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PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO LITHOGRAPHIC PRINTING PLATES.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH RAJF MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED
BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

This is an invention by BALKUNJE ANANTH SHENOI, Scientist, SRINIVASAN CHAKRAPANI, Junior Scientific
Assistant, RAMASUBBU VENKATACHALAM, Junior Scientific Assistant and SUBRAMANIAM
NATARAJAN, Senior Laboratory Assistant, all are citizens of India, employed in the Central
Electrochemical Research Institute, Karaikudi-3, India.

The following specification describes the nature of this invention.

This invention relates to improvements in or relating to trimetallic lithographic printing plates and more particularly to mild steel-copper-chromium type plates.

Hitherto it has been proposed to use aluminium or zinc lithoplates bearing a hardened photoresist which acts as the ink receiving image area while the clean metal surface functions as an ink repeller. Such plates yield, when skillfully handled, only around 100,000 impressions on smooth papers. Their grains are susceptible to be damaged by friction during printing. They would, further, suffer oxidation if not properly stored and the pH of the fountain solution is not maintained during printing.

In the other types of existing plates, the metal support usually mild steel or aluminium, has overcoats of copper and chromium. The principal underlying the process is that copper can be made to receive and chromium to repel the greasy printing inks. Since in this case, printing is done from a metal surface, viz. copper, the printed impressions are absolute and true reproductions of the master image over a very large number of impressions, which is usually 300,000 to 5,00,000, if the supporting metal sheet is rigid and dimensionally stable. The remarkable resistance of such plates to the printing press environments adds to their storage life and, particularly, when the processed plates are stored for future use for the same work. Conventionally they are produced by electroplating the copper and chromium to the required thickness from the conventional electrolytes.

Though this method is employed to meet almost all the demand of such plates there are several factors which govern their quality and durability. The copper surface, for example, does not readily receive ink and certain pre-etch operations are necessary to make the copper surface satisfactorily ink-receptive and to desensitise the chromium surface. The printing property of these two metals depends to a considerable extent on the methods of and electrolytes for depositing these two layers. Further, the greater the hardness of the metal deposits the longer do the plates run on the press.

In the present invention, the principal aim has been to provide cold rolled mild steel sheets of 0.012" to 0.024" thick (depending upon the press for which it is meant) with electro-deposits of copper and chromium having a good grain structure.

The present invention broadly consists in first electroplating copper over a smooth electrocleaned mild steel sheets of size, say, 38.3" × 31.3" × 0.012". The mild steel sheet is first given a copper strike in the conventional cyanide bath or a pyrophosphate electrolyte containing little amount of nitrate. Over this 1—2 mil copper is plated from a copper sulphate-sulphuric acid electrolyte which contains aliphatic monohydric or dihydric alcohols and/or their amine derivatives or aromatic amines and their derivatives and other grain refining agents like casein, glue and gelatin. Chromium is then deposited to a thickness of 3—5 microns from the conventional or the tetrachromate bath where the operating conditions are so chosen that a grey grained chromium deposit is obtained.

The following examples are given to further illustrate the invention :

EXAMPLE 1

Cold rolled mild steel sheets without any surface defects and machine marks of thickness 0.012" are degreased and electrocleaned in a carbonate-hydroxide electrolyte as follows :

- | | |
|--|----------------------|
| 1. Sodium hydroxide : | 25 g/l |
| Sodium carbonate : | 35 g/l |
| Temperature : | 70°C |
| Current density : | 15 A/dm ² |
| Time : | |
| Cathodic : | 2 minutes |
| Anodic : | 1 minute |
| 2. Swill and rinse | |
| 3. Cathodic strike in a conventional cyanide solution as usual for three minutes | |
| 4. Double rinse | |
| 5. Dip in 5% (by volume) H ₂ SO ₄ for one minute | |
| 6. Rinse | |

Price : TWO RUPEES

7. Copper plate from :

Copper sulphate :	150 g/l
Sulphuric acid :	75 g/l
Gelatin/glue	1 g/l
Absolute alcohol	25-100 ml/l
Temperature :	Room Temperature
Time :	100 minutes
Current density :	48 asf

8. Rinse

9. Dip in 5% (by wt) sulphuric acid for 1 minute

10. Rinse

11. Chromium plating from a conventional chromium plating solution, as follows :

Chromium trioxide :	250 g/l
Sulphate added as sulphuric acid :	2.5 g/l
Trivalent chromium formed by cathodic reduction :	5 g/l
Current density :	15 A/dm ²
Temperature :	Room temperature
Time :	
Anode :	Antimonial lead containing 8%
Anode cathode ratio :	1 : 1

12. Rinse and dry
A grey deposit is obtained.

EXAMPLE 2

- Degreased and electrocleaned as in Example 1.
- Rinse
- Strike in a pyrophosphate bath as follows :

Copper pyrophosphate :	150 g/l
Copper nitrate :	70 g/l
Sodium pyrophosphate :	325 g/l
pH adjusted with ammonia (electrometric)	10
Current density :	2 A/dm ²
Time :	5 minutes

4. Rinse

5. Acid copper plating from a conventional bath for a thickness of 25-35 microns

6. Rinse

7. Dip in 5% (by wt) sulphuric acid

8. Rinse

9. Chromium plating from tetrachromate bath as follows :

Chromium trioxide :	250 g/l
Calcium carbonate :	50 g/l
Calcium sulphate :	20 g/l
Temperature :	30°C
Current density :	1 A/dm ²
Anode :	Antimonial lead containing 1% Antimony
Anode cathode ratio :	1 : 1
Time :	10 minutes

EXAMPLE 3

The procedure is the same as in Example 2 except for the pyrophosphate striking operation which is now replaced by striking in the following manner .

Copper sulphate :	40 g/l
Triethanolamine :	50 g/l
Ammonium sulphate :	50 g/l
Ammonia :	to pH 11
Sodium oxalate :	5 g/l
Temperature :	30°C
Current density :	1 A/dm ²
Time :	2 minutes

The grain structure of the deposits enhances the ease of sensitisation (of the copper printing areas) and desensitisation (of the chromium, non-printing surfaces). Further, this enables chromium to retain sufficient fountain solution to keep away the ink. Such a finish on copper offers a two-fold advantage. Apart from retaining the required amount of ink, it offers itself for the finest screen work. Besides printing on paper for greater number of impressions, they can be utilised to a great extent for printing on tinplates, plastic and other polyester sheets and to a less extent for making durable photographic designs, sign panels etc.

R BHASKAR PAL

PATENT OFFICER

Council of Scientific and Industrial Research

Dated this 14th day of October 1971.

COMPLETE SPECIFICATION

IMPROVEMENTS IN OR RELATING TO LITHOGRAPHIC PRINTING PLATES.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH RAJI MARG, NEW DELHI-1, AN INDIAN REGISTERED BODY
INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist SRINIVASAN CHAKRAPANI, Junior Scientific Assistant, RAMASUBBU VENKATACHALAM, Junior Scientific Assistant and SUBRAMANIAN NATARAJAN, Senior Laboratory Assistant, all are citizens of India employed in Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India.

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

This invention relates to improvements in or relating to trimetallic lithographic printing plates and more particularly to mild steel-copper-chromium type plates.

Hitherto it has been proposed to use aluminium or zinc plates bearing a hardened photo-resist which acts as the ink receiving image areas while clean metal surface functions as an ink-repeller. Such plates yield, when skilfully handled, only around 1,00,000 impressions on smooth papers. Their grains are susceptible to friction during printing. They would further oxidise, if they are not properly stored and the pH of the fountain solution is not properly maintained during printing.

In the other types of existing plates viz. bimetal and trimetal plates, the following is the principle that is adopted. In a bimetal plate system, one of the two metals acts as supporting metal 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 a printing area of the system and aluminium and stainless steel as non-printing area as well as supporting metal for the systems. In the case of trimetal system, chromium-copper and mild steel type is used where, chromium acts as non-printing area, copper, printing area and mild steel supporting base metal. Aluminium and stainless steel are not used very much in bi and trimetal systems at present for the reasons that the plating of copper on the former is comparatively difficult and the latter for its high cost. The mild steel has been chosen mainly for its cheapness and dimensional stability while printing.

The maximum number of impressions on paper that can be had, is in the order of 5,00,000 to 10,00,000. The remarkable resistance of such plates to the printing as well as storage life and particularly when the processed plates are stored for further use for the same work. Conventionally, they are produced by electroplating copper and chromium to the required thickness from the conventional baths.

Though this method is employed to meet all the demand of such plates, there are several factors which govern their quality and durability. The copper surface does not readily receive ink and certain pre-etch operations are necessary to make the copper surface satisfactorily ink-receptive and to desensitise the chromium surface. The printing properties of these two metals depend to a considerable extent on the methods of preparation and the electrolyte used for depositing these two layers. Further, the greater the hardness of the metal deposits the longer the plates run in the press. However, there is an upper limit for the hardness because too high a hardness tends to make the deposit especially copper brittle.

In this present invention, the principal aim has been to provide cold rolled mild steel sheets of 0.012" to 0.024"

thick (depending on the press for which it is meant) with electrodeposits of copper and chromium having a good grain structure.

The present invention broadly consists in first electroplating copper over a smooth electrocleaned mild steel sheet of size say 38.3" x 31.3" x 0.012". The mild steel sheet is first given a copper strike in a conventional cyanide bath or a pyrophosphate bath containing a little amount of nitrate. Over this 1-2 mil copper is plated from a copper sulphate-sulphuric acid electrolyte containing aliphatic monohydric or dihydric alcohols having carbon atoms 1-5 and/or their amine derivatives or aromatic and their derivatives and other grain refining agents like caesin, glue and gelatin. Chromium is then deposited to a thickness of 2-5 microns from a conventional or the tetrachromate bath where the operating conditions are so chosen as to give gray grained deposit.

The following examples are given to further illustrate the invention :

EXAMPLE 1

Cold-rolled mild steel sheet without any surface defects and machine marks of thickness 0.012" are degreased and electrocleaned in a carbonate-hydroxide electrolyte as follows :

- | | |
|---|-------------------------|
| 1. Sodium hydroxide : | 25 g/l |
| Sodium carbonate : | 35 g/l |
| Temperature : | 70°C |
| Current density : | 15 A/dm ² |
| Time (cathodic) | 2 minutes |
| (anodic) | 1/2-1 minute |
| 2. Swill and rinse | |
| 3. Cathodic strike in conventional cyanide solution | |
| Copper cyanide : | 22.5 g/l |
| Sodium cyanide : | 34 g/l |
| Sodium carbonate : | 15 g/l |
| Free cyanide : | 7.5 g/l |
| Current density : | 1-1.5 A/dm ² |
| Temperature : | 25-35°C |
| Time : | 3-5 minutes |

4. Double rinse
5. Dip in 5% sulphuric acid (by vol.) for one minute
6. Rinse
7. Copper plate from :

Copper sulphate :	150 g/l
Sulphuric acid :	75 g/l
Gelatin/glue	0.1—1 g/l
Absolute alcohol	45 ml/l
Temperature	25-35°C
Time :	50 minutes
Current density	4.8 A/dm ²
Thickness	2 mil (0.002 inch)
8. Rinse
9. Dip in 5% sulphuric acid (by vol.) for one minute
10. Rinse
11. Chromium plating from a conventional chromium plating bath :

Chromium trioxide :	250 g/l
Sulphate added as sulphuric acid	2.5 g/l
Trivalent chromium formed by cathodic reduction	5 g/l
Current density	15 A/dm ²
Temperature	25-35°C
Time	5 minutes
Thickness	0.0002 inch (5 microns)
Anode	Antimonial lead containing 6—8% antimony
Anode to cathode ratio	2:1 to 1:1

12. Rinse and dry

A gray deposit is obtained. By using a mixture of glue and ethanol in the acid copper plating bath, the hardness value of copper is increased to a value between 90 VPN and 100. If copper deposit is given on the mild steel surface from an acid copper plating bath with prior cyanide strike without the above-said additions, the hardness value of copper is around 80 VPN. The hardness of chromium deposit always is above 400 VPN, whatever be the nature of the bath and operating conditions. The wear and tear of the surface of two metals (i.e. chromium and copper) is less owing to the higher hardness. This is the reason for larger number of operations in the press.

EXAMPLE 2

1. Degreased and electrocleaned as in Example 1.
2. Rinse

3. Strike in a pyrophosphate bath as follows :

Copper pyrophosphate :	150 g/l
Copper nitrate :	70 g/l
Sodium pyrophosphate :	325 g/l
pH (adjustment made by ammonia electrometrically)	10
Current density :	2 A/dm ²
Time :	5 minutes

4. Rinse
5. Acid copper plating from a bath as indicated in Example 1.
6. Rinse
7. Dip in 5% (by vol.) sulphuric acid
8. Rinse
9. Chromium plating from tetrachromate bath under the following conditions :

Chromium oxide :	250 g/l
Calcium carbonate :	50 g/l
Calcium sulphate :	20 g/l
Temperature	30°C
Current density	1 A/dm ²
Anode :	Antimonial lead with 8% of antimony
Anode-cathode ratio :	1:1 to 2:1
Time :	10 minutes
Thickness :	0.0001 in or 2.5 microns
10. Rinse and dry

EXAMPLE 3

The procedure is the same as in Example 2 except for the pyrophosphate strike operation which is now replaced by strike in the following manner.

Copper sulphate :	40 g/l
Triethanolamino :	50 g/l
Ammonium sulphate :	50 g/l
Ammonia :	to pH 11
Sodium oxalate :	5 g
Temperature :	30°C
Current density :	1 A/dm ²
Time :	2—3 minutes

We claim :

1. A process for the production of triemetal printing plates by electroplating copper on mild steel from a low cyanide copper bath and this copperised mild steel is further built up with copper to a uniform thickness of 0.01 inch to 0.002 inch from a bath consisting of copper sulphate, sulphuric acid, absolute alcohol and glue and over this thick copper chromium of dull and grey appearance is deposited uniformly to a thickness of 0.0001 inch to 0.0002 (2-5 microns) from a bath of chromic acid and sulphuric acid or from a bath of chromic acid calcium carbonate and calcium sulphate.

2. A process as claimed in Claim 1 wherein copper is built up from a bath containing copper sulphate 150 g/l and sulphuric acid 70 g/l with the operating current density 4.8 A/dm² at room temperature (i.e.25-35°C).

3. A process as claimed in Claims 1 and 2 wherein the build up copper contains 40-50 ml/l of absolute alcohol and

0.1-1 g/l glue and the combined addition of these two constituents in the bath is to increase the hardness of the copper deposit from 80 VPN to 90-100 VPN with an improvement in throwing power of the bath.

4. A process as claimed in Claim 1 wherein for the plating of chromium for dull and grey appearance, the bath consisting of either chromic acid 250 g/l and sulphuric acid 2.5 g/l or a bath containing chromic acid 250 g/l, calcium carbonate 50 g/l and calcium sulphate 20 g/l, is used with current density of 1 A/dm².

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Dated this 15th day of January 1973.