GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

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B 41 n 1/04

"Improved process for the manufacture of lithographic printing plates and more particularly multilayer printing plates".

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).

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and SUBBIAH JOHN, Senior Technical Assistant, both are Indian Nationals and employed in the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India.

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

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This invention relates to improvements in or relating to lithographic printing plates and more particularly to multilayer type printing plates.

Hitherto it has been proposed to use aluminium plates processed by chemical or electrochemical graining with the subsequest 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 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 base metal.

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

The difficulties associated with the fist method are that the grains are susceptible to friction during printing and hence the impression 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.

In the case of conventional bimetallic and trimetallic printing systems, each printing plate can be brought into use for printing only one type of picture or image. If more than one type of picture or image is required, i.e. as in the case of multicolour printing, more than one printing plate is required to print each one of the required colours. In the normal practice after the use of a printing plate for printing a particular picture, the plate has to be discarded. Hence, the process is expensive.

The main object of the present invention is to obviate these disadvantages by using a suitable base metal wherein the base plate is deposited with several sets of alternate layers of copper and chromium. Hence, in actual usage each set (i.e. copper and chromium can be brought into use for printing a particular picture or image. Thus, for example, in a printing plate containing three sets of alternate layers of copper and chromium can be used for printing three different pictures or images or colours. Thereby, the multilayer plates are cheaper and economic than the conventional bi and trimetallic systems.

A further object of the present invention is to provide a method of plating copper on chromium. It is well known that the high corrosion resistance of chromium in decorative plating is attributed to the formation of a thin oxide layer of chromium. This passive layer forms immediately after plating and hence further adherent plating of copper is very difficult. Hence, in this invention there is provided a method of activating chromium prior to further plating of copper.

Figure 1 is an enlarged cross-sectional view of a partially manufactured plate in accordance with the invention.

Figure 2 is an enlarged cross sectional view of a complete plate containing three set of alternate layers of copper and chromium on mild steel base plate in accordance with the invention, and

Figure 3 is an enlarged cross sectional view of a complete plate with three sets of layers of copper and chromium on aluminium base plate in accordance with the invention;

Thus in Fig. 1, base metal (mild steel) is represented by 4, alkaline copper 3, acid copper 2 and chromium 1. This is actually a trimetallic system which can be used for printing a particular image or picture.

In Fig. 2, base(mild steel) is represented by 10, alkaline copper 9, acid copper 8, chromium 7, nickel strike 6, acid copper 5, chromium 4, nickel strike 3, acid copper 2 and chromium 1. Thus, the printing plate is provided with three sets of alternate layers of copper and chromium with intermediate nickel strike.

In Fig.3, base(aluminium) is presented by 11, zinc or bronze strike 10, alkaline copper 9, acid copper 8, chromium 7, nickel flash 6, acid copper 5, chromium 4, nickel flash 3, acid copper 2 and chromium 1.

Thus, in actual practice, a sheet of mild steel or aluminium plated with copper and then with a layer of chromium is coated with a photo-resist, 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. After removal of chromium image is coated with photoresist exposed, developed and etched with suitable etchants to remove copper in the non-printing areas. Thus, in the multilayer printing plate system, the successive layers of chromium and copper can be brought into use for separate pictures or tones.

The present invention broadly consists in plating the base metal with a thin adherent deposit of bronze in the case of aluminium base metal and alkaline copper strike in the case of mild steel and copper plated to a thickness of 5 to 10 microns and chromium plated to a thickness of 2-5 microns from conventional baths. The chromium plated base metal is activated and plated with a thin deposit of copper or nickel from suitable flash baths and copper plated to a thickness of 5-10 microns. It is then chromium plated. This plating sequence is repeated to produce alternate layers of copper and chromium with an intermediate copper or nickel flash.

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

EXAMPLE 1

3S aluminium alloy(containing 1.2% Mn) plates (10 cm x 7.5 cm) without any surface defects were mechanically polished, degreased, etched, rinsed and given a zinc coating by double immersion treatment. These were then given copper strike from conventional cyanide copper strike baths, acid copper plated to a thickness of 10 microns and then chromium plated to a thickness of 5 microns from conventional baths

For plating subsequent deposit of copper, the chromium plated surface was nickel flash plated from the bath of the following composition:

Nickel chloride:	240 g/1
Hydrochloric acid (sp.gr: 1.18):	70 ml/1
Sodium fluoride:	10 g/1
Temperature:	30°C
Anode:	Nickel
Current density:	2 A/dm^2
Time:	5 minutes

The plates were then rinsed, copper plated and chromium plated. Three sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence and there were no blistering as indicated by holding the plated sample for 10 minutes at 200°C.

EXAMPLE 2

2S aluminium alloy(99% aluminium) plates (10 cm x 7.5 cm) were polished, degreased, etched, bronze strike plated, and strike copper plated from conventional baths. The plates were then copper plated to 7.5 microns and chromium plated to 2.5 microns from conventional plating baths. For plating subsequent layer of copper, the chromium plated surface was strike copper plated from the following bath:

Copper sulphate:	50 g/1
Hydrochloric acid: (sp.gr: 1.18)	100 ml/1
Anode:	graphite or carbon
Current density:	2 A/dm²
Time:	2 minutes

The plates were rinsed, copper plated and chromium plated. Four sets of alternate layers of copper and chromium were deposited in the above sequence. The plated samples were then held for 10 minutes at 200°C and there were no blistering. No blistering also was observed in the bend-test.

EXAMPLE 3

10 cm x 7.5 cm mild steel panels were polished, degreased, anodically cleaned, acid dipped, copper strike plated and copper plated to a thickness of 7.5 microns and chromium plated to 2.5 microns thickness from conventional baths.

For plating subsequent deposit of copper, the chromium plated surface is activated and copper strike plated from the following bath:

Copper carbonate:	40 g/1
Hydrochloric acid (sp.gr: 1.18):	200 ml/1
Gum arabic:	0.05 g/1
Temperature:	35°C
Anode:	Graphite
Current density	2 A/dm²
Time:	5 minutes

The plates were then washed, copper and chromium plated from the conventional baths. Three sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence as indicated by the bend test and heat-baking test.

EXAMPLE 4

10 cm x 7.5 cm brass panels were polished, degreased, cathodically cleaned, acid dipped, and then copper and chromium plated from conventional baths. For plating subsequent deposit of copper, the chromium plated surface was copper strike plated from the following bath:

Cupric chloride:	20 g/1
Hydrochloric acid: (sp.gr: 1.18):	100 ml/1
Anode:	graphite
current density:	1 A/dm^2
Time:	2 minutes

The plates were then washed, copper and chromium plated from the conventional baths. Four sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence as indicated by the bend test and heat-baking test.

EXAMPLE 5

Polished and degreased stainless steel plates of size 10 cm x 7.5cm were electrolytically cleaned, acid dipped, given copper strike or nickel flash and then copper and chromium plated from the conventional plating baths. An adherent deposit of copper was plated on chromium from the following bath:

Nickel chloride:	240 g/1
Hydrochloric acid:	100 ml
Temperature:	30°C
Anode	Nickel
Current density:	2 A/dm^2
Time:	3 minutes

The plates were washed, copper and chromium plated. Three sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence as indicated by the bend test and heat baking test.

The main advantage of the present invention is that the multilayer printing plate with successive layers of copper and chromium can be used for printing more than one type of picture or colour and thus making the process cheap and economical.

Dated this 5th day of August, 1976.

Sd/-
Asstt. Patents Officer,
Council of Scientific & Industrial Research

146435

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

"Process for the manufacture of improved lithographic printing plates and more particularly multilayer printing plates".

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 BALKUNJE ANANTHA SHENOI, Scientist and SUBBIAH JOHN, Senior Technical Assistant, both are Indian Nationals and employed in the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India.

146435

This invention relates to process for the manufacture of improved lithographic printing plates and more particularly multilayer 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 and shellac. Zinc plates are also being used in the place of aluminium. The main principle is that the aluminium of zinc plates bearing a hardened photo

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resists acts as the ink receiving image areas while the clean metal surface function 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.

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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 impression obtained with them are low in comparison with the bimetallic and trimetallic plates. They would also further ~~oxides~~ oxidise if they are not properly stored and the pH of the fountain solution is not properly maintained during printing.

In the case of conventional bimetallic and trimetallic printing systems, each printing plate can be brought into use for printing only one type of picture or image. If more than one type of picture or image is required, i.e. as in the case of multicolour printing, more than one printing plate is required to print each one of the required colours. In the normal practise after the use of a printing plate for printing a particular picture, the plate has to be discarded. Hence, the process is expensive.

The main object of the present invention is to obviate these disadvantages by using a suitable base metal wherein the base plate is deposited with several sets of alternate layers of copper and chromium. Hence, in actual usage each set (i.e. copper and chromium) can be brought into use for printing a particular picture or image. Thus, for example, a printing plate having three sets of alternate layers of copper and chromium can be used for printing three different pictures or images or colours. Thereby, the multilayer plates are cheaper and economic than the conventional bi and trimetallic systems.

A further object of the present invention is to provide a method of plating copper on chromium. It is well known that the high corrosion resistance of chromium in decorative plating is attributed to the formation of a thin oxide layer of chromium. This passive layer forms immediately after plating and hence further adherent plating of copper is very difficult. Hence, in this invention there is provided a method of activating chromium prior to further plating of copper.

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The present invention consists of a process for the manufacture of improved lithographic printing plates and more particularly of multilayer printing plates which comprises polishing and cleaning of a metal base plate, depositing these on a layer of zinc, bronze or copper; subsequently obtaining thereon layers of copper and chromium by successive conventional copper and chromium plating processes, characterised in that the said chromium layer is activated by treatment with an activating solution containing 20 to 50 g/l of a soluble copper salt and 100 to 200 ml/l of hydrochloric acid at a current density of 1 to 5 A/dm for 2 to 5 minutes at 25 to 35 ^{o}C.

In the accompanying drawings with provisional specification, Figure 1 is an enlarged cross-sectional view of a partially manufactured plate in accordance with the invention containing one layer each of copper and chromium on mild steel base metal.

Figure 2 is an enlarged cross sectional view of a complete plate containing three sets of alternate layers of copper and chromium on mild steel base plate in accordance with the invention, and figure 3 is an enlarged cross sectional view of a complete plate with three sets of layers of copper and chromium on aluminium base plate in accordance with the invention.

Thus in Figure 1 base metal (mild steel) is represented by 4, alkaline copper 3, acid copper 2 and chromium 1. This is actually a trimetallic system which can be used for printing a particular image or picture.

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In Fig. 2, base metal (mild steel) is represented by 10, alkaline copper 9, acid copper 8, chromium 7, nickel strike 6, acid copper 5, chromium 4, nickel strike 3, acid copper 2 and chromium 1. Thus, the printing plate is provided with three sets of alternate layers of copper and chromium with intermediate nickel strike over chromium.

In Fig. 3, base metal (aluminium) is presented by 11, zinc or bronze strike 10, alkaline copper 9, acid copper 8, chromium ~~ax~~ 7, nickel flash 6, acid copper 5, chromium 4, nickel flash 3, acid copper 2 and chromium 1. Thus, the printing plate is provided with three sets of alternate layers of copper and chromium with intermediate nickel strike over chromium and an initial strike of bronze or zinc on aluminium.

Thus, in actual practice, a sheet of mild steel or aluminium plated with copper and chromium is coated with a photo-resist, 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. After the removal of first set of copper and chromium image is again coated with photoresist, exposed, developed and etched with suitable etchants to remove chromium in the printing areas. The printing plate thus formed is again brought into use. Thus, in the multilayer printing plate system, the successive layers of chromium and copper can be brought into use for separate pictures or tones.

The present invention broadly consists in plating the base metal with a thin adherent deposit of zinc or bronze in the case of aluminium base metal and alkaline copper strike in the case of mild steel and copper plated to a thickness of 5 to 10 microns and chromium plated to a thickness of 2-5 microns from conventional baths. The chromium plated base metal is activated and plated with a thin deposit of copper or nickel from suitable flash baths and copper plated to a thickness of 5-10 microns. It is then chromium plated. This plating sequence is repeated to produce alternate layers of copper and chromium with an intermediate copper or nickel flash on chromium.

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

EXAMPLE – 1

3S aluminium alloy (containing 1.2% Mn) plates (10 cm x 7.5 cm) without any surface defects were mechanically polished and buffed, degreased, etched, rinsed and given a zinc coating by double immersion treatment. These were then given copper strike from conventional cyanide copper strike baths, acid copper plated to a thickness of 10 microns and then chromium plated to a thickness of 5 microns from conventional baths.

For plating subsequent deposit of copper, the chromium plated surface was nickel flash plated from the bath of the following composition:

Nickel chloride	..	240 g/l
Hydrochloric acid (sp.gr: 1.18)	..	70 ml/l
Sodium fluoride	..	20 g/l
Temperature	..	30°C
Anode	..	Nickel
Current density	..	2 A/dm^2
Time	..	5 Min.

The plates were then rinsed, copper plated and chromium plated. Three sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence and there were no blistering as indicated by holding the plated sample for 10 minutes at 400°C.

EXAMPLE – 2

2S aluminium alloy (99% aluminium) plates (10 cm x 7.5 cm) were polished, degreased, etched, bronze strike plated, and strike copper plated from conventional baths. The plates were then copper plated to 7.5 microns and chromium plated to 2.5 microns from conventional plating baths. For plating subsequent layer of copper, the chromium plated surface was strike copper plated from the following bath:

Copper sulphate	.. 50 g/l
Hydrochloric acid (sp.gr. 1.18)	.. 100 ml/l
Temperature	.. 25°C
Anode	.. graphite or carbon
Current density	.. 5 A/dm^2
Time	.. 2 minutes

The plates were rinsed, copper plated and chromium plated. Four sets of alternate layers of copper and chromium were deposited in the above sequence. The plated samples were then held for 10 minutes at 200°C and there were no blistering. No blistering also was observed in the bend-test.

EXAMPLE - 3

10 cm x 7.5 cm mild steel panels were polished, degreased, alkaline cleaned, acid dipped, copper strike plated and copper plated to a thickness of 7.5 microns and chromium plated to 2.5 microns thickness from conventional baths.

For plating subsequent deposit of copper, the chromium plated surface is activated and copper strike plated from the following bath:

Copper carbonate	.. 40 g/l
Hydrochloric acid (sp.gr. 1.18)	.. 200 ml/l
Gum arabic	.. 0.05 g/l
Temperature	.. 35°C
Anode	.. Graphite
Current density	.. 2 A/dm^2
Time	.. 5 min.

The plates were then washed, copper and chromium plated from the conventional baths. Three sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence as indicated by the bend test and heat-baking test.

10 cm x 7.5 cm brass panels were polished, degreased, cathodically cleaned, acid dipped, and then copper and chromium plated from conventional baths. For plating subsequent deposit of copper, the chromium plated surface was copper strike plated from the following bath:

Cupric chloride	.. 20 g/1
Hydrochloric acid (sp.gr. 1.18)	.. 100 ml/1
Temperature	.. 35°C
Anode	.. graphite
Current density	.. 1 A/dm^2
Time	.. 2 min.

The plates were then washed, copper and chromium plated from the conventional baths. Four sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence as indicated by the bend test and heat-baking test.

EXAMPLE - 5

Polished and degreased stainless steel plates of size 10 cm x 7.5 cm were electrolytically cleaned, acid dipped, given copper strike or nickel flash and then copper and chromium plated from the conventional plating baths. An adherent deposit of copper was plated on chromium from the following bath:

Nickel chloride	.. 240 g/1
Hydrochloric acid	.. 100 ml
Temperature	.. 30°C
Anode	.. Nickel
Current density	.. 2 A/dm^2
Time	.. 3 Minutes

The plates were washed, copper and chromium plated. Three sets of alternate layers of copper and chromium were deposited in the above sequence. The deposits had good adherence as indicated by the bend test and heat baking test.

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The main advantage of the present invention is that the multilayer printing plate with successive layers of copper and chromium can be used for printing more than one type of picture or colour and thus making the process cheap and economical.

WE CLAIM:

1. Process for the manufacture of improved lithographic printing plates and more particularly of multilayer printing plates which comprises polishing and cleaning of a metal base plate, depositing thereon a layer of zinc, bronze or copper; subsequently obtaining thereon layers of copper & chromium by successive conventional copper and chromium plating processes, characterised in that the said chromium layer is activated by treatment with an activating solution contain 20 to 50 g/l of a soluble copper salt and 100 to 200 ml/l of hydro-chloric acid at a current density of 1 to 5 A/dm^2 for 2 to 5 minutes at 25 to 35°C.
2. Process as claimed in claim 1 wherein the activating solution contains as copper salt, copper sulphate.
3. Process as claimed in claim 1 and 2 wherein the copper salt used is copper carbonate.
4. Process as claimed in claim 1 wherein the copper salt used is cupric chloride.
5. Process for the manufacture of improved lithographic printing plates and more particularly of multi layer printing plates subsequently as herein before described and illustrated.
6. Improved lithographic printing plates and more particularly multi-layer printing plates ~~as~~ when prepared by process described herein.

Dated this 23rd day of August, 1977

(I.M.S. MAMAK)
SCIENTIST 'E' (PATENTS) C.S.I.R.

PROVISIONAL SPECIFICATION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

No 146435.

No. OF SHEETS :- 1
SHEET No :-

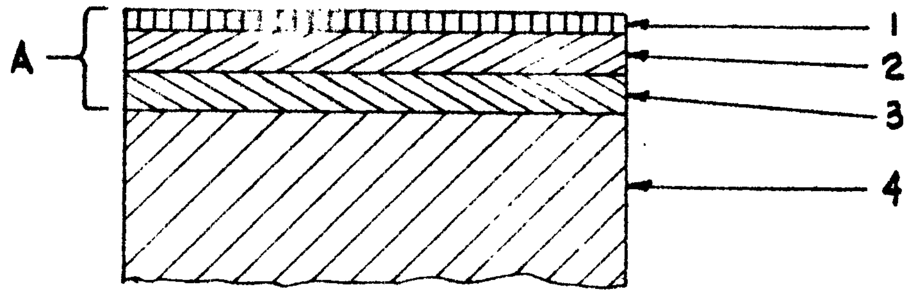

FIG. 1

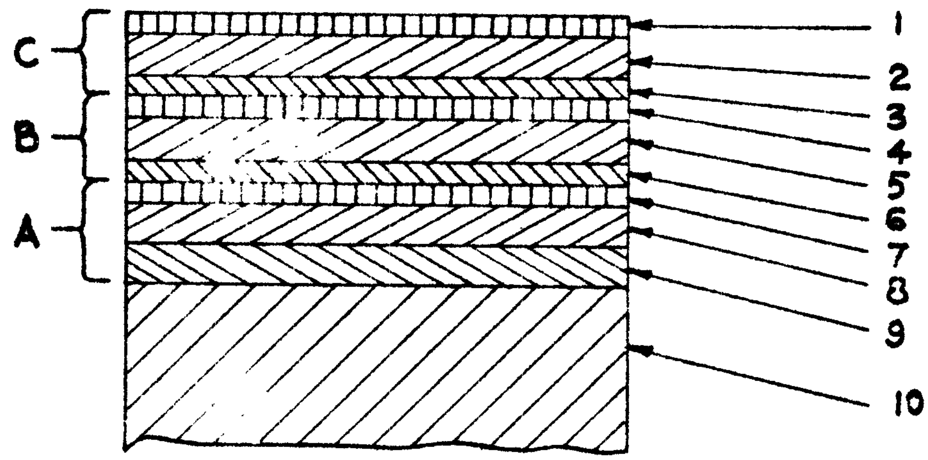

FIG. 2

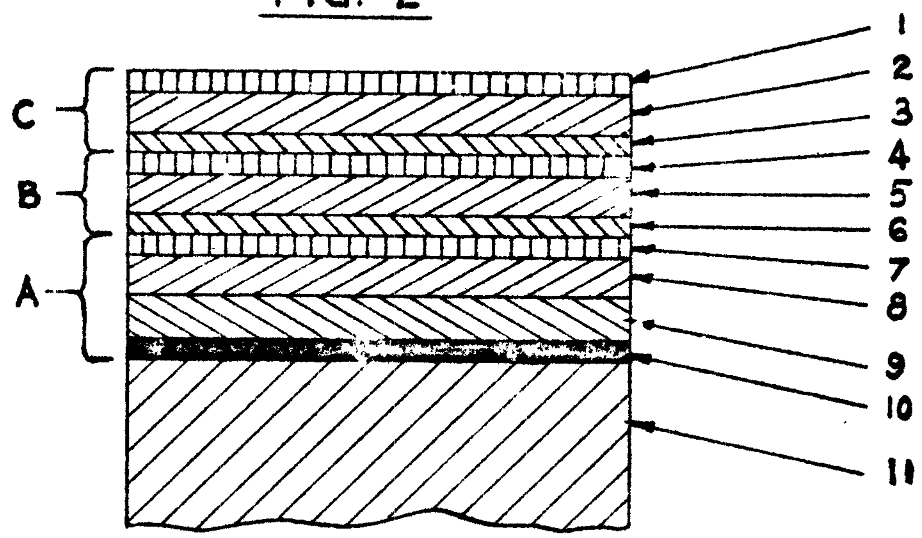

FIG. 3

[R.B. PAI]
Asst. PATENTS OFFICER,
C.S.I.R.