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"IMPROVEMENTS IN OR RELATING TO POWDERLESS ETCHING OF ALUMINIUM AND ITS ALLOYS FOR PHOTO-ENGRAVING AND BLOCK MAKING"

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, Scientist, a citizen of India and employed in the Central Electrochemical Research Institute, Karaikudi—3, Tamil Nadu, India.

This invention relates to improvements in or relating to powderless etching of aluminium and its alloys for photo engraving and block making.

Hitherto it has been proposed to use aluminium and its alloys for photo-engraving and block making purposes for which some suitable etching solutions are developed under trade names in foreign countries.

This is open to the objection that the etching solutions developed in foreign countries for photo-engraving and block making for aluminium are proprietary and are available only in trade names and hence, there is a need to develop our own composition for the powderless etching of aluminium for the above purpose.

The object of this invention is to obviate the above disadvantage by using the etching solutions described in this patent which are cheap and indigenously available for powderless etching of aluminium and its alloys for photo-engraving and block making.

To these ends, the invention broadly consists in etching aluminium and its alloys for the purpose of photo-engraving and block making after applying the acid resistant photoresist and developing the image adopting the conventional methods given in the art of photoengraving and block making using ferric chloride solution of specific gravity 1·26 to 1·38(30°—40°Be) containing a water immissible solvent consisting of aliphatic or aromatic hydrocarbons or naphthenic hydrocarbons which has got high flash point and which substantially unreactive with the etching solutions like kerosene or petroleum ether or diesel or toluene or naphthalene or diethyl benzene or trichloroethylene. In addition to the above, the etching solution also contains a film forming substance, surface active agents and accelerators. Copper chloride or suphate and other chloride salt of tin and cadmium are individually or in combination with ammonium thiocyanate is used as accelerator in the etching composition without which the etching rate is sluggish. The surface active agents like lignin sulphonic acid, lauryl sulphate, cetyl trimethyl ammonium bromide or chloride, "amphocerine BD" (a surface active agent produced by M/s HICO Products Ltd., Bombay), teepol, tetramethyl ammonium chloride, sulphonated castor oil, are used individually or in combination in the etching solution. Compounds like ethylene glycol, ethylene glycol monoethyl ether, triethanol or monoethanolamine, amines and esters of asteric acid, palmitic acid are also used in the etching solution to control the etching rate and to avoid lateral cutting of the image on the photoresist. The pH of the etching electrolyte was adjusted to 0·2 with hydrochloric acid or ammonia as the case may be.

The following are the examples given to illustrate the invention and not to limit the scope of the invention :

2S aluminium alloy was degreased and acid resistant photoresist was applied and the image was developed using the conventional methods available in the art of photoengraving. After developing the image it was etched in the following etching solution :

Ferric chloride	..	30° Be (Specific gravity 1·26) pH adjusted to 1·5 with hydrochloric acid
Kerosene ..	..	1—5%
Teepol ..	..	1%
Temperature ..	..	30—35°C
Time of etching	..	15 minutes

The image was not affected due to lateral cutting due to etching.

EXAMPLE 2

The photoresist was applied as in Example 1 over 26s aluminium alloy and the image was developed in the same way. Then the plate was etched using the undermentioned etching solution :

Ferric chloride	..	40°Be (Specific gravity : 1·38) pH adjusted to 1 with hydrochloric acid
Petroleum ether	..	2%
Sodium lauryl sulphate	..	0·2 g
Ethylene glycol	..	1%
Temperature ..	..	35—38°C
Etching time ..	..	15 minutes

In the above solution, etching was good and the image was not spoiled.

EXAMPLE 3

The photoresist was applied over 65S aluminium alloy and the image was developed as in Example 1. The plate was etched in the following etching solution :

Ferric chloride ..	..	35°Be (Specific gravity : 1·32) pH adjusted to 1 with ammonia
Diesel or kerosene	...	2%
Lignin sulphonic acid	..	0·5%
Cupric chloride or stannous chloride or cadmium chloride ..	..	0·4%
Ammonium thiocyanate	..	0·02%
Ethylene glycol monoethyl ether ..	..	2%
Operating temperature	..	30—35°C
Etching time ..	..	15 minutes

PRICE : TWO RUPEES

The image was not at all affected and the etch factor was good.

EXAMPLE 4

The acid photoresist was formed over high purity aluminium sheet and the image was prepared as in Example 1. After preparing the image, it was etched in the following etching solution :

Ferric chloride	38° Be (Specific gravity : 1·355) pH
pH adjusted to ..	1·5 with hydrochloric acid
Kerosine	2%
Sulphonated castor oil ..	0·2%
Triethanolamine ..	1%
Ethylene glycol ..	1%
Copper chloride ..	0·4%
Ammonium thiocyanate ..	0·2%
Working temperature ..	30—38°C
Etching time	15 minutes

The image was perfect and unaffected by the etching solution. No lateral corrosion was observed. The etch factor was good.

EXAMPLE 5

2S aluminium alloy plate was electrolytically grained and then anodised in sulphuric or chromic acid and then the picture was developed by photographic method and etched in the following solution :

Ferric chloride	38° Be (Specific gravity : 1·355)
pH adjusted to ..	1·5 with hydrochloric acid
Kerosine	2%
Sulphonated castor oil ..	0·2%
Triethanolamine ..	1%
Ethylene glycol ..	1%
Copper chloride ..	0·4%
Ammonium thiocyanate ..	0·2%
Working temperature ..	30—38°C
Etching time	15 minutes

The block produced was very fine.

EXAMPLE 6

Ferric chloride	35°Be (Specific gravity : 1·32)
pH adjusted to ..	1 with hydrochloric acid
Trichloroethylene ..	2%
Trimethyl benzene ..	6—8%
Methyl salicylate ..	0·3%
Triethanomaline ..	1%
Sulphonated castor oil ..	0·5%
Sodium lauryl sulphate ..	0·3%
Temperature	30—35°C
Etching time	15 minutes

3S aluminium alloy plate was degreased and acid resistant photoresist was applied as in Exampe 1 and the image was developed according to the conventional methods available in the art of block making and photo engraving. Then the plate was etched in the above mentioned etching solution. The image was unaffected and etching was perfect.

EXAMPLE 7

Al-Zn-Mg alloy was used and the image was formed as in the above examples.

Ferric chloride ..	30°Be (Specific gravity : 1·26)
pH adjusted to ..	1 with hydrochloric acid
Toluene	6%
Turpentine	2%
Methyl sulpho-succinate ..	0·3%
Cupric chloride ..	0·4%
Ammonium thiocyanate ..	0·02%
Sodium salt of lignin sulphonic acid	0·5%
Teepol	0·2%
Bath temperature ..	32—35°C
Etching time	15 minutes

The image was unaffected and no lateral undercutting of the image was observed.

The following are among the main advantages of the invention :

1. Aluminium and aluminium based alloys can be made use of for block making and photo engraving purposes using the etching solutions mentioned in this patent.

2. The etching solution mentioned in this patent has got good etching characteristic and it does not spoil the image by lateral or undercutting type of corrosion.

3. The etching solution is composed of freely available chemicals.

4. The etching solution described in this patent can be used for photo-engraving and block making electrolytically grained and anodised aluminium and its alloys.

Dated this 28th day of October, 1972

PATENTS OFFICER,

Council of Scientific and Industrial Research

INDIAN PATENTS AND DESIGNS ACT 1970

Complete Specification

"IMPROVEMENTS IN OR RELATING TO THE MANUFACTURE OF ALUMINIUM PHOTO ENGRAVURE PLATE AN BLOCK BY POWDERLESS ETCHING OF ALUMINIUM AND ITS ALLOYS"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi—1, India, an Indian registered body incorported 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, a citizen of India and employed in the Central Elecrochemical Research Institute, Karaikudi—623006, Tamil Nadu, India.

This invention relates to improvements in or relating to the manufacture of photoengravure plate and block by aluminium and its alloys.

Hitherto it has been proposed to use aluminium and its alloys for photo engraving and block making purposes for which some suitable etching solutions are developed under trade names in foreign countries.

The limitations connected with the prior knowledge are that the composition of the etching solutions are proprietary and are only available in trade names. Hence, there is a need for developing an etching composition for powderless etching of aluminium and its alloy for photo engraving and block making.

The main object of this invention is to obviate the above disadvantages by developing an etching solution which is cheap and indigenously available for powderless etching of aluminium and its alloys for photo engraving and block making.

According to the present invention, there is provided a process for the manufacture of aluminium photo engravure plate and block which consists in etching (a) aluminium (minium 99%) and its alloys containing magnesium 1—5% or copper 0·5—5% or zinc 0·5—15% or tin 0·2—2% or combination of more than one said alloying ingredients with aluminium are etched in (b) an etching solution containing ferric chloride (specific gravity 1·26 to 1·38) with a water immiscible solvent with a high flashpoint and substantially unreactive with etching solutions like kerosene, petroleumiether, diesel, toluene, napthalene, diethul benzene or triehlorethulene.

A film forming substance like ethylene glycol, ethulene glycol monoethyl ether, triethanol or mono ethanolamine and amines and esters of steric acid and palmitic acid may be added to the etching solution.

A surface active agent such as lignin sulphonic acid, lauryl sulphate, cetyl trimethyl ammonium bromide or chloride, teepol, tetramethyl ammonium chloride, sulphonated castor oil and "amphocerine BD" may be added to the etching solution.

Accelerators like copper chloride or sulphate and other chloride salts such as tin chloride and cadmium chloride with or without ammonium thiocyanate may be added to the etching solution.

In the invented process, etching of aluminium and its alloys for the purpose of photo engraving and block making after applying acid resistant photoresist and developing the image adopting the conventional methods given in the part of photo engraving and block making using feric chloride solution of specific gravity 1·26—1·38 (30—40° Be) along with a water immiscible solvent consisting of aliphatic or aromatic hydrocarbons of naphthenic hydrocarbons which have got high flash point and which are substantially unreactive with the etching solutions like kerosene or petroleum ether or diesel or toluene or nephthalene or diethul benzene or thrichlorethulene. In addition to the above, the etching solution also contains a film forming substance, surface active agents and accelerators. Copper chloride or sulphate and other chloride salt of tin and cadmium are individually or in combination with ammonium thiocyanate are used as accelerator in the etching composition without which the etching rate is sluggish. The surface active agents like lignin sulphonic acid, laurul sulphate, cetul trimethul ammonium bromide or chloride, 'amphocerine BD" (a surface active agent produced by M/s HICO Products Ltd., Bombay), teepol, tetramethul ammonium chloride, sulphonated castor oil, are used individually or in combination in the etching solution. Compounds like ethulene glycol, ethulene glycol monoethyl ether, triethanol or monoethanolaline, amines and esters of steric acid, palmitic acid are also used in the etching solution to control the etching rate and to avoid lateral cutting of the image on the photoresist. The pH of the etching electrolute was adjusted to 0 to 2 with hydrochloric acid or as the case may be.

The following are the examples given to illustrate the invention and not to limit the scope of the invention :

2S aluminium alloy was degreased and acid resistant photoresist was applied and the image was developed using the conventional methods available in the art of photoengraving. After developing the image, it was etched in the following solution :

Ferric chloride ...	...	30°Be (Specific gravity : 1·26)
pH adjusted to	...	1·5 with hydrochloric acid
Kerosene ...	...	1—5%
Teepol ...	...	1%
Temperature ...	...	30—35°C
Time of etching	...	15 minutes

The image was not affected due to lateral cutting due to etching.

EXAMPLE 2

The photoresist was applied as in Example 1 over 26S (copper : 4·25%) aluminium alloy and the image was developed in the same way. Then the plate was etched using the undermentioned etching solution :

Ferric chloride ...	...	40°Be (Specific gravity : 1·38)
pH adjusted to	...	1 with hydrochloric acid
Petroleum ether	...	2%
Sodium laurul sulphate	...	0·2%
Ethulene glycol	...	1%
Temperature ...	...	35—38°C
Etching time ...	...	15 minutes

In the above solution, etching was good and the image was not spoiled.

EXAMPLE 3

The photoresist was applied over 65S sluminium alloy (Mg 1%, Cu 0·25%, Si 0·5% and Cr 0·25%) and the image was developed as in Example 1. The plate was etched in the following etching solution :

Ferric chloride ...	...	35° Be (Specific gravity : 1·32)
pH adjusted to	...	1 with amonia
Diesel or kerosene	...	2%
Lignin sulphonic acid	...	0·5%
Cupric chloride or stannous chloride or cadmium chloride ...	...	0·4%
Ammonium thiocyanate	...	0·02%
Ethulene glucol monoethul ether ...	...	2%
Operating temperature	...	30—35°C
Etching time ...	...	15 minutes

The image was not at all affected and the etch factor was good.

EXAMPLE 4

The acid photoresist was formed over high purity aluminium sheet and the image was prepared as in Example 1. After preparing the image it was etched in the following etching solution :

Ferric chloride ...	...	38°Be (Specific gravity : 1·335)
pH adjusted to	...	1·5 with hydrochloric acid
Kerosene ...	...	2%
Sulphonated castor oil	...	0·2%
Triethanolamine	...	1%
Ethulene glycol	...	1%
Copper chloride	...	0·4%
Ammonium thiocyanate	...	0·2%
Working temperature	...	30—38°C
Etching time ...	...	15 minutes

The image was perfect and unaffected by the etching solution. No lateral corrosion was observed. The etch factor was good.

EXAMPLE 5

2S (99% aluminium) aluminium alloy plate was electrolutically grained and then anodised in sulphuric or chromic acid and then the picture was developed by photographic method and etched in the following solution :

Ferric chloride ...	...	38°Be (Specific gravity : 1·355)
pH adjusted to	...	1·5 with hydrochloric acid
Kerosene ...	...	2%
Sulphonated castor oil	...	0·2%
Triethanolamine	...	1%
Ethulene glucol	...	1%
Copper chloride	...	0·4%
Ammonium thiocyanate	...	0·2%
Working temperature	...	30—38°C
Etching time	...	15 minutes

The block produced was very fine.

EXAMPLE 6

Ferric chloride ...	...	35°Be (Specific gravity : 1·32)
pH adjusted to	...	1 with hydrochloric acid
Trichloroethulene	...	2%
Trimethul benzene	...	6—8%
Methul salicylate	...	0·3%
Triethanolamine	...	1%
Sulphonated castor oil	...	0·5%
Sodium laurul sulphate	...	0·3%
Temperature ...	...	30—35°C
Etching time ...	...	15 minutes

3S aluminium alloy (1·25% manganese) plate was degreased and aid resistant photoresist was applied as in Example 1 and the image was developed according to the conventional methods available in the art of block making and photoengraving. Then the plate was etched in the above mentioned etching solution. The image was unaffected and etching was perfect.

EXAMPLE 7

A1-Zn-Mg alloy was used and the image was formed as in the above examples.

Ferric chloride	...	30°Be (Specific gravity) 1·26
pH adjusted to	...	1 with hydrochloric acid
Toluene ...	...	6%
Turpentine ...	...	2%
Methul sulphosuccinate	...	0·3%
Cupric chloride ...	...	0·4%
Ammonium thiocyanate	...	0·02%
Sodium salt of lignin sulphonic acid ...	...	0·5%
Teepol ...	...	0·2%
Bath temperature	...	32—35°C
Etching time ...	...	15 minutes

The image was unaffected and no lateral undercutting of the image was observed.

In all the above seven examples each factor was approximately 20.

The following are among the main advantages of the invention :

1. Aluminium and aluminium based alloys can be made use of for block making and photo engraving purposes using the etching solutions mentioned in this patent.

2. The etching solution mentioned in this patent has got good etching characteristics and it does not spoil the image by lateral or undercutting type of corrosion.

3. The etching solution is composed of indigenously available chemicals.

4. The etching solution described in this patent can be used for photo-engraving and block making electrolytically grained and anodised aluminium and its alloys.

WE CLAIM :

1. A process for the manufacture of aluminium photo engravure plate and block which consists in etching (*a*) aluminium (minimum 99%) and its alloys containing magnesium 1—5% or copper 0·5—5% or zinc 0·5—15% or tin 0·2—2% or combination of more than one said alloying ingredients with aluminium in (*b*) an etching solution comprising ferric chloride (specific gravity 1·26 to 2·38) with a water immiscible solvent with a high flashpoint and substantially unreactive with etching solutions like Kerosene, petroleum ether, diesel, toluene, napthalene, diethyl benzene or trichlorethylene.

2. A process as claimed in Claim 1 wherein a film forming substance like ethulene glycol, ethylene glycol monoethyl ether, triethanol or mono ethanolamine and amines and esters of steric acid and palmitic acid are added to the etching solution.

3. A process as claimed in Claim 1 to 2 whrein a surface active agent such as lignin sulphonic acid, lauryl sulphate, cetul trimethyl ammonium bromide or chloride, teepol, tetramethul ammonium chloride, sulphonated castor oil and "amphocerine BD" is added to the etching solution.

4. A process as claimed in any of the preceding claims wherein accerators like copper chloride or sulphate and other chloride salts such as tin chloride and cadmium chloride with or without ammonium thiocyanate are added to the etching solution.

Dated this 24th day of January 1974.

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