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[54] **PHOTOSENSITIVE ALUMINUM PLATE OF IMPROVED STORAGE STABILITY**

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[58] **Field of Search** ..... 96/86, 109 CA, 109

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

A photosensitive aluminum plate of improved storagability in which an anodically oxidized aluminum is used as a support and a silver halide is contained as a photosensitive material in the micropores of the oxide film formed on the support by anodic oxidation.

9 Claims, No Drawings

PHOTOSENSITIVE ALUMINUM PLATE OF IMPROVED STORAGE STABILITY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to a photosensitive aluminum plate using an anodically oxidized aluminum as a support and containing a silver halide as a photosensitive material in the micropores of the oxide film formed by anodic oxidation of the aluminum support. More particularly, this invention relates to such a photosensitive aluminum plate having improved storage stability.

2. Description of the Prior Art

Aluminium is a very advantageous metal because it is relatively cheap, easy to process due to its superior malleability and ductility, easy to handle due to its low specific gravity and light weight and resistant to corrosion due to the formation, upon exposure to air, of a stable oxide film resulting from reaction with oxygen in the air.

The demand for aluminum has recently been increasing more and more due to the various good properties and usefulness as described above.

In spite of these preferred properties, however, metallic aluminum also has the disadvantage that it can be easily damaged by abrasion or pressure exerted against its surface due to its poor hardness, i.e., to its softness, and moreover, since the oxide film naturally formed thereon is generally extremely low in thickness, e.g., about 5×10^{-5}mm to 1.5×10^{-4}mm, abnormal generation of corrosion may occasionally take place.

These drawbacks, however, have been completely eliminated as a result of the invention of the method for anodic oxidation of aluminum now practiced, because the aluminum oxide film thus formed artificially has great resistance to external, physical and chemical influences.

The above-described aluminum oxide film may be prepared by passing electricity through an aqueous or nonaqueous solution, either alone or in combination of one or more such solutions, of an inorganic acid such as sulfuric acid, phosphoric acid, chromic acid or boric acid, or of an organic acid such as oxalic acid or sulfamic acid, in which the aluminium is immersed in the solution as the anode. Thereby an oxide film is formed on the surface of the aluminum. As to the aluminum oxide film formed in this manner, many reports have been made, and in particular a detailed explanation on the structure thereof is made in *Journal of the Electrical and Chemical Society*, 100, (9), 411.

According to the report made in the above-described reference, the oxide film is composed of hexagonal prism units, i.e., cells, vertically standing on the surface of the metallic aluminum, with a pore being present in the central portion of the cells.

The dimensions of these cells and pores will vary depending upon the conditions under which the oxide film is formed. The following table indicates the wall thickness of the cell and the size of the pore obtained when using the various electrolytic solutions as specified in the table.

TABLE 1

Electrolytic Solutions (Temperature)	Wall Thickness of Cell (A/V)	Pore Size (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

Silver halide photosensitive materials in which an anodically oxidized aluminum plate is used are well known and are described for example in U.S. Pat. Nos. 2,115,339, 2,126,017 and 2,766,119.

The characteristics of such photosensitive materials are that the silver image may be protected by the corrosion resistance and durability of the oxide film, resulting in the formation of a relatively stable image recording. Therefore, it is necessary not only to simply apply the photosensitive silver salt to the aluminum oxide film, but also to incorporate it into the micropores of the oxide film.

The photosensitive silver salt in general may be formed by reacting silver nitrate in a solution of gelatin with an alkali metal halide. The silver salt prepared in such a conventional manner, however, will be of a particle size within the range of from about 0.05 μ to several microns, although the particle size may depend upon the solution mixing method, mix ratios, gelatin concentrations or the like. Since the pore size of the cell is, as shown in the hereinabove described Table 1, within the range of from about 0.01 to 0.05 μ, even the smallest silver salt particle prepared in the conventional manner will be too large, thus making it impossible to incorporate it into the pores.

However, as is disclosed in the above-described patent references, this problem can be solved by successive application and impregnation of the silver nitrate solution and alkali halide solution in that order, whereby the photosensitive silver salt can be incorporated into the pores of cells.

The silver salt particles incorporated into the pores tend to be reduced by the surrounding aluminum due to the difference in redox potentials between the silver salt and the aluminum. This may cause fogging and thereby shorten the shelf life. In an attempt to eliminate this disadvantage, a method has been proposed in which contact between the substances can be avoided by using a polymeric binder. This method is also described in the above-described patent specifications. Although a shelf life on the order of 3 to 6 months may be obtained by this method, it is still unsatisfactory from the standpoint of selling or using it.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to provide a photosensitive aluminum plate having an improved shelf life, together with a high sensitivity and a low generation of fog. Another purpose is to provide a method for the preparation of a photosensitive aluminum plate of superior shelf life.

These objects have now been accomplished according to the present invention by applying a 3-mercapto-5-methyl-4-phenyl-1,2,4-triazole, simultaneously with or subsequently to the step of photosensitive silver salt formation in the micropores of the oxide film. Thus, the shelf life can be extended to 1 to 2 years according to the method of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The photosensitive aluminum plate according to this

invention contains a photosensitive silver salt(in a hydrophilic colloid)and a 3-mercapto-5-methyl-4-phenyl-1,2,4-triazole in the micropores of the aluminum oxide film formed on the surface of the aluminum.

As the aluminum support described above pure aluminum or any aluminum alloy may be used. Suitable aluminum alloys are alloys of aluminum with alloying metals, e.g. zinc, silicon, iron and copper can be used. A copper aluminum alloy is preferred. The alloying metal can be present at a level of from about 0.5–1.0 by weight to the aluminium. Preferably from about 0.12 to 0.3 by weight of the alloying metal is used.

The photosensitive silver salt suitably can be silver bromide, silver chloride, or a mixed silver halide, i.e., silver chlorobromide. In particular silver bromide is preferred as the silver halide.

Examples of hydrophilic colloids which can be used include gelatin, polyvinyl alcohol, methyl cellulose, gum arabic and agar-agar, although in particular gelatin is preferred. The amount of hydrophilic colloid which can be used ranges from about 0.1 to 1%, preferably from about 0.2 to 0.5%, by weight based on the silver solution or the halide solution used in preparing the photosensitive silver salt.

3-Mercapto-5-methyl-4-phenyl-1,2,4-triazoles include not only 3-mercapto-5-methyl-4-phenyl-1,2,4-triazole but also the derivatives thereof, as well as their analogous compounds having substantially the same effect. Suitable such derivatives and analogous compounds are 3-mercapto-4-phenyl-1,2,4-triazole, 3-mercapto-4,5-dimethyl-1,2,4-triazole, 3',5-dimercapto-3,5'-diphenyldihydro-1,2-triazolotriazole, and 3',5'-dimercapto-3,5'-diethyldihydro-1,2-triazolotriazole. 3-Mercapto-5-methyl-4-phenyl-1,2,4-triazole is especially preferred. This additive may be added into the halide solution used in the photosensitive silver salt formation at a level of about 0.05 to 1.0 g., preferable about 0.1 to 0.5 g, per liter of the halide solution and ultimately adsorbed onto the photosensitive silver salt formed in the micropores of the oxide film formed by anodic oxidation. Alternatively, it may be brought into substantial contact, after formation of the photosensitive silver salt in the micropores, with the oxide film formed by anodic oxidation as an aqueous solution containing, per liter of solution, the same amounts of the additive described above, and thereby adsorbed onto the already formed photosensitive silver salt.

The photosensitive aluminum plate according to the present invention shows high sensitivity and reduced fog and is also excellent in shelf life.

The present invention will be further illustrated by the following nonlimitative examples.

EXAMPLE 1

An electrolytic solution containing 5% of oxalic acid and 3% of potassium oxalate was subjected to electrolysis by impressing a direct current of 2A/dm² for 30 minutes on a corrosion resistant aluminum alloy plate containing 0.15% of copper as the anode, while keeping the temperature of the solution at 60°) C.

The resulting support was rinsed and dried and subsequently a silver nitrate solution of the following composition was applied thereto and dried.

Silver Nitrate	300 g
Gelatin	5 g
Distilled Water	1 liter

Subsequently, a halide solution of the following composition was applied thereto and dried.

Potassium Bromide	100 g
Red Prussiate	50 g
Distilled Water	1 liter

Furthermore, a solution of the following composition was applied thereto, followed by a 30 second rising and then by drying.

Potassium Bromide	50 g
3-Mercapto-5-methyl-4-phenyl-1,2,4-triazole	1 g
Distilled Water	1 liter

There was obtained a photosensitive aluminum plate which can be stored for more than one year without formation of any fog.

EXAMPLE 2

Onto the plate electrolyzed in the manner as described in Example 1 was applied a silver nitrate solution of the following composition, followed by drying.

Distilled Water	1 liter
Silver Nitrate	200 g
Polyvinyl Alcohol	5 g

A halide solution of the following composition was then applied, followed by rinsing for 30 seconds.

Potassium Bromide	25 g
Sodium Chloride	15 g
Distilled Water	1 liter

Subsequently, an aqueous solution containing 0.2 g/l of 3-mercapto-5-methyl-4-phenyl-1,2,4-triazole, was applied and this was followed by drying.

The resulting photosensitive aluminum plate was found to be intact after storage for 1 to 2 years, without formation of any fog and deterioration in any other photographic properties.

The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What is claimed is:

1. In a photosensitive aluminum plate comprising an aluminum plate containing a silver halide in the micropores of an aluminum oxide film formed by anodic oxidation on the surface of said plate, the improvement which comprises further incorporating at least one of 3-mercapto-4-phenyl-1,2,4-triazole, 3-mercapto-5-methyl-4-phenyl-1,2,4-triazole, 3-mercapto-4,5-dimethyl-1,2,4-triazole, 3',5-dimercapto-3,5'-diethyldihydro-1,2-triazolotriazole, 3',5-dimercapto-3,5'-diphenyldihydro-1,2-triazolotriazole into said micropores.

2. The photosensitive aluminum plate as claimed in claim **1** in which said aluminum plate is pure aluminum of an aluminum alloy.

3. The photosensitive aluminum plate as claimed in claim **2** in which said aluminum alloy is an aluminum-copper alloy.

4. The photosensitive aluminum plate as claimed in claim **1** in which said silver halide is selected from the

group consisting of silver bromide, silver chloride and mixed silver halides.

5. The photosensitive aluminum plate as claimed in claim 4 in which said silver halide is silver bromide.

6. The photosensitive aluminum plate as claimed in claim 1 in which said 3-mercapto-5-methyl-4-phenyl-1,2,4-triazole.

7. The photosensitive aluminum plate as claimed in claim 1 in which a hydrohyilic colloid is additionally incorporated into said micropores.

8. The photosensitive aluminum plate as claimed in claim 7 in which said hydrophilic colloid is selected from the group consisting of gelatin, polyvinyl alcohol, methyl cellulose, gum arabic and agar-agar.

9. The photosensitive aluminum plate as claimed in claim 8 in which said hydrophilic colloid is gelatin.

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