic plates. They would also further oxidise if they are not properly stored and the pH of the fountain solution is not properl maintained during printing.

Aluminium and stainless steels are not used very much in bi and trimetal systems at present for the reason that the plating of copper on the former is compartively difficult and the latter for its high cost. In the conventional trimetal system namely mild-steel-copper-chromium, an initial sublayer of alkaline copper is usually plated from cyanide baths. But the waste treatment of cyanide is a problem.

The main object of the present invention is to obviate these disadvantages by using mild steel base wherein the plate is deposited with an initial sublayer of nickel from a synthetic nickel plating bath.

The novel feature of the present invention resides in providing a non-porous nickel layer as the sublayer inasmuch as this increases the overall hardness of the plate and precludes possible migration of moisture to the underside of the copper.

Thus, in actual practice, a sheet of mild steel is plated with a nickel sublayer and then with a layer of copper and chromium. It is then coated with a photoresist, exposed through a negative transparency, developed, coated with asphalt, washed to remove the remaining photosensitive coating left after development, etched with suitable etchants to remove chromium in the printing areas. The printing plate thus formed is brought into use.

The present invention broadly consists in plating the base metal with a non-porous deposit of nickel to a thickness of 5 microns and copper plated to a thickness of 5 to 10 microns and chromium plated to a thickness of 2-5 microns.

The following typical examples are given to further illustrate the invention, but not to limit the scope of this invention:

EXAMPLE 1

Steel sheets of 20 cm x 20 cm were first mechanically polished, degreased with a solvent, cathodically cleaned, acid dipped, neutralised and nickel plated from the following bath:

Nickel sulphate:	240 g/l
Nickel chloride:	45 g/l
Boric acid	37.5 g/l
Current density:	3 A/dm^2
pH	5 ± 0.5
Temperature	45°C
Time	10 minutes

A matte finish nickel layer of about 5 microns was obtained having a smooth, uniform, opaque surface.

The sheets were then copper plated under the following conditions:

Copper sulphate:	180 g/l
Sulphuric acid:	75 g/l
Addition agent	
Phenol sulphonic acid:	5 g/l
or glue	0.1 g/l
or gelatin	0.2 g/l
Temperature	40°C
Current density:	2.5 A/dm^2

A copper plate of 5 microns thick. was obtained in 10 min having good appearance, uniformity and smoothness.

The copper plated sheets were chromium plated under the following conditions:

Chromic acid:	250 g/l
Sulphuric acid:	2.5 g/l
Current density:	19 A/dm^2
Temperature	40°C

Chromium was deposited to a thickness of 2 microns in in 12.5 min and had a remarkably uniform surface.

EXAMPLE II

The first part of Example 1 was followed through the step of washing the steel sheet after the pickling operation. The thus degreased, pickled and washed sheet was directly taken to the bright nickel plating vat having the following composition:

Nickel sulphate:	300 g/l
Nickel chloride:	60 g/l
Boric acid	40 g/l
Butynediol or	0.5 g/l
2,7-naphthalene sulphonic aid or proprietary brighteners:	1 g/l
Temperature	65°C
Current density:	4.0 A/dm^2

A bright nickel layer of about 5 microns was produced in 7.5 min. It had a smooth and uniform surface.

The sheets were then bright copper plated under the following conditions:

Copper sulphate:	220 g/l
Sulphuric acid	60 g/l
Thiourea or	0.01 g/l
proprietary brighteners:	to the amount specified by the trade firm
Current density:	3.5 A/dm^2
Temperature	50°C

A bright, smooth, small crystal, dense layer of copper having an average thickness of above 5 microns was obtained in 7 min.

The copper plated sheet, after washing with water was immersed in the chromium plating bath given in Example 1. A current density of 18 A/dm^2 was passed for about 15 minutes at a temperature of 45°C. The chromium coating was of 2 microns thick. and had a remarkably hard, uniform bright surface.

EXAMPLE III

The first part of Example 1 was followed through the step of washing the steel sheet after the pickling operation. The thus-degreased, pickled and washed sheet was directly taken to the nickel plating vat having the following composition:

Nickel sulphate:	200 g/1
Nickel sulphamate	120 g/1
Nickel chloride	40 g/1
Boric acid	35 g/1
Temperature	50°C
Current density	4 A/dm^2

A nickel layer of about 5 microns was obtained in 7.5 min. It had a smooth and uniform surface.

The sheets were then copper plated under the following conditions:

Copper sulphate:	240 g/1
Sulphuric acid	90 g/1
Potassium aluminium sulphate:	10 g/1
Current density:	2.5 A/dm^2

A smooth, fine-grained, matte surface layer of copper with an average thickness of 5 microns was obtained in 10 minutes.

The matte copper plated sheet was chromium plated according to the details of Example 1 with the exception that a plating time of about 20 minutes was used. A matte chromium coating having a thickness of about 2 microns was obtained.

The following are the main advantages of the invention:

1. The nickel sublayer produced according to this specification particularly increases the hardness and thereby the serviceability of the printing plate.
2. The addition agents mentioned in this specification produce a smooth and uniform fine-grained surface.
3. The use of addition agents eliminate the need for buffing the copper layer prior to chromium plating.
4. The addition agents used in this specification are readily available in the market.

Dated this 7th day of August, 1976

— Sd/- [signature]

Asst. Patents Officer
Council of Scientific & Industrial Research

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

" AN ELECTROCHEMICAL PROCESS FOR PREPARATION OF LITHOGRAPHIC PRINTING TRIMETALLIC PLATES".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
Rafi Marg, New Delhi-1, India, an India registered body incorporated under the Registration of Societies Act.

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

146615

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India, Indian National.

This invention relates to the preparation of improved lithographic trimetallic printing plates.

Hitherto it has been proposed to use aluminium plates processed by chemical or electrochemical graining with the subsequent anodic treatment for the formation of thin oxide film over the surface to make them suitable for printing work employing dichromated colloids of albumin, gum, polyvinyl alcohol, glue, casein or shellac. Zinc plates are also being used in the place of aluminium. The main principle is that the aluminium or zinc plates bearing a hardened photo resists acts as the ink receiving image areas while the clean metal surface functions as an ink repeller.

The other type of printing plates are the bimetallic and trimetallic. In a bimetal plate system, one of the two metals acts as support as well as non printing area for the system and the other metal acts as printing area for the system. For instance, in systems of copper-aluminium and copper-stainless steel, copper acts as printing area of the system and aluminium and stainless steel as non printing area as well as supporting metal for the system. In the case of trimetal system, for example, chromium - copper - mild steel, chromium acts as non printing area, copper the printing area and mild steel the supporting basemetal.

The main drawbacks of the hitherto known process are given below:

The difficulties associated with the first method are that the grains are susceptible to friction during printing and hence the number of impressions obtained with them are low in comparison with the bimetallic and trimetallic plates. They would also further oxidise if they are not properly stored and the pH of the fountain solution is not properly maintained during printing.

Aluminium and stainless steels are not used very much in bi and trimetal systems at present for the reasons that the plating of copper on former is comparatively difficult and the latter for is high cost. In the conventional tri metal system namely mild steel copper - chromium, an initial sub layer of alkaline copper is usually plated from cyanide baths. But the waste treatment of cyanide is a problem.

The main object of the present invention is to obviate these disadvantages by using mild steel base metal which is deposited with an initial sub layer of nickel which substantially increases the over all hardness of the printing plate and also minimise the possible migration of moisture to the base metal. It is copper plated and then chromium plated to form the trimetallic printing plate.

The main finding underlying the invention consists of plate an initial sub layer of nickel from an aqueous electrolysing bat containing Nickel sulphate 200-300 g/1, Nickel chloride 15-60 g/1, Nickel sulphamate 125-300 g/1, Boric acid 30-55 g/1 at current densities of the order of 2-8A/dm^2 at temps of 50-65°C and then copper plated from an aqueous copper plating bath containing current sulphate 150-250 g/1 sulphuric acid 60-150 g/1 alongwith 0.01 to 10 g/1 addition agents at current densities of the order of 2-6 A/dm^2 at temps. of 35-60°C and finally chromium plated from an aqueous plating solution containing chromic acid 250-450 g/1, sulphuric acid 1.5-40 g/1, strontium sulphate 2-10 g/1, soidium or

Potassium silico fluoride 2-15 g/l at current densities of 10-30 A/dm^2 at temps. of 45-60°C to form the trimetallic printing plate.

The new result flowing from the new finding is that the provision of initial sublayer of nickel on the basic metal improves the over all hardness of the printing plate which ultimately improves the life of the printing plate. Also the nickel sub layer prevents the possible migration of moisture to the underside of copper which spoils the life of the printing plate.

According to this invention an electrochemical process for the preparation of lithographic trimetallic printing plates which comprises mechanical polishing of mild steel sheet followed by degreasing, electrolytic cleaning and dipping, copper plating and final chromium plating characterised in that an initial sub-layer of nickel is plated on the mild steel prior to copper plating.

Thus in actual practice, a sheet of mild steel is plated with a nickel sublayer and then with a layer of copper and chromium. It is then coated with a photo resist, exposed through a negative transparency, developed, coated with asphalt, washed to remove the remaining photo sensitive coating left after development, etched with suitable etchants to remove chromium in the printing areas. The printing plate thus formed is brought into use.

The present invention consists of a process for the preparation of lithographic trimetallic printing plates which comprises the steps of mechanical polishing and buffing of mild steel sheets, degreasing with trichloroethylene, electrolytic cleaning in alkaline solution, acid dipping and subsequently ~~xx~~ nickel strike plating to a thickness of 1-2.5 microns from an aqueous solution containing nickel sulphate 200-300 g/l, nickel chloride 15-60 g/l, nickel sulphamate 125-300 g/l, Boric acid 30-55 g/l at current densities of the order of 2-8 A/dm^2 at temps. of 50-65°C and copper plating to a thickness of 5-10 microns from an aqueous solution containing copper sulphate 150-250 g/l, sulphuric acid 60-150 g/l alongwith 0.01 to 10 g/l of addition agents at current densities of the order of 2-6 A/dm^2 at temps. of 35-60°C and finally chromium plating to a thickness of 0.5-2.5 microns from an aqueous solution containing chromic acid 250-450 g/l, ~~strontium sulphate 2-10 g/l~~ sulphuric acid 1.5-4.0 g/l, sodium or potassium silicofluoride 2-15 g/l, stronium sulphate 2-10 g/l at current densities of 10-30 A/dm^2 at temps. of 45-60°C to from the trimetallic printing plate where in the provision of initial sub layer of nickel substantially improve the over all hardness of the plate and also prevent the migration of moisture to the underside of the copper which factors ultimately imporve the life of the printing plate.

The following typical examples are given to further illustrate the invention, but not to limit the scope of this invention.

EXAMPLE-1

Mild steel sheets of size 20 cm x 20 cm were mechanically polished and buffed, degreased with a solvent such as trichloro ethylene, cathodically cleaned under the following conditions:

Sodium carbonate	..	25 g/1
Sodium phosphate	..	20 g/1
Sodium metasilicate	..	15 g/1
Temp	..	70°C
Current density	..	5 A/dm^2
Time	..	2 minutes

It is then acid dipped in 20% hydrochloric acid for 30 sec. and then nickel plated from the following bath:

Nickel sulphate	..	200 g/1
Nickel chloride	..	60 g/1
Boric acid	..	35 g/1
pH	..	4.0 ± 0.5
Temp.	..	50°C
Current density	..	2 A/dm^2
Time	..	5 min.

A matt finish nickel layer of about 2 microns was obtained, having a smooth, uniform, opaque surface.

The sheets were then copper plated under the following conditions:

pper sulphate	..	150 g/1

Sulphuric acid		75 g/1
Addition agent phenol sulphonic acid		5 g/1
Glue	..	0.1 g/1
Gelatin	..	0.2 g/1
Temp.	..	40 °C
Current density	..	2.5 A/dm^2

A copper plate of 5 microns thickness was obtained in 10 min. having good appearance, uniformity and smoothness.

The copper plated sheets were chromium plated under the following conditions:

Chromic acid	..	250 g/1
Sulphuric acid	..	2.5 g/1
Current density	..	19 A/dm^2
Temp.	..	40 °C

Chromium was deposited to a thickness of 2 microns in 12.5 min. and had a remarkably uniform surface.

EXAMPLE - II

The first part of Example 1 was followed through the step of washing the steel sheet after the pickling operation. The thus degreased, pickled and washed sheet was directly taken to the bright metal plating vat having the following composition:

Nickel sulphate	..	300 g/1
Nickel chloride	..	60 g/1
Boric acid	..	40 g/1
Butynediol	..	0.5 g/1
or		
2,7-Naphthalene Sulphonic acid		1 g/1
or		
Other proprietary brightners		
pH	..	4.0 ± 0.5

Temperature	..	65°C
Current densities	..	6.0 A/dm²

A bright nickel layer of about 5 microns was produced in 4 min. It has a smooth and uniform bright surface.

The sheets were then bright copper plated under the following conditions:

Copper sulphate	..	200 g/1
Sulphuric acid	..	150 g/1
Thio urea	..	0.01 g/1
or		
Proprietary brighteners	..	to the amount specified by the trade firm
Current density	..	6 A/dm²
Temperature	..	50°C

A bright, smooth, small crystal, dense layer of copper having an aboverage thickness of about 5 microns was obtained in 4 min.

The copper plate sheet, after washing with water was immersed in the chromium plating bath given in Example I. A current density of 18 A/dm² was passed for about 15 min. at a temp. of 45°C. The chromium coating was of 2 microns thickness and had a remarkably hard, uniform bright surface.

EXAMPLE -III

The first part of Example-1 was followed through the step of washing the steel sheet after the pickling operation. The thus degreased, pickled and washed sheet was directly taken to the nickel plating vat having the following composition:

Nickel sulphate	..	200 g/1
Nickel sulphamate	..	125 g/1
Nickel chloride	..	40 g/1
Boric acid	..	30 g/1
Temperature	..	50°C
Current density	..	4 A/dm²

A nickel layer of about 5 microns was obtained in 7.5 min. It had a smooth and uniform surface.

The sheets were then copper plated under the following conditions:

Copper sulphate ..	250 g/1
Sulphuric acid ..	90 g/1
Potassium aluminium sulphate ..	10 g/1
Temperature ..	40°C
Current density ..	2.5 A/dm^2

A smooth, fine grained, matte surface layer of copper with an average thickness of 5 microns was obtained in 10 min.

The matte copper plated sheet was chromium plated from the following bath.

Chromic acid ..	250 g/1
Sulphuric acid ..	1.5 g/1
Sodium or potassium silico fluoride ..	6 g/1
Temperature ..	40°C
Current density ..	12 A/dm^2

A matte chromium coating of 2 microns was obtained after 20 min.

EXAMPLE-IV

The first part of Example 1 was followed through the step of washing the steel sheet after the pickling operation. It was nickel plated from the following bath:

Nickel sulphamate ..	300 g/1
Nickel chloride ..	15 g/1
Boric acid ..	45 g/1
pH ..	3.5 - 4.5
Temperature ..	55°C
Current density ..	8.0 A/dm^2

A matte white layer of nickel about 5 microns was produced in 4 min.

The sheet was then copper plated according to Example III and chromium plated from the following bath.

Chromic acid	..	450 g/1
Strontium sulphate		5 g/1
Potassium fluo-silicate		15 g/1
Temperature	..	50°C
Current density	..	30 A/dm^2

A matte chromium deposit of 2 microns was obtained in 10 minutes.

The following are the main advantages of the inventions

1. The nickel sublayer produced according to this pecification particularly increases the hardness and thereby the serviceability of the printing plate.
2. The addition agents mentioned in this specification produce a smooth and uniform fine grained surface. Thereby the use of addition agents eliminate the need for buffing the copper layer prior to chromium plating.
3. The addition agents used in this specification are readily available in the market.

WE CLAIM:

(1) An electrochemical process for the preparation of lithographic trimetallic printing plates which comprise mechanical polishing of mild steel sheet followed by degreasing, electrolytic cleaning and dipping, copper plating and final chromium plating characterised in that an initial sub-layer of nickel is plated on the mild steel prior to copper plating.

(2) A process as claimed in claim 1 wherein the mechanically polished and buffed mild steel sheets are subjected to degreasing, electrolytic cleaning in alkaline solution, acid dipping followed by a nickel strike plating from an aqueous solution containing nickel sulphate 200-300 g/1, Nickel chloride 15-60 g/1, Nickel sulphamate 125-300 g/1 boric acid 30-55 g/1 employing current densities of the

order of 2-8 A/dm^2 at temperatures of 50-65°C and copper plating from an aqueous solution containing copper sulphate 150-250 g/1, sulphuric acid 60-150 g/1 alongwith 0.01 to 10 g/litre of addition agents at current densities of the order of 2-6 A/dm^2 at temperatures of 35-60°C and finally chromium plating from an aqueous solution containing chromic acid 250-450 g/1, sulphuric acid 1.5 - 40 g/1, sodium or potassium silico fluoride 2-15 g/1, strontium sulphate 2-10 g/1 at current densities of 10-30 A/dm^2 at temperatures of 45-60°C to form the trimetallic printing plate.

(3) An electrochemical process for the preparation of lithographic trimetallic printing plates with Nickel, copper and chromium on mild steel sheet substantially as hereinbefore described.

(4) Lithographic trimetallic printing plates whenever obtained according to a electrochemical process substantially as hereinbefore described.

Dated this 17th day of August 1977

Sd/-
PATENTS OFFICER,
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH