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[54] **PHOTOSENSITIVE ALUMINUM PLATE AND PROCESS FOR PREPARING THE SAME**

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[52] **U.S. Cl.** .... **96/86 R,** 96/67, 96/75

[51] **Int. Cl.** **G03c 1/94**

[58] **Field of Search** .... 204/58; 75/139; 96/86, 96/86 P, 75, 67, 90, 33; 101/459

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[57] **ABSTRACT**

A photosensitive plate comprising an aluminum support containing from 0.05 to 1.0 percent by weight copper and having thereon a finely porous oxide layer formed by the anodization of said support, said oxide layer carrying a photosensitive material, is disclosed. A process for preparing the photosensitive aluminum plate is also disclosed.

3 Claims, 1 Drawing Figure

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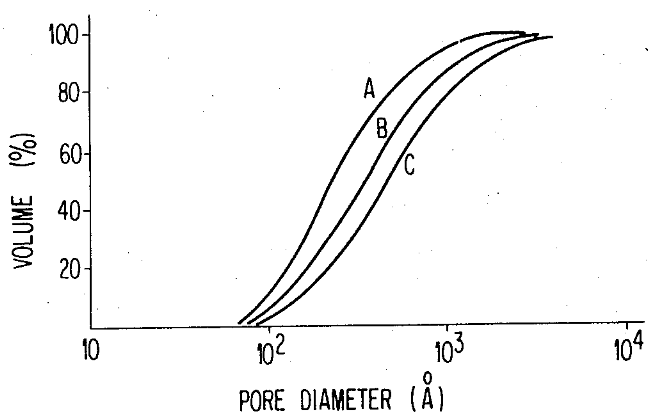

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PHOTOSENSITIVE ALUMINUM PLATE AND PROCESS FOR PREPARING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a photosensitive plate using anodized aluminum as a support. More particularly, this invention relates to a photosensitive aluminum plate having on an aluminum alloy an anodized finely porous oxide layer carrying in the fine pores a photosensitive material such as silver halide, and the like. This invention also relates to the process for preparing the photosensitive plate.

An object of the present invention is to provide a photosensitive plate which is high in its photographic properties, is inexpensive to manufacture and can be manufactured under mild anodizing conditions.

2. Description of the Prior Art

Aluminum is a metal which is relatively inexpensive, easily workable because of its excellent ductility, light and easily handled due to its low specific gravity, silver in color and beautiful, and corrosion resistant because it easily reacts with oxygen in the air forming a stable oxide film. Use of aluminum has recently progressed rapidly because of these advantages. However, on the other hand, since aluminum is low in hardness (soft) and easily damaged (scratches and dents) and because the oxide film which is naturally produced is generally from 5×10^{-5} to 1.5×10^{-4} mm in thickness, corrosion occasionally occurs in an unusual manner.

A method of anodizing aluminum has been devised to overcome such disadvantages and, since the aluminum oxide film produced thereby minimizes the scratching and corroding of aluminum, the above-mentioned defects have been eliminated.

By passing an electric current through a system using aluminum as an anode in an aqueous solution or a non-aqueous solution of inorganic acid, such as sulfuric acid, phosphoric acid, chromic acid, boric acid, and the like, and organic acid, such as oxalic acid, sulfamic acid, and the like, alone or in combination of two or more such acids, an oxide film is formed on the surface of the aluminum.

Much research has been reported on the aluminum oxide film so obtained. For example, the structure of the aluminum oxide film is described in the J. Elec. Chem. Soc., 100 (9) 411.

The oxide film is composed of a unit cell which is a hexagonal post perpendicular to the metallic surface. In the central part of the hexagonal post a pore exists.

The sizes of the cell and the pore vary depending upon the conditions of film formation. The thickness of the cell wall and the size of the pore when various electrolytes are used are as shown in Table 1.

TABLE 1

Thickness of Cell Wall and Size of Pore When Anodized in Various Electrolytes

Electrolyte	Thickness of Cell Wall (A/V)	Diameter of Pore (A)
15% Sulfuric Acid 50°F	8.0	120
3% Chromic Acid 100°F	10.9	240
4% Phosphoric Acid 75°F	10.0	330
2% Oxalic Acid 75°F	9.7	170

A photosensitive material utilizing anodized aluminum is conventionally known and is described in the specification of U.S. Pat. Nos. 2,126,017 and 2,766,119.

Heretofore, aluminum and aluminum alloys used for these purposes are not specified in terms of the alloy components and conditioning, and, even though the method of anodizing is under the same conditions, a stable and satisfactory result is not necessarily obtained, and it has been difficult from a number of standpoints to industrialize such a method.

Although other photosensitive materials can be used as the sensitizing agent, an example using silver halide will be explained herein.

One of the most important characteristics in this type of photosensitive aluminum plate is the optical density of the image obtained by the following general treatment where the sensitizing agent is silver halide:

Exposing → Developing → Fixing →
Washing with Water → Intensifying →
Washing with Water → Sealing

Of course, with respect to the image concentration it is desired to show the maximum image concentration for a given amount of exposure.

Considering aluminum as a support, the elements affecting the image concentration are believed to be as follows:

1. Total volume of pores enclosing the photosensitive material;
2. Stereostructure of the pores affecting the development efficiency (for example, the effective percentage (*m*/M) of silver (*m*) existing as an image after treatment for the amount (M) of silver halide in the pores before development);
3. Trace amounts of the components in the aluminum affecting it photographically.

SUMMARY OF THE INVENTION

The present inventors have found that, when preparing a photosensitive plate from, in addition to pure aluminum, a binary alloy of Al-Mg, Al-Cu, Al-Mn, Al-Sn, Al-Fe, Al-Zn, and the like, and a ternary alloy based on two binary alloys by the method described below and creating an image thereon, a specific range of copper content is extremely effective for improving the color in the image areas and the non-image areas. That is, it has been found that if the copper content is increased within a certain range the developed silver image is increased in neutral black optical density to a greater extent and the aluminum oxide film in the non-image areas is colored to a lesser extent by anodizing.

In order to determine the influence of the copper in the aluminum alloy on image concentration, the following experiment was conducted.

First, in order to confirm that copper has an influence upon the pore volume enclosing the photosensitive material, an electromicrograph of the cross section of the oxide film was taken, and the volume of pore corresponding to each diameter was calculated. In the two experiments the latter is considered to show the volume of the pore more correctly. Therefore, a description of the latter will be given as follows:

the volume of a pore of γ in diameter, which is given as a function of the pressure by the following formula

$$\gamma = 75,000/P\,A\ ,$$

can be determined from the change of the volume of mercury pressured into the pores of the oxide film by pressure P, the change being shown in dilato meters, wherein the surface tension of the mercury is 480 dyne/cm and the contact angle is 140°.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

The drawing shows the relationship graphically of the pore diameter and the volume percentage in aluminum oxide film.

From the drawing and Table 2 it has been found that the higher the copper content, the larger the diameter and volume of the pore. That is, the higher the copper content in the aluminum alloy, the larger the amount of the photosensitive agent can be placed in the pore.

DETAILED DESCRIPTION OF THE INVENTION

Next, as to the developing efficiency, the silver content in the silver halide before developing, M mg/100 cm^3, and that after developing and fixing, *m* mg/100 cm^3, were compared on the photosensitive plates prepared using three types of aluminum alloys differing in copper content and under the same conditions according to the above described method and exposed to light using a Plano Printer (manufactured by the Fuji Photo Film Co., Ltd.) and developed and fixed using an Alphoto Auto Processor (manufactured by the Fuji Photo Film Co., Ltd.).

Table 2 shows the elemental analysis of these three types of aluminum alloys and Table 3 shows $\overline{M}$, $\overline{m}$, and $\overline{m}/\overline{M}$ values when using these aluminum alloys.

However, these values are average values of M and *m* obtained on annealed aluminum (O), half hard aluminum (H-14) and half hard aluminum (H-18) which have the same composition but differ in conditioning.

Table 4 shows the average values of M and *m* of each material under each tempering condition.

TABLE 2

Elemental Analysis

Sample	Element Cu	Fe	Si	Mg	Mn	Zn	Cr	Ti
	%	%	%	%	%	%	%	%
A	0.16	0.46	0.09	<0.01	<0.01	<0.01	<0.01	<0.01
B	0.27	0.47	0.10	<0.01	<0.01	<0.01	<0.01	<0.01
C	0.50	0.46	0.10	<0.01	<0.01	<0.01	<0.01	<0.01

TABLE 3

Amount of Silver on the Plate Before and After Development and Developing Efficiency

Sample	Amount of Silver After Development	Before Development	Developing Efficiency
	$\overline{m}$ (mg/100cm³)	$\overline{M}$ (mg/100cm³)	$\overline{m}/\overline{M}$
A	5.8	14.7	0.39
B	7.3	16.5	0.44
C	9.0	18.3	0.49

TABLE 4

Amount of Silver in Conditioned Material and Developing Efficiency

Material	Amount of Silver After Development	Before Development	Developing Efficiency
	$\overline{m}$ (mg/100cm³)	$\overline{M}$ (mg/100cm³)	$\overline{m}/\overline{M}$
O	6.5	16.3	0.39
H-14	7.8	16.7	0.47
H-18	7.8	16.4	0.47

Table 3 shows that the higher the copper content the higher is the developing efficiency (the production efficiency of reduced silver). Although the reason is not completely understood, it is believed that the movement to the right in the following relationship is probably varied depending upon the stereo structure of the pore.

$$AgX \rightarrow Ag + X\ ,$$

wherein X represents Cl, Br or I.

As is well known, with the general silver halide photosensitive material, copper ion has an influence upon the sensitization. However, it was not obvious that, in the silver halide photosensitive material as in the present invention, the copper in the aluminum acts directly on the silver halide resulting in a photographic influence.

As was described above, it has been found that the higher the copper content of the aluminum alloy to be used, the higher is the concentration of the image area and the closer the photosensitive aluminum plate obtained is to colorless.

The effective range of the copper content is from 0.05 to 1.0 percent and the preferred content is from 0.12 to 0.30 percent.

If the copper content is too high, a reduction reaction (so called "fog") shown by the above formula tends to take place and the quality of the anodized film (abrasion resistance and corrosion resistance) tends to become worse.

The anodizing in the present invention is carried out as described in the specification of U.S. Pat. No. 2,766,199 using a solution of a mixture of oxalic acid and an oxalate of an alkali metal such as sodium oxalate and potassium oxalate as an electrolyte and passing an electric current of 0.5 to 5 amp/dm^2 therethrough while maintaining the temperature of the liquid at from 40 to 70°C at pH of from 1 to 5. The electric current used at this point can be either DC or a mixture of DC and AC. An aqeuous solution of sulfuric acid, chromic acid, or phosphoric acid, and the like can be used as the electrolyte. The anodized aluminum plate is immersed into an aqueous solution of silver nitrate and a hydrophilic colloid, or such liquid can be coated on the aluminum plate.

Suitable hydrophilic colloids are polyvinyl alcohol, methyl cellulose, gum arabic, gelatin, and the like.

Preferably, the concentration of the silver nitrate is from 30 to 50 percent and that of hydrophilic colloid is from 0.1 to 0.5 percent.

0.01 to 0.03 percent of the oxidizing agent such as ferricyanates of alkali metal, bichromates, chromate, and the like can be added to this liquid.

When, after immersing in the silver nitrate solution or coating the solution, removing as much as possible of the liquid adhering to the surface of plate and drying the plate, and thereafter, immersing the plate into an aqueous solution of an alkali halide, such as potassium bromide and potassium chloride, and the like, silver halide is formed in the pore.

In addition to the above method, the anodized plate can be treated with the above described oxidizing agents, and these oxidizing agents can be used together with the alkali halide or a silver salt of the above described oxidizing agents can be used together with silver nitrate.

When employing the aluminum alloy of the present invention as shown in Table 5, the reflection concentration of the image is higher in comparison with that of a conventional material 1100 (American Aluminum Association) having a 0.02 percent copper content.

TABLE 5

Relationship of Copper Content of Aluminum Alloy and Reflection Concentration of Image

Copper Content (%)	Reflection Concentration
0.02(material 1100)	0.6
0.16	1.7
0.50	1.9

In the above, the reflection concentration of the image is one obtained by exposing a plate through a filter of 0.85 in concentration for 10 seconds by a Quick Copy Printer (made by the Fuji Photo Film Co., Ltd.) and treating it with an Alphoto Processor.

Thus, the present invention is characterized in that a sufficient image density can be obtained even by treatment under mild conditions of anodizing since a high image density can be obtained when the copper content is within the specific range as described above.

In general, in a photosensitive material prepared by forming a photosensitive material in a pore of anodized aluminum, a satisfactory image cannot be obtained unless the anodizing is at a relatively high temperature, for a long period of time, and a concentrated electrolyte is used. The oxide film prepared under such conditions has disadvantages such as being poor in film quality and being expensive to manufacture.

However, the present invention has the advantages that a photosensitive plate high in photographic ability can be manufactured cheaply under mild anodizing conditions.

The aluminum alloy can be manufactured using conventional methods. One method will be summarized as follows.

The desired quantity of copper is added to aluminum of 99.5 percent in purity and an ingot is made therefrom. After a homogenizing treatment (540°C × 4 hr.) the ingot is cold-rolled or hot-rolled to obtain a plate having the desired thickness. At this point, addition of a trace amount of manganese, magnesium, silicon, iron, and the like, other than copper, does not affect reversely on the photosensitive plate.

In addition to silver halides, a diazo compound, ammonium iron citrate and a red prussiate, an organic halogen compound such as CBr_4, and diphenylamine, a compound changing color depending upon the pH and a compound converting to an acid or base by a light irradiation, as described in, for example, Japanese Patent Publication No. 40-2203, a quinone diazaido derivative such as diazo salicylic acid, a leuco compound such as 4,4'-tetra-methyldiphenylmethane, Michler's hydrol, Michler's hydromethylether, bix-(4,4'-bis-dimethylamine benzhydryl)ether, 4,4'-tetramethyl diaminodiphenyl methyl benzoate, tetramethyl benzidine, crystal violet lactone, crystal violet carbinol base, and the like and an organic halogen generator such as CB_4, and a photochromic dye, for example, the 1,3,3-trimethylindolinobenzospiropyrans, the 1,3,3-trimethylindolino-β-naphthospiropyrans, the benzo-β-naphthospiropyrans and the xantho-β-benzospiropyrans as described in, for example, Belgian Patent No. 683,188, and the like can be used as the photosensitive material in the present invention.

As to these photosensitive materials, the present invention can be conducted by the methods described in the present specification and by methods well known in the photographic art similar to the use of silver halide.

EXAMPLE 1

Material H-14 (corresponding to A in the Table and the Drawing) having a copper content of 0.16 percent was electrolyzed using a combination of alternating current and direct current at a current density of $2A/dm^2$ in an electrolyte of 5 percent oxalic acid and 3 percent potassium oxalate at 60°C for 30 minutes.

The oxide film so obtained was washed sufficiently with water and dried, and then the following composition (Solution 1) was impregnated into the pores of the oxide film:

Solution 1	
Silver Nitrate	300 g
Gelatin	1 g
Potassium Bichromate	0.2 g
Distilled Water	1 l

After squeezing the excess liquid from the surface of the oxide film and drying it, the oxide film was immersed into the following solution (Solution 2) for 10 seconds:

Solution 2	
Sodium Chloride	300 g
Potassium Bichromate	50 g
Distilled Water	1 l

After washing with water, the oxide film was immersed into the following solution (Solution 3) for 60 seconds:

Solution 3

Red Prussiate	125 g
Potassium Bromide	100 g
Sodium Bichromate	20 g
Distilled Water	1 l

and, after washing with water, was stored in a dark and cold place.

The plate thus obtained was exposed under a negative film, developed in a photographic developer, fixed, and washed with water, and, thereafter, was intensified with a golden intensifier, and, if necessary, was dyed, and finally was sealed in a hot solution of nickel salt or boiling water for filling up the pores to obtain a distinct photo copy which is higher in contrast. The photographic image so obtained is characterized by being particularly fast to light and weather.

Incidentally, this plate before toning had an image density corresponding to the copper content of 0.16 percent in Table 5.

EXAMPLE 2

Material H-18 (corresponding to B in the Table and the Drawing) having a copper content of 0.27 percent was electrolyzed using a direct current at a current density of $2A/dm^2$ in an electrolyte of 2 percent oxalic acid and 3 percent sodium oxalate at 45°C for 20 minutes.

The oxide film so obtained was washed sufficiently with water and dried, and, thereafter, was immersed into Solution 4 as follows:

Solution 4

Chromic Acid Anhydride	200 g
Distilled Water	1 l

at 40°C for 5 minutes, and, after drying, the following Solution 5 was impregnated into the pores of the oxide film:

Solution 5

Silver Nitrate	300 g
Gelatin	5 g
Concentrated Nitric Acid	1 cc
Distilled Water	1 l

After squeezing the excess liquid from the surface of the oxide film and drying it, the oxide film was immersed into the following solution (Solution 6) for 60 seconds:

Solution 6

Potassium Bromide	50 g
Potassium Bichromate	50 g
Distilled Water	1 l

After washing with water and drying, the oxide film was stored in a dark and cold place.

When treating the plate so obtained in the same manner as used in Example 1, the plate before intensification had an image density corresponding to a copper content of 0.16 percent in Table 5.

EXAMPLE 3

Material H-18 (corresponding to C in the Table and the Drawing) having a copper content of 0.50 percent was electrolyzed in each of the liquid compositions and in the same manner as in Example 1 and the liquid was impregnated into the pore. The plate so obtained had an image density corresponding to the copper content of 0.50 percent in Table 5.

EXAMPLE 4

After anodizing material H-14 (corresponding to A in the Table and the Drawing) having a copper content of 0.16 percent under the same condition as used in Example 1, with the liquid consisting of the following compositions

(1)	Ethyl Cellulose	5 g
	Ethyl Alcohol	20 cc
	Toluene	20 cc
	Carbon Tetrabromide	2 g

and

(2)	3-Dibenzyl Amino-7-diethylamino-florane	2 g
	Ethylene Dichloride	10 cc

was impregnated into the pores of oxide film and, after drying, the film gave a distinct green image on exposure under a negative film under arc light.

The distinction of the image so obtained was remarkably excellent in comparison with one obtained by anodizing an aluminum material containing only a small amount of copper.

What is claimed is:

1. A photosensitive aluminum plate, consisting of an aluminum support containing therein, from 0.05 to 1.0 percent by weight of copper, and having thereon, a finely porous oxide layer formed by the anodization of said support, said oxide layer carrying a photosensitive material and said photosensitive material further being characterized as having filled the pores of said finely porous oxide layer,

said aluminum support consisting of (1) aluminum, (2) a binary alloy selected from the group consisting of Al-Cu, Al-Mn, Al-Sn, Al-Fe and Al-Zn, or (3) a ternary alloy based on two binary alloys selected from the group consisting of Al-Cu/Al-Mn, Al-Sn/Al-Fe and Al-Zn.

2. The photosensitive plate as claimed in claim 1 wherein said photosensitive material is selected from the group consisting of a silver halide; a diazo compound; ammonium iron citrate and a red prussiate; an organic halogen compound and diphenylamine; a compound changing color depending upon the pH and a compound converted to an acid or base upon light irradiation; a quinone diazaido derivative; a leuco compound and an organic halogen generator; and a photochromic dye.

3. The photosensitive plate as claimed in claim 1, wherein said copper ranges from 0.12 to 0.30 percent by weight.

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