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Electrophotographic photoreceptor.

An electrophotographic photoreceptor comprising a conductive substrate carrying a photoconductive layer, said substrate being obtainable by etching aluminium or an aluminium alloy with an alkaline etchant comprising (i) an alkali metal hydroxide and (ii) a weakly-acidic salt of an alkali metal and/or an alkaline earth metal, followed by anodizing the thus etched substrate.

The present invention relates to electrophotographic photoreceptors, especially conductive substrates for electrophotographic photoreceptors. More particularly, it relates to the conductive substrates for the electrophotographic photoreceptors used in an apparatus wherein an electrophotography is applied using a coherent light as a light source for forming images, especially a laser printer.

In recent years, the electrophotography has been applied to copying machines as well as various printers, because they can give images with high qualities without delay. As a photoreceptor which plays an important role in the electrophotography, the photoreceptor comprising an inorganic photoconductive substance such as selenium, arsenic-selenium alloy, cadmium sulfide, zinc oxide, amorphous silicon and the like has been used. More recently, various photoreceptors composed of various combinations of charge generation materials which comprise organic photoconductive substances with charge transport materials are developed and widely employed.

When the prior photoreceptor is set in the copying machine and the printer wherein a LED light is used as the light source, the good image can be obtained without any trouble. However, when it is set in the electrophotographic apparatus wherein the coherent light such as a laser is used as the light source, it is frequently impossible to obtain the good image, because the resultant image has a moire fringe pattern. As a cause that the good image cannot be obtained, the following is considered:

Because the coherent light is illuminated, an interference occurs between a light reflected on the surface of the photoreceptor and a light reflected from within the photoreceptor. The reflected light from within the photoreceptor includes that from the substrate and (in case of a laminate-type photoreceptor comprising a charge generation layer and a charge transport layer and an amorphous silicon photoreceptor comprising multiple layers) that from an interface between layers. The above occurrence of the interference is accompanied with an inconstant intensity of light. As the result, the photoreceptor is unevenly illuminated by light and a residual potential is also uneven, leading to the appearance of the moire fringe pattern on the image. This phenomenon is noticeable when the image is halftone.

Hitherto, various methods are proposed in order to resolve the moire fringe pattern. For example, a method comprising treating an aluminium substrate with a black alumite so as to reduce a reflectance of the substrate (JP-A-59-158); a method comprising subjecting a substrate to a stain finish by machining its surface; a method comprising subjecting a substrate to a sand blasting finish; and a method comprising subjecting a substrate to an etching treatment (JP-A-1-188860) are known. However, these methods have defects that insufficient effects are obtained

due to the surface of the substrate being contaminated during the treatment and other causes.

An object of the present invention is to provide the electrophotographic photoreceptor which can give the good image without producing the moire fringe pattern even if it is used in the electrophotography using the coherent light as the light source.

The present invention provides a conductive substrate for an electrophotographic photoreceptor, the conductive substrate comprising aluminium or its alloy which is subjected to an etching treatment using an alkaline etchant containing a hydroxide of alkali metal and a weakly-acidic salt of alkali metal and/or alkaline earth metal followed by anodizing.

The conductive substrate for the electrophotographic photoreceptor according to the present invention comprises aluminium or its alloy. The aluminium alloy includes Al-Mn and Al-Mg-Si. The conductive substrate of the invention should be that treated with the etching treatment with the alkaline etchant and the anodization.

Before the substrate is subjected to the etching treatment, it is preferably degreased using a conventional degreaser such as acid, alkali, organic solvent, surfactant or emulsion or by electrolyzing.

Next, the substrate is subjected to the etching treatment. The etching treatment is carried out by immersing the substrate in an aqueous solution comprising the alkaline etchant. The alkaline etchant used contains the hydroxide of alkali metal and the weakly-acidic salt of alkali metal and/or alkaline earth metal. The preferable alkali metal hydroxide includes sodium hydroxide and potassium hydroxide. The weakly-acidic salt of alkali metal and/or alkaline earth metal may be a normal salt or a hydrogen salt. The preferable alkali metal and the preferable alkaline earth metal in the weakly-acidic salt includes sodium, potassium, magnesium and calcium. The preferable weakly-acid which forms the weakly-acidic salt with the alkali metal and/or alkaline earth metal includes inorganic acids such as carbonic acid, silic acid and phosphoric acid as well as organic acids such as acetic acid, tartaric acid and succinic acid. The acid having $-\log K_a$ (K_a : dissociation constant of acid) of more than 2, especially more than 3 is more preferable. The concentrations of the alkali metal hydroxide and the weakly-acidic salt of alkali metal and/or alkaline earth metal in the alkaline etchant may be suitably varied. The preferable concentration of the alkali metal hydroxide in the alkaline etchant is 60 to 85 % by weight, more preferably 70 to 85 % by weight. While, the preferable concentration of the weakly-acidic salt of alkali metal and/or alkaline earth metal in the alkaline etchant is 10 to 30 % by weight, more preferably 10 to 25 % by weight.

The above alkaline etchant may contain a surfactant and/or an alkali metal chloride as an agent for improving properties of the etchant, in order to attain an

uniform etching.

The etching conditions are not particularly limited, provided that the above alkaline etchant is used. For example, an aqueous solution comprising the alkaline etchant has a concentration of 0.5 to 10 % by weight, preferably 0.5 to 5 % by weight. A temperature is 40 to 80°C, preferably 40 to 60°C. A period is generally 1 to 15 minutes.

Desirably, the aqueous solution comprising the alkaline etchant further contains an aluminium ion, thereby the etching rate can be suitably controlled. Otherwise, the substrate is etched immediately after it is immersed in the aqueous solution comprising the alkaline etchant. The aluminium ion concentration is preferably 0.1 to 2 % by weight.

In the present invention, the use of the alkaline etchant containing the hydroxide of alkali metal and the weakly-acidic salt of alkali metal and/or alkaline earth metal is important. Using such an alkaline etchant, an etching degree is easily controlled and the substrate whose surface has a suitable roughness is easily obtained, as compared with the use of only the alkali metal hydroxide. The roughness, expressed as R_{\max} (JIS B 0601-1970), of the surface of the conductive substrate which is subjected to the etching treatment, before the anodization is preferably about 2 to 4 μm . The etching degree is preferably controlled so that the roughness of the surface of the conductive substrate which is subjected to the anodization, before the provision of the photoconductive layer is 0.2 to 1.5 μm , especially 0.5 to 1 μm , expressed as R_{\max} (JIS B 0601-1970). When the roughness of the etched substrate is lower, the interference is easily occurred. While, when it is higher, the surface of the substrate subjected to the anodization is still rough. In case of that the anodized substrate has the rough surface, the resultant image has defects such as a fog.

After the etching treatment, the substrate is generally post-treated, for example by washing with water, neutralizing with an acid and again washing with water.

Next, the substrate is subjected to anodizing. Generally, the anodization is carried out in an acid such as chromic acid, sulfuric acid, oxalic acid, boric acid and sulfamic acid. The use of sulfuric acid is preferable. When the anodization is carried out in sulfuric acid, the preferable conditions are as follows: the concentration of sulfuric acid is 100 to 300 g/l; the concentration of aluminium ion is 2 to 15 g/l; the liquid temperature is 10 to 30°C, preferably 10 to 25°C; the bath voltage is 5 to 20 V; the current density is 0.5 to 2 A/dm².

The coating resulted from the anodization has generally an average thickness of 20 μm or less, preferably 10 μm or less.

After the anodization, the substrate having the above coating is treated by a low temperature sealing

or a high temperature sealing.

The low temperature sealing is carried out by immersing the substrate in an aqueous sealant solution at the temperature of 25 to 40°C, preferably 30 to 35°C. The aqueous sealant solution for the low temperature sealing is generally that containing nickel fluoride. The concentration of nickel fluoride in the aqueous solution is suitably varied, preferably 3 to 6 g/l. The pH of the aqueous solution of nickel fluoride is 4.5 to 6.5, preferably 5.5 to 6. For adjusting the pH of the aqueous solution of nickel fluoride, oxalic acid, boric acid, formic acid, acetic acid, sodium hydroxide, sodium acetate or aqueous ammonia may be used. The addition of cobalt acetate, nickel sulfate, surfactant and the like is effective for improving the properties of the coating. The time involved in the low temperature sealing is 1 to 3 minutes per μm of average thickness of the coating.

The high temperature sealing is carried out by immersing the substrate in an aqueous sealant solution containing a sealant at the temperature of 65 to 100°C, preferably 80 to 98°C. The aqueous sealant solution for the high temperature sealing is that containing metal salt such as nickel acetate, cobalt acetate, lead acetate, nickel acetate-cobalt, barium nitrate, preferably nickel acetate. The concentration of nickel acetate in the aqueous solution is suitably varied, preferably 3 to 20 g/l. The pH of the aqueous solution of nickel acetate is 5 to 6, preferably 5.5 to 6. For adjusting the pH of the aqueous solution of nickel acetate, aqueous ammonia or sodium acetate may be used. The addition of sodium acetate, organic carboxylate, anionic or nonionic surfactant and the like is effective for improving the properties of the coating. The time involved in the high temperature sealing is 2 to 10 minutes per μm of average thickness of the coating.

Finally, the substrate is worked up, for example by washing with water, drying in normal air or hot air and cooling to room temperature.

On the conductive substrate treated in the above, the photoconductive layer is provided. The photoconductive layer may comprise an inorganic or organic material. The inorganic material includes selenium, arsenic-selenium alloy, cadmium sulfide, zinc oxide and amorphous silicon. The inorganic photoconductive layer is applied on the conductive substrate according to the known process such as deposition, sputtering and coating. The organic photoconductive layer may be a laminated-type photoconductive layer which is formed by laminating the charge generation layer and the charge transport layer in any order, or a dispersion-type photoconductive layer which is formed by dispersing the charge generation material in a medium containing the charge transport material. The charge generation layer is formed by depositing an organic pigment such as phthalocyanine and azo pigment or applying a dispersion of the organic pig-

ment in a binder resin according to a conventional method such as dipping, spraying and spiral coating. While, the charge transport layer is similarly formed using a dispersion of the charge transport material such as hydrazone derivative and aromatic amine derivative in the binder resin or a polymeric charge transport substance such as polyvinyl carbazole. Alternatively, a composite-type photoconductive layer comprising the inorganic photoconductive layer as the charge generation layer and the organic photoconductive layer as the charge transport layer may be used.

If necessary, an intermediate layer having a barrier function and an adhesive function is provided between the conductive substrate and the photoconductive layer.

The electrophotographic photoreceptor according to the present invention which has the conductive substrate comprising aluminium or its alloy subjected to an etching treatment using a specific alkaline etchant followed by anodizing can give a very good image without producing a moire fringe pattern which occurs in the prior electrophotographic photoreceptor, even if it is set in an apparatus wherein the coherent light is used as the light source, such as a laser printer. The resultant image has no defect such as fog, black spot and white spot, because fine defects and contaminations on the surface of the substrate are completely removed according to the present invention.

Examples

The following examples will more fully illustrate the embodiments of the present invention. It will be apparent to one of those skilled in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention. All parts and percentages referred to herein are by weight unless otherwise indicated.

Example 1

An aluminium (material #6063) cylinder having a mirror finished surface (outer diameter of 30 mm, length of 250 mm and thickness of 1 mm) was degreased with an aqueous solution containing a degreaser (trade name NG-#30, ex. Kizai K.K.) in a concentration of 30 g/l at 60°C for 5 minutes.

After washing with water, the aluminium cylinder was subjected to an etching treatment by dipping in a liquid for etching for 4 minutes. The liquid comprised an aqueous solution which contained 1.2 % of an alkaline etchant [P₃T651, ex. Henkel Hakusui K.K.] consisting of 76 % of sodium hydroxide, 18 % of sodium carbonate, 3 % of sodium phosphate and 3 % of sodium chloride and was heated to 50°C, to which 0.3 % of aluminium (material #6063) was dissolved. Immediately, the aluminium cylinder was washed with

water and then dipped in 7 % of nitric acid at 25°C for 1 minute. It was washed with water again and then subjected to an anodization in an electrolyte of sulfuric acid in a concentration of 180 g/l (dissolved aluminium ion concentration being 7 g/l) at a current density of 1.2 A/dm², thereby an anodic oxide coating having an average thickness of 6 µm was formed. After washing with water, the aluminium cylinder was subjected to a sealing by dipping in an aqueous solution containing a nickel acetate based high temperature sealer (trade name TOPSEAL DX-500, ex. Okuno Seiyaku K.K.) at 95°C for 30 minutes. Finally, the aluminium cylinder was washed with water while an ultrasonic waves being applied thereto and then dried.

A dispersion was prepared by adding 500 parts of 1,2-dimethoxy ethane in 10 parts of oxytitanium phthalocyanine and 5 parts of polyvinyl butyral (trade name Denka Butyral 6000C, ex. DENKI KAGAKU KOGYO KABUSHIKI KAISHA) and grinding and dispersing using a sand grind mill. In this dispersion, the above aluminium cylinder having the anodic oxide coating was dipped, thereby a charge generation layer having a dry thickness of 0.4 µm was formed on the aluminium cylinder.

Next, the aluminium cylinder was dipped in a solution of 56 parts of N-methylcarbazol-3-carbaldehyde diphenylhydrazone, 14 parts of 3,3-di(4-methoxyphenyl)acrolein diphenylhydrazone, 1.5 parts of 4-(2,2-dicyanovinyl)phenyl-2,4-5-trichlorobenzene sulfonate and 100 parts of polycarbonate resin (Novalex® 7030A ex. MITSUBISHI KASEI CORPORATION) dissolved in 1000 parts of 1,4-dioxane, thereby a charge transport layer having a dry thickness of 17 µm was formed. Thus, a photoreceptor (A) was prepared.

Example 2

The procedures in Example 1 were repeated, except that the etching temperature was 56°C. Thus, the photoreceptor (B) was prepared.

Example 3

The procedures in Example 1 were repeated, except that 0.6 % of aluminium was dissolved in the aqueous solution containing the alkaline etchant. Thus, the photoreceptor (C) was prepared.

Example 4

The procedures in Example 1 were repeated, except that the etching temperature was 50°C and the aqueous solution contained 2.0 % of the alkaline etchant. Thus, the photoreceptor (D) was prepared.

Example 5

The procedures in Example 1 were repeated, except that the etching temperature was 45°C, the aqueous solution contained 3.0 % of the alkaline etchant and 0.6 % of aluminium was dissolved in the aqueous solution containing the alkaline etchant. Thus, the photoreceptor (E) was prepared.

Example 6

The procedures in Example 1 were repeated, except that the etching temperature was 45°C, the aqueous solution contained 3.0 % of the alkaline etchant and 0.9 % of aluminium was dissolved in the aqueous solution containing the alkaline etchant. Thus, the photoreceptor (F) was prepared.

Example 7

The procedures in Example 1 were repeated, except that the etching temperature was 45°C, the aqueous solution contained 4.0 % of the alkaline etchant and 0.6 % of aluminium was dissolved in the aqueous solution containing the alkaline etchant. Thus, the photoreceptor (G) was prepared.

Example 8

The procedures in Example 1 were repeated, except that the etching temperature was 45°C, the aqueous solution contained 4.0 % of the alkaline etchant and 0.9 % of aluminium was dissolved in the aqueous solution containing the alkaline etchant. Thus, the photoreceptor (H) was prepared.

Comparative Example 1

On an aluminium (material #6063) cylinder having a mirror finished surface (outer diameter of 30 mm, length of 250 mm and thickness of 1 mm), the charge generation layer and the charge transport layer identical with those in Example 1 were directly formed, without subjecting to either the etching treatment or the anodization. Thus, the photoreceptor (I) was prepared.

Comparative Example 2

The procedures in Example 1 were repeated, except that the etching treatment was omitted. Thus, the photoreceptor (J) was prepared.

Comparative Example 3

The procedures in Example 1 were repeated, except that the aqueous solution contained 3 % of sodium hydroxide as the alkaline etchant. Thus, the

photoreceptor (K) was prepared.

Example 9

The procedures in Example 1 were repeated, except that the alkaline etchant consisting of 85 % of sodium hydroxide and 15 % of sodium acetate was used. Thus, the photoreceptor (L) was prepared.

Example 10

The procedures in Example 1 were repeated, except that the alkaline etchant consisting of 85 % of sodium hydroxide and 15 % of sodium bicarbonate was used. Thus, the photoreceptor (M) was prepared.

Example 11

The procedures in Example 1 were repeated, except that the alkaline etchant consisting of 85 % of sodium hydroxide and 15 % of sodium dihydrogenphosphate was used. Thus, the photoreceptor (N) was prepared.

Comparative Example 4

The procedures in Example 1 were repeated, except that the aqueous solution contained 1.02 % of sodium hydroxide as the alkaline etchant. Thus, the photoreceptor (O) was prepared.

Test

Each of the above photoreceptors was set in a commercial laser printer of a reversal development system (PC-PR1000 ex. NEC Corporation) and its performances under different environmental conditions were evaluated.

Each of the conductive substrates after subjected to the etching treatment in Examples 1, 9 and 10 showed the roughness, R_{\max} (JIS B 0601-1970), of 3.6, 2.2 and 3.8 μm , respectively. The conductive substrate after subjected to the anodization in Example 1 showed the roughness, R_{\max} (JIS B 0601-1970), of 0.8 μm . Each of the conductive substrates after subjected to the etching treatment in Comparative Examples 3 and 4 showed the roughness, R_{\max} (JIS B 0601-1970), of 5.0 and 4.6 μm , respectively.

When the photoreceptors (A to H and L to N) prepared in Examples were used, the good images irrespective of a white or black background were obtained with producing no moire fringe pattern, under the environmental conditions of 5°C/10 % (RH), 25°C/60 % (RH) and 35°C/85 % (RH). When the photoreceptor (I) prepared in Comparative Example 1 was used, the moire fringe pattern was produced all over the half-tone image. When the photoreceptor (J) prepared in Comparative Example 2 was used, the moire fringe

pattern was also produced, provided that its extent was slight as compared with that of the photoreceptor (I). When the photoreceptors (K and O) prepared in Comparative Examples 3 and 4 were used, the moiré fringe pattern was not produced. However, a fog was produced, that is, black spots appeared all over the white background and therefore, the good images were not obtained. As a cause that the fog was produced, it is considered that because the surface of the conductive substrate was excessively roughened by the etching treatment, points to which charges were injected from the conductive substrate when the photoreceptor was charged were produced and these points appeared as the black points on the image.

It is judged from the results in Examples and Comparative Examples that the electrophotographic photoreceptor according to the present invention has the very excellent performances.

Claims

1. An electrophotographic photoreceptor comprising a conductive substrate carrying a photoconductive layer, said substrate being obtainable by etching aluminium or an aluminium alloy with an alkaline etchant comprising (i) an alkali metal hydroxide and (ii) a weakly-acidic salt of an alkali metal and/or an alkaline earth metal, followed by anodizing the thus etched substrate.
2. A photoreceptor according to claim 1 wherein the substrate has been subjected to a sealing treatment during or after the anodization.
3. A photoreceptor according to claim 1 or 2 wherein the substrate has a surface roughness (R_{\max}) of 0.2 to 1.5 μm .
4. A process for preparing an electrophotographic photoreceptor comprising forming a photoconductive layer on a conductive substrate which has been prepared by etching aluminium or an aluminium alloy with an alkaline etchant comprising (i) an alkali metal hydroxide and (ii) a weakly-acidic salt of an alkali metal and/or an alkaline earth metal, followed by anodizing the thus etched substrate.
5. A process according to claim 4 wherein the weakly-acidic salt is at least one alkali metal or alkaline earth metal carbonate, silicate, phosphate or carboxylate.
6. A process according to claim 4 or 5 wherein the alkaline etchant comprises the alkali metal hydroxide in a concentration of 60 to 85% by weight and the weakly-acidic salt in a concentration of 10

to 30% by weight.

7. A process according to any one of claims 4 to 6 wherein the alkaline etchant is used in the form of an aqueous solution which further comprises aluminium ions.
8. A conductive substrate for an electrophotographic photoreceptor, as defined in any one of claims 1 to 3.
9. A process for preparing a conductive substrate, said process being as defined in any one of claims 4 to 7.
10. Apparatus comprising a photoreceptor as defined in any one of claims 1 to 3.