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# IMPROVEMENTS IN OR RELATING TO LITHOGRAPHIC ALUMINIUM PLATES.

## PROVISIONAL SPECIFICATION

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 BALKUNJE ANANTHA SHENOI, Scientist, SRINIVASAN CHAKRAPANI, Junior Scientific Assistant and RAMASUBBU VENKATACHALAM, Junior Scientific Assistant, citizens of India and employed in the Central Electrochemical Research Institute, Karaikudi-3, India.

This invention relates to improvements in or relating to the surface preparation of aluminium plates for the lithographic printing industry with special reference to printing from "presensitised plates".

Hetherto it has been proposed to use aluminium plates processed by chemical and|or electrochemical graining and| or chemical and|or electrolytic methods of forming oxide films over the surface to make them suitable for printing work employing dichromated colloids of albumen, gum, polyvinyl alcohol, glue. casein, shellac and the like. It has also been the procedure hitherto to provide aluminium with an oxide or hydroxide layer with or without silicate ion being incorporated in the film, for purposes of making the presensitised plates. In such plates, the light sensitive diazo resin-coat remains on the aluminium surface for a considerably long period, say, six months to one year, before it is exposed to a stencil or a transparency. The primary aim of providing this type of barrier film has been to prevent the interaction of the diazo compound and aluminium and to prevent the aluminium getting stained thereby.

This is open to the objection in that the presensitised plates do not often possess a long printing life. The main reason for this shortcoming is the lack of adhesion of the diazo resist to the oxide layer and hence to the printing plate. For the resist to be adherent, the oxide layer must contain a larger number of pores of a sufficiently large size, so that the bonding takes place through the pores. Often, the oxide layer that is found on the existing plates are not readily hydrophilic and offer a slight resistance to the quick development of the image and to the easy desensitisation of the non-image areas.

The chief object of the invention has been, therefore, to obviate these disadvantages by using a chemical or an electrochemical method for obtaining a surface on aluminium suitable for printing, especially for printing by the presensitised plates.

The other object of the invention is to provide aluminium with an oxide layer having very good hydrophilic qualities, which enable easy desensitisation of the non-image areas of the surface.

Another object of this invention is to provide an oxide layer with which the light hardened stencil makes a good bonding even though the plate has not been previously machanically, chemically or electrochemically grained.

To these ends, the process according to this invention. broadly consists in giving an oxide layer on the cleaned aluminium surface by chemical or electrochemical means, so that the light sensitive diazo resin layer is firmly held over the surface, at the same time preventing the aluminium surface reacting with the organic diazo compounds, resulting in the staining of the non-image areas which would then be difficult to desensitise and would present a dull background for the image area.

According to this invention, the aluminium plates—2S, 3S, 26S or 52S—are first thoroughly cleaned from all organic and other surface impurities by dipping in an alkali solution. Over this clean surface, oxide film is built up chemically and| or electrochemically in solutions of silicates, borates, inorganic acids like sulphuric, phosphoric, chromic, nitric acids or organic acids like oxalic, malonic, acetic acid and|or their salts from mixtures of these acids or salts or by dipping in a solution of alkali silicate and after drying again dipping in or spraying a solution of organo-titanium, zirconium or silicon compounds, for example, of the formula $M(OR)_4$ where 'M' is the metal and 'R' is an alkyl or aryl group, whereby a composite layer of aluminium oxide and titanium, silicon or zirconium hydroxide is obtained which, not only offers a highly hydrophilic surface, but retains the hydrophilic quality for a longer period.

The following examples are given to illustrate the present invention :

*Example 1*

The aluminium plates —2S, 3S, 26S or 52S— are cleaned first in 5-10% sodium hydroxide to remove grease and other surface impurities.

They are then treated in the following solution :

Sodium silicate : 3-15% and|or
Trisodium phosphate : 3-15%
Temperature : 80-100°C
Time : 15-45 minutes

After the plates have been so treated they are ready to be coated with the diazo resins.

*Example 2*

The plates after cleaning as given in Example 1, are made anodic first in the following solution :

Sulphuric acid : 10-25% by w|v
Temperature : 20-30°C
Time : 10-20 minutes
Current density : 1.2-2.4 A|dm²
Cathode : Lead or stainless steel

After rinsing, they are made anodic using lead or stainless steel as cathode in the following solution :

Phosphoric acid : 10-50% by w|v
Current density : 1-3 A|dm²
Temperature : 25-35°C
Time : 10-20 minutes

The plates are removed, washed thoroughly and are coated with the radiation sensitive diazo resin emulsions.

*Example 3*

The aluminium sheets cleaned by alkaline dips are first treated by immersion in

Sodium silicate : 1-3% in water
Temperature : 80-100°C
time : 15-30 minutes

and after rinsing and drying treated by spraying the solution with tetraisopropyl titanate (2-8% by weight in isopropyl alcohol) and drying at 80-120°C. After the plate is dry, it is ready to be coated with the diazo compound to be sent to the consumer.

The following are among the main advantages of this invention :

The oxide layer offsets the chemical action of the diazo compounds with aluminium. Thus, the staining of the aluminium surface is avoided and the background (the

non-image area) is bright and white leaving the image clear and distinct. This would make the proof corrections, if any, easy. Since the surface is hydrophilic (in the case of films from phosphate ion containing solutions remarkably high), the development of the image in water is quick and easy. The porous nature of the oxide film offers a firm bonding of the stencil to the surface, the pore acting as "teeth" providing good "anchorage" to the hardened photo resist. Thus, the adherence of the resist to the surface increases with the increase in number and size of the pores. This quality is appreciably high if processed by the "double anodising" method described under Example 2 where sulphuric acid provides a large number of tiny pores which grow in diameter in the subsequent anodising in phosphoric acid.

Thus aluminium plates can be provided with an oxide layer possessing the properties of ease of developing, ease of desensitisation of non-image areas and good anchorage to the aluminium support by employing the process hereinbefore described. The process is particularly useful for making presensitised plates and for other methods of printing like the albumen and the deep etch processes and for the so called "wipe-on" plates.

A further advantage of this process is that it can be used in photographic preparation of name-plates, instruction panels, wiring and design diagrams, dials, scales, advertising specialities and the like.

R. BHASKAR PAI

*Patents Officer,*

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

*Dated this 8th day of September 1971.*

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# COMPLETE SPECIFICATION

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 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, SRINIVASAN CHAKRAPANI, Junior Scientific Assistant and RAMASUBBU VENKATACHALAM, Junior Scientific Assistant, all are citizens of India and employed in the Central Electrochemical Research Institute, Karaikudi-623006, India.

This invention relates to improvements in or relating to the surface preparation of aluminium plates for lithographic printing from pre-sensitised resin coated plates.

Hitherto it has been known 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. It has also been known to use aluminium sheets or foils with an oxide film or a hydroxide layer with or without a dip in a solution of sodium silicate before it is coated with pre-sensitised resin coat for printing. In such cases, the light sensitive diazo resin remains on the aluminium surface for considerably long period, say, six months to one year before it is exposed to a stencil or transparency. The primary aim of providing this type of barrier film has been to prevent aluminium from getting stained thereby. Preference to these plates over the other types of plates employing the dichromated colloids lies in that the equipment required in the printing shop is less.

Further, the processing of the plates is quick, because the plates are already coated and ready for processing. These pre-sensitised plates suffer from, however, a series of shortcomings. They do not possess a long printing life, the main reason being that there is lack of good adhesion of diazo resin coat to the oxide layer of aluminium. Often, the oxide films on the plates are not readily hydrophilic in nature and offer a slight resistance to the quick development of the image areas and to the easy de-sensitisation of the non-image areas.

The main object of the invention has been, therefore, to obviate these disadvantages by employing an electrochemical method for obtaining, on the surface of aluminium, an oxide film of uniform thickness with large number of pores of sufficiently wider diameter to hold pre-sensitised resin coat very tightly.

To achieve an oxide film with large pore number and pore diameter as claimed in this new investigation, the cleaned aluminium surface free from scratches, dents and grease, is anodised in two different electrolytes at different times. That is to say, to anodise in one electrolyte at first and after thorough rinsing with cold water, anodise in the second electrolyte. After this double anodising operation in two different electrolytes, the plate is dipped or sprayed with a solution of tetra isopropyl titanate of 1-10% w|v in one litre of isopropyl alcohol.

After these treatments, the plates are dried well and at this stage, they are ready for further processing in printing process with a thin and uniform layer of light sensitive diazo resin coat on the surface.

For preparing aluminium plates according to this invention, alloys of aluminium above 99% purity can be used for this treatment. For producing an oxide film with larger pore number and pore diameter on the surface of aluminium with above-said purity, the plate is anodised in two stages. Firstly, the plate is anodised in sulphuric acid of 10-20% w|v and after rinse with cold water, it is again anodised in phosphoric acid of 10-50% by w|v in a separate tank. The anodisation in sulphuric acid gives a large number of pores to the oxide films on the surface of aluminium and anodising in phosphoric acid gives a large pore diameter. The oxide film obtained as above holds the resin coat tightly. The following examples of sequence of operations illustrate the process.

*Example 1*

1. Degrease with trichloroethylene or benzene,
2. Alkali cleaning for 1-2 minutes at 60°C,
3. Rinse with cold water,
4. Anodic electrolytic treatment in sulphuric acid is given as per conditions indicated below :
   Sulphuric acid : 12% by weight
   Current density : 12 A|dm²
   Cathode : Lead
   Temperature : 25°C
   Time : 15 minutes
5. Rinse with cold water,
6. Second anodic treatment in phosphoric acid. The composition and condition are given below :
   Phosphoric acid : 12% by weight
   Current density : 1.2 A|dm²
   Temperature : 30°C
   Time : 15 minutes
   Cathode : Lead
7. Rinse and dry
8. Then the above plate is dipped in isopropyl titanate of 4% by weight in isopropyl alcohol,
9. Dry.

*Example 2*

The aluminium plate is treated similarly as given in Example 1 except sequences given in 4 and 6.

4. Sulphuric acid : 25% w|v
Current density : 2 A|dm²
Temperature : 20°C
Time : 10 minutes
Cathode : Lead

6. Phosphoric acid : 30% w|v
Current density : 2 A|dm²
Temperature : 20°C
Time : 10 minutes

Following are among the main advantages of this invention :

1. The oxide film offsets the chemical action of the diazo compound on aluminium surface. Thus, the staining of the surface is avoided and the background (non-image area) is bright and white leaving the image clear and distinct.

2. Since the surface is hydrophilic (remarkably high in the case of films from phosphate containing solutions) the development of the image areas is quick and easy.

3. The porous structure of the film offers a firm bonding of the stencil to the surface. the pores acting as "teeth" providing good anchorage to the hardened diazo resin coat. Greater the number and size of pores, better the adherence of the resin coat to the surface. This quality is appreciably high, if processed by the "double anodising" method where sulphuric acid provides a large number of tiny pores which grow larger in diameter in phosphoric acid.

4. Since there is secure bonding of the resin coat to the surface, the number of impressions obtainable is great. This is approximately double the number obtainable without such a treatment.

5. Since the oxide layer imparts hardness to the surface the life of the plate increases. The plate is less prone to frictional forces.

6. The oxide layer increases the resistance of the plate to corrosive atmospheres.

7. All the materials except the organic metallic compounds are manufactured in India and are readily available.

We claim :

1. A process for the surface preparation of aluminium lithographic plates for printing from presensitised diazo resin coating in which the cleaned aluminium surface is subjected to anodic treatment in sulphuric acid and then in phosphoric acid at different times using direct current with a view to increasing the pore number as well as pore diameter of oxide film on the surface of aluminium in order to make very good bonding between the resin coat and the anodised surface.

2. A process as claimed in Claim (1) wherein the concentration of sulphuric acid used is in the range of 5-35% w|v and the concentration range of phosphoric acid used is 5-35% w|v.

3. A process as claimed in Claim (1) or (2) wherein the anodic treatment is carried out in sulphuric acid at first and then after washing in cold water the aluminium plate is anodised in phosphoric acid.

R. BHASKAR PAI

*Patents Officer,*

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

*Dated this 14th day of August 1972.*

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