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PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO PREPARATION OF LITHOGRAPHIC ALUMINIUM 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 describes the nature of this invention:—

This is an invention by BALKUNJE ANANTHA SHENOI, RAMACHANDRA SUBRAMANIAN and SRINIVASA CHAKRAPANI OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI-3, S. I. RAILWAY, INDIA, ALL INDIAN CITIZENS.

This invention relates to improvements in or relating to the method of preparation of Aluminium Lithoplate.

Hitherto it has been proposed to 'grain' mechanically the zinc plates or use imported aluminium lithoplates.

This is open to the objection that the grains are not uniform, the image is not fine and the processes are very costly on aluminium.

The object of this invention is to obviate these disadvantages by using a simple electrochemical technique for the preparation of aluminium lithoplates with properties suitable for lithographic purposes.

To these ends, the invention broadly consists in 'graining' the aluminium plates either (1) mechanically, or (2) chemically, or (3) electrochemically and/or (I) anodically treating the 'grained' plates in an aqueous solution containing fluorides, chromates, carbonates, phosphates of sodium, potassium and/or ammonium in concentrations not exceeding 15 per cent. by total weight of solids in solution, the current maintained by an applied voltage ranging from 10 to 200 volts d.c. or a.c. or superimposed a.c., over d.c., (II) or suitably modifying the composition and operating conditions of the conventional anodizing baths namely sulphuric, chromic or oxalic or phosphoric acid baths or a combination of these acids in appropriate proportions, and then making the film hydrophillic either by incorporating such substances as dextrin, glucose, starch, dialdehyde starch, carboxy methly cellulose with the anodizing baths or in the subsequent sealing step.

The following typical examples are given to illustrate the invention:

EXAMPLE 1.

The cleaner solution is 5 per cent. KOH or NaOH or 3 per cent. $Na_2 CNO_4$ and 3 per cent. $Na_2 CO_3$.

Temp	80° C.
Time of immersion:	2-5 min
Anodising solution containing	
alkali chromate	1 to 20 g/l
alkali carbonate	1 to 15 g/l
Temp	40°C. to 75° C.
Voltage	150 volts d.c.

EXAMPLE 2.

After cleaning as above, the aluminium plate is etched by immersion for 1-5 min. in a fluoride solution of ammonia kept at 90° C. and then anodising in an aqueous solution containing alkali carbonate

1 to 20 g/l
alkali chromate 1 to 15 g/l
alkali phosphate 1 to 20 g/l
kept 40°-60°C. and voltage at 100-150 volts.

The following are among the main advantages of the invention:

1. The 'graining' is uniform
2. The grain size can be controlled to any desired limit
3. Number of impressions per plate is very high that it can be used for longer runs
4. All the materials are indigenous
5. It is very cheap, elegant and less time consuming
6. The finer details of the image is clear and hence the impressions are better than from zinc lithoplates
7. The lightness of aluminium makes it possible to reduce the freight charges, etc.
8. Highly resistant to atmospheric corrosion during storage and idle period.

R. BHASKAR PAI

Patents Officer,

Council of Scientific & Industrial Research.

Dated this 6th day of November 1964.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO PREPARATION OF LITHOGRAPHIC ALUMINIUM PLATES.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA (AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT NO. 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; Ramachandra Subramanian, Senior Scientific Assistant and Srinivasa Chakrapani, Senior Laboratory Assistant, Citizens of India and employed in the Central Electrochemical Research Institute, Karaikudi-3, S. Rly, India.

This invention relates to improvements in or relating to the method of surface preparation of aluminium plates for lithoprinting works.

Hitherto, it has been proposed to use mechanically grained zinc plates or imported aluminium lithoplates. The mechanical graining is done in a horizontal rocking machine with a slurry of fine abrasives and a number of marble balls for nearly one hour. Cost of such graining operation may be Rs. 2 to 3 per plate. The grains produced are not uniform. The process is rather crude and time-consuming. Further, this process cannot be used on aluminium plates as it is open to the objection that the surface tends to develop "white dots" due to non-uniform oxidation. The process is also costlier on aluminium plates than on zinc plates. For roto-printing very thin sheets of aluminium are used which cannot withstand such a drastic treatment.

Price : TWO RUPEES.

The object of this invention is to obviate these disadvantages by using a simple, chemical or electrochemical technique for the surface preparation of aluminium lithoplates with properties suitable for printing and at the same time with an eye on the economics of the technique, elegance and ease of operation.

Another object of this invention is to prevent the defects due to atmospheric oxidation of the aluminium surface and the development of white spots which makes the life of such plates short.

The present invention is based on the principle that the surface of an aluminium plate gets etched when treated chemically or electrochemically in solutions containing alkali salts, chromates, phosphates, halides producing a uniformly grained surface. This is subsequently oxidized anodically in an electrolyte containing sulphuric acid, chromic acid or phosphoric acid either individually or in combination in suitable quantities.

Accordingly the invented process for preparing lithographic aluminium plates comprises graining an aluminium plate chemically or electrochemically in an aqueous solution of alkali salts, chromates, phosphates or halides followed by anodically oxidising the grained surface in an electrolyte containing one or more of the following, namely, sulphuric acid, chromic acid or phosphoric acid.

By this process, the surface of the aluminium offset lithoplate is smoothly and uniformly grained to a controlled size and depth producing a porous structure. This makes a firm bonding with the dichromate-gum arabic coating. After subsequent development in the usual way, the light-hardened portions receive ink and the non-exposed portions being hydrophilic get dampened with sufficient water. The impressions produced from such a surface are true to the original even in finer details. Thus instead of other expensive planographic methods, after simple chemical and electrochemical treatment, aluminium plates can be used with improved results.

However, the subsequent electrochemical oxidation anodically in a suitable electrolyte under optimum conditions apart from retaining the optimum grain size and pore structure to properly absorb and retain the ink and water in the respective areas increases the mechanical hardness of the surface and is also resistant to corrosive atmosphere.

For preparing the aluminium plates according to this invention alloys of aluminium such as the following can be used provided the surface structure of aluminium plates is homogeneous and does not contain any inclusions, i.e., free from surface defects:

2S . 99.8 per cent. aluminium

3S . Manganese 1.2 per cent. balance aluminium

57 S . Magnesium 2.5 per cent.; chromium 0.3 per cent.; balance aluminium

65S . Copper 0.3 per cent.; magnesium 1.0 per cent.; silicon 0.6 per cent.; chromium 0.3 per per cent.; balance aluminium.

The process broadly consists in performing the operation as described hereunder. The aluminium plates supplied by the rolling mills is degreased to remove organic impurities by using a suitable organic solvent like trichloroethylene.

Then it is dip-cleaned at 25 to 35° C. in a 5 to 10 per cent aqueous solution of sodium hydroxide for one to two minutes. It is rinse in running water and chemically etched in any one of the aqueous solutions given below:

(a) Alkali chromate	1 to 4%
Alkali carbonate	2 to 5%
Temperature	60 to 100° C.
Time	2 to 5 minutes

rinsed,followed by a dip in

Alkali or ammonium fluorides or acid fluorides	5 to 10%
Temperature	35 to 50° C.
Time	1 minute
(b) Hydrochloric acid	10 to 20%
Temperature	30 to 35°C.
Time	2 to 3 minutes
(c) Hydrofluoric acid	5 to 10% by volume
Nitric acid	5 to 10% "
Temperature	35 to 50° C.
Time	1 to 2 min.
(d) Alkali pyrophosphates	5 to 8% by weight
Ammonium or alkali fluoride or bifluoride	1 to 2% "
pH	2 to 3
Temperature	30 to 35°C.

(e) etching can also be performed in a solution of "b" or "c" by use of alternating current with two aluminium plates connected to the current leads into the electrolyte. The concentration of the chemicals may be varied within the following limits:

Hydrochloric acid	0.1 to 5% by vol
Current density	0.3 to 1.0 A/sq. in.
Temperature	25 to 60°C.
Hydrofluoric acid	0.2 to 0.3% by volume
Nitric acid	0.2 to 0.3% "
Current density	0.3 to 1.0 A/sq. in.
Temperature	25 to 60°C.

After thoroughly rinsing from any one of the previous steps, the plate is treated electrolytically in any one of the following solutions under suitable conditions. The plate is made anodic with a similar plate placed at a distance of 10 to 15 cm. apart as the cathode.

(f) Alkali carbonate	2 to 5 g/l
Alkali chromate	1 to 4 g/l
Temperature	50 to 60°C.
Applied voltage	150 to 200 V d.c.
Time	4 to 15 min.

The voltage is gradually and continuously raised but as quickly as possible to the required voltage. Mechanical agitation or circulation of electrolyte is essential.

(g) Phosphoric acid	5 to 10% by volume
Temperature	30 to 35° C.
Voltage	50 V d.c.
Time	20 min.
(h) Phosphoric acid	3 to 6% by volume
Chromic acid	3 to 6% by weight
Balance water	
temperature	30 to 35°C.
Current density	10 to 15 a.s.f.
Time	20 min.
(i) Chromic acid	10 to 25% by weight
Voltage	40 to 50 V d.c.
Temperature	50 to 65°C.
Time	10 to 20 min.
(j) Sulphuric acid	10 to 20% by volume
Temperature	30 to 35°C.
Current density	8 to 20 a.s.f.
Time	10 to 20 min.

After the electrolytic treatment in any one of the said solutions under the conditions described, current is switched off, the plates are removed, thoroughly rinsed in running water and dried by warm air. The plates are now ready for further processing for printing in the usual way.

The time of treatment for one plate is about 40 to 45 min. if one plate alone is processed at a time in a tank. Depending on the capacity of the tank., the number of plates processed may be increased. Further the process is also suitable for thin sheets of aluminium in the form of rolls and can be made continuous by proper design.

The following examples are given to illustrate the invention.

EXAMPLE I.

Degreased with trichloroethylene.
Dip cleaned in 5 per cent. alkali solution at room temperature for two minutes.
Rinsed.
Chemically etched in an aqueous solution containing

Hydrofluoric acid	5% by volume
Nitric acid	5% by volume
at 40° C. for two minutes	

Rinsed.
Anodic treatment in a solution containing

Alkali chromate	1 to 3 min.
Alkali carbonate	2 to 6 min.
Temperature	40 to 75° C.
Applied voltage	180 V d.c.
Time	5 to 10 min.
Mechanical agitation.	
Rinsed well	
Air dried.	

EXAMPLE II.

Degreased in trichloroethylene
Dip cleaned in 5% sodium hydroxide as above
Chemically etched in 5% aqueous solution of hydrofluoric acid.
Rinsed
Anodically treated in an aqueous solution containing

Chromic acid	5 to 10%
Voltage	50 V d.c.
Temperature	50°C.
Time	15 min.
Mechanical agitation.	

The following are some of the advantages of this invention:

1. The 'graining' is uniform.
2. The grain size can be controlled to any desired limit.
3. Number of impressions per plate is very high that it can be used for longer runs.
4. All the materials are indigenous.
5. It is way cheap, elegant and less time-consuming.
6. The finer details of the image are clear and hence the impressions are better than from zinc lithoplates.
7. The lightness of aluminium makes it possible to reduce the freight charges, etc.
8. Highly resistant to atmospheric corrosion during storage and idle period.

We claim:

1. A process for preparing lithographic aluminium plates which comprises graining an aluminium plate chemically or electrochemically in an aqueous solution of alkali salts, chromates, phosphates or halides followed by anodically oxidising the grained surface in an electrolyte containing one or more of the following, namely, sulphuric acid, chromic acid or phosphoric acid.

2. A process as claimed in Claim 1 wherein the surface of aluminium lithoplate is grained chemically or electrochemically in any one of the aqueous solutions given below under the conditions of operation mentioned against each:

a	Alkali chromate	1 to 4%
	Alkali carbonate	2 to 5%
	Temperature	60 to 100°C.
	Time	2 to 5 minutes
	rinsed, followed by a dip in Alkali or ammonium fluorides or acid fluorides	5 to 10%
	Temperature	35 to 50°C.
	Time	1 minute
or b	Hydrochloric acid	10 to 20%
	Temperature	30 to 35° C.
	Time	2 to 3 minutes
or c	Hydrofluoric acid	5 to 10% by volume
	Nitric acid	5 to 10% „
	Temperature	35 to 50°C.
	Time	1 to 2 min.
or d	Alkali pyrophosphates	5 to 8% by weight
	Ammonium or alkali fluoride or bifluoride	1 to 2%
	pH	2 to 3
	Temperature	25 to 60° C.

3. A process as claimed in Claim 2 wherein etching is performed in the solution of (b) or (c) by use of altering current with two aluminium plates connected to the current leads into the electrolyte.

4. A process is claimed in any of the preceding claims wherein the concentration of the chemicals may be varied within the following limits:

Hydrochloric acid	0.1 to 5% by vol.
or Hydrofluoric acid	0.2 to 0.3% by volume
Nitric acid	0.2 to 0.3% „
Current density	0.3 to 1.0 A/sq. in.
Temperature	25 to 60° C.

5. A process as claimed in any of the preceding claims wherein the grained plates are anodically treated in tny one of the aqueous solutions given below under the conditions of operation mentioned against each:

y	Alkali carbonate	2 to 5 g/I
	Alkali carbonate	2 to 5 g/1
	Temperature or	50 to 60°C.
	Applied voltage	150 to 200 V d.c.
	Time	4 to 15 min.

the voltage is gradually and continuously raised but as quickly as possible to the required voltage, mechanical agitation or circulation of electrolyte is essential:

or g	Phosporic acid	5 to 10% by volume
	Temperature	30 to 35°C.
	Voltage	50 V d.c.
	Time	20 min.
or h	Phosphoric acid	3 to 6% by volume
	Chromic acid	3 to 6% by weight
	Balance water temperature	30 to 35° C.
	Current density	10 to 15 asf
	Time	20 minutes
or i	Chromic acid	10 to 25% by weight
	Voltage	40 to 50 V d.c.
	Temperature	50 to 65°C
	Time	10 to 20 min
or j	Sulphuric acid	10 to 20% by volume
	Temperature	30 to 35°C.
	Current density	8 to 20 asf
	Time	10 to 20 min.

6. A process for graining and anodizing the aluminium plate for lithographic work substantially as hereinbefore described.

7. An aluminium offset plate produced by the process as substantially described herein.

R. BHASKAR PAI

Patents Officer,

Council of Scientific and Industrial Research.

Dated this 2nd day of September 1965.

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