United States Patent [19]

Hukase et al.

[11] **3,850,632**

[45] **Nov. 26, 1974**

[54] **ELECTROPHOTOGRAPHIC PHOTOSENSITIVE PLATE**

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[22] Filed: **July 26, 1972**

[21] Appl. No.: **275,212**

[30] **Foreign Application Priority Data**

July 26, 1971 Japan 46-55877

[52] **U.S. Cl.** **96/1.8,** 96/1.5, 117/218

[51] **Int. Cl.** **G03g 5/00,** G03g 5/02

[58] **Field of Search** 96/1.5, 1.8; 117/215, 218

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[57] **ABSTRACT**

Electrophotographic photosensitive plate of improved moisture fastness having on its photoconductive layer a protective coating comprising polyvinyl butyral and a cellulose derivative which provides the plate with protection from abrasion and deterioration in resolving power under either high or low humidity conditions.

6 Claims, No Drawings

ELECTROPHOTOGRAPHIC PHOTOSENSITIVE PLATE

This invention relates to an electrophotographic photosensitive plate, more particularly to an electrophotographic photosensitive plate having a novel protective coating.

In general, the conventional electrophotographic process is carried out in such a manner that a photosensitive plate, prepared by forming a photoconductive layer on an electroconductive support, is positively or negatively charged (according to the characteristics of the photosensitive plate) by means of corona discharge, and then exposed to electromagnetic waves, e.g. light or X-ray, to form a latent electrostatic image by utilization of the photoconductivity of the photosensitive plate. This latent image is developed with a toner which has been charged with a polarity opposite to that of said latent image, and, if the developed image is carried on the photosensitive layer (this means that the photosensitive layer serves as a recording layer as in the Electrofax process), this is fixed as is by application of heat or solvent vapors, while if the recording layer is used separately from the photosensitive layer (as in the Xerox system using a selenium photosensitive plate or the like), the developed toner image is transferred, according to the electrostatic image transfer process, to a recording layer, ordinarily on a separate paper, and is then fixed. After the fixing, the photosensitive plate is subjected to cleaning and is reused. Thus, a single photosensitive plate is subjected to a copying cycle comprising charging, imagewise exposure, toner development and fixing optionally with image transfer, repeatedly, as often as several thousand times.

The present invention is concerned with an improvement of the photosensitive plate to be used in the latter process.

Photosensitive plates used in the latter process are abraded or injured during cleaning, transfer, and the like mechanical operations. Such troubles become fatal drawbacks for the photosensitive plates. Particularly in xeroradiography, relatively many operations are effected manually, so that such troubles as mentioned above tend to take place.

Among photosensitive layers, the photoconductive selenium plate, which is the one most commonly used, is particularly susceptible to mechanical abrasion and injury because of its ductility. In order to protect the photoconductive layer from mechanical abrasion and injury, it has been well known to form a thin protective coating on said layer, as disclosed in, for example, Japanese Pat. Publication Nos. 15,446/63 and 20,697/63, and U.S. Pat. Nos. 2,860,048, 2,892,708, 2,901,348 and 3,092,493.

However, the protective coating should, of course, not deprive the photosensitive plate of its inherent characteristics, and should satisfy such conditions as mentioned below.

1. The coating should not react with the photoconductive substance used.
2. The coating should adhere well to the photoconductive layer.
3. In case the photoconductive layer is composed of selenium or its alloy, the heat treatment for forming the protective coating should not be effected over a long period of time when the heating temperature is above 40°C.

4. The coating should not have an electric conductivity in the horizontal direction so as not to degrade the photosensitive plate in contrast or resolving power.
5. The coating should not have a volume electric resistivity of more than $10^{15}\Omega$ cm, because in winter, when the air is dry, the photosensitive plate is deteriorated in resolving power due to high electric resistance.
6. The coating should be excellent in abrasion resistance.
7. The coating should have such a thickness as not to deteriorate the photosensitive plate in resolving power and abrasion resistance.
8. The coating should be excellent in moisture fastness.

However, the protective coatings disclosed in the aforesaid prior art literature are composed of polystyrene, polycarbonate, polyvinyl formal, polyvinyl acetal, cellulose acetate, etc. which heretofore have not been satisfactory. Although these known protective coatings are relatively satisfactory in abrasion resistance, they are low in moisture fastness and hence cannot be used throughout the year, including summer, when the temperature and humidity are high and winter when the temperature and humidity are low.

The present invention provides a novel protective coating which has overcome the drawbacks of the conventionally known protective coatings. That is, the present invention is concerned with an electrophotographic photosensitive plate prepared by using, as a support, a metal such as aluminum, zinc, brass or copper, or an electroconductive glass, forming, on said electroconductive support, a photoconductive layer composed of selenium, selenium-tellurium or the like selenium alloy, zinc oxide, lead oxide or cadmium sulfide, and further forming on said photoconductive layer a protective layer comprising a mixture of polyvinyl butyral and a cellulose derivative which is compatible with the polyvinyl butyral and which itself has a low volume resistivity.

Polyvinyl butyral having a butyralation degree within the range of 57 to 65 mole percent gives particularly favorable results. Representative examples of suitable cellulose derivatives include ethyl cellulose, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose acetobutyrate and cellulose nitrate. Satisfactory results are obtainable when the proportion of the above-mentioned cellulose derivative based on the amount of polyvinyl butyral is, for example, 20 to 50 percent by weight in the case of cellulose nitrate, 10 to 30 percent by weight in the case of cellulose diacetate, 20 to 28 percent by weight in the case of cellulose triacetate, and 10 to 30 percent by weight in the case of cellulose acetobutyrate. Thus, the proportion of the cellulose derivative used is not fixed but varies depending on the nature of the cellulose derivative employed.

In forming the protective layer according to the present invention, a mixture of the above-mentioned two components is dissolved in dioxane or the like organic solvent therefor and then coated on the photoconductive layer of the photosensitive plate. When it is desired to form the protective layer by a dipping method, the said mixture may be dissolved in a proportion of 3 to 4 g. per 100 cc. of the solvent.

If the protective coating is made thicker, the photosensitive plate is deteriorated in resolving power and

increased in residual potential. When the thickness of the protective coating is about 1 μ, the photosensitive plate shows a resolving power of about 8 lines per mm. and is satisfactory in intensity, abrasion resistance and resolving power.

When a protective layer-forming solution identical in composition with that used in the dipping method is coated by means of a whirler, innumerable radial wrinkles are formed on the resulting protective layer. If, in this case, more than 3 percent by weight of ethyl cellulose is incorporated into said solution, the resulting protective layer will be free of radial wrinkles and will provide a uniform surface. However, when the content of ethyl cellulose is excessively high, undesirable results are brought about under conditions of low humidity. Ordinarily, therefore, an ethyl cellulose content of about 3 to 8 percent by weight is preferred.

The photosensitive plate of the present invention not only has a high resolving power under high humidity conditions but also is greatly improved in image characteristics even under low humidity conditions, and thus is high in resolving power and excellent in resistance to abrasion and injury. For example, the photosensitive plate of the present invention is 3 to 4 times higher in abrasion resistance than a photosensitive plate having a protective coating composed of only the cellulose derivative. Furthermore, a photosensitive plate having a protective coating composed of only the cellulose derivative is deteriorated in resolving power under high humidity conditions, whereas the photosensitive plate of the present invention shows a high resolving power at a humidity within the range of from 30 to 90 percent. For obtaining a good image, a resolving power of at least 8 to 10 lines per mm. is necessary.

Photosensitive selenium plates having protective layers, wherein polyvinyl butyral and typical cellulose derivatives were singly used, were tested in resolving power under various humidity conditions. The results obtained were as set forth in Table 1, in which the values of resolving power are represented by lines per mm.

Table 1

Type of protective coating on selenium			Resolving Power at the given humidity				
			38%	57%	68%	81%	90%
Not-protected			12.5	12.5	10–12.5	10–12.5	10
	(Butyralation degree, mole%)	(Residual acetyl content, mole%)					
Polyvinyl butyral	57 ± 3	Less than 3	5.0	8–10	8–10	8–10	8.0
do.	62 ± 3	do.	4.0–5.0	8–10	8–10	8–10	8.0
do.	More than 67	4–6	4.0	8.0	6.3	6.3	5.0
Cellulose diacetate			6.0	4.0	2.0	0	0
Cellulose nitrate			10.0	8–10	2.0	0	0

As is clear from Table 1, polyvinyl butyrals having a butyralation degree within the range of from 57 to 65 mole percent give favorable results, and those having a butyralation degree of more than 67 mole percent give somewhat inferior results.

For preventing the degradation in resolving power under low humidity conditions, it might be thought that the addition of an ionic surface active agent would be useful. This, however, is not practical because adsorption of water and absorption of moisture would be increased under high humidity conditions.

As will be understood from Table 1, the present invention provides a protective layer which can be rendered free of the drawbacks of conventionally known protective layers. It is very surprising that the drawbacks encountered when a polyvinyl butyral or a cellulose derivative is used alone by itself can be removed by the joint use of these two.

The present invention is illustrated in further detail below with reference to the following representative, non-limiting examples.

Example 1

3 grams of a mixture constituting a protective coating composition comprising 70 percent by weight of polyvinyl butyral (Eslec BM-2 produced by Sekisui Chemical Co.) and 30 percent by weight of cellulose nitrate (FQ produced by Daicel Co.) was dissolved in 100 cc. of dioxane. The resulting solution was coated in accordance with a conventional dipping method on a photosensitive selenium plate to a thickness of about 1 μ, whereby the photosensitive plate showed an excellent abrasion resistance and a high resolving power of 8 to 10 lines per mm. at a humidity within the range from 30 to 90 percent.

Example 2

3 grams of a mixture comprising 75 percent by weight of polyvinyl butyral (Eslec BM-2 produced by Sekisui Chemical Co.) and 25 percent by weight of cellulose diacetate (L-AC produced by Daicel Co.) was dissolved in 100 cc. of dioxane. The resulting solution was coated in accordance with a conventional dipping method on a photosensitive selenium plate to a thickness of about 1 μ, whereby the photosensitive plate showed the same characteristics as in Example 1.

Example 3

4 grams of a mixture comprising 75 percent by weight of polyvinyl butyral (Eslec BM-2 produced by Sekisui Chemical Co.) and 25 percent by weight of cellulose diacetate (L-AC produced by Daicel Co.) was dissolved in 100 cc. of dioxane. Into the resulting solution was incorporated 3 percent by weight, based on the weight of the mixture, of ethyl cellulose (Etcel produced by Dow Chemical Co.), and said resulting solution was then coated, by means of a whirler, on to the photosensitive selenium plate to a thickness of about 1

μ, whereby the photosensitive plate showed the same characteristics as in Example 1.

Example 4

3 grams of a resin mixture comprising 80 percent by weight of polyvinyl butyral (Eslec BM-2 produced by Sekisui Chemical Co.) and 20 percent by weight of cellulose acetobutyrate (Kodapak II produced by Eastman Kodak Co.) was dissolved in 100 cc. of dioxane. The resulting solution was coated in accordance with a conventional dipping method on a photosensitive selenium plate to a thickness of about 1 μ, whereby the photosensitive plate showed the same characteristics as in Example 1.

Example 5

3 grams of a resin mixture comprising 65 percent by weight of polyvinyl butyral (Eslec BM-2 produced by Sekisui Chemical Co.) and 35 percent by weight of cellulose nitrate (FQ produced by Daicel Co.) and 5 percent by weight, based on the weight of said resin mixture, of ethyl cellulose (Etcel produced by Dow Chemical Co.) were dissolved in 100 cc. of dioxane. The resulting solution was coated by means of a whirler onto a photosensitive selenium plate to a thickness of about 1 μ, whereby the photosensitive plate showed the same characteristics as in Example 1.

Example 6

3 grams of a resin mixture comprising 65 percent by weight of polyvinyl butyral (Eslec BM-2 produced by Sekisui Chemical Co.) and 35 percent by weight of cellulose nitrate (FQ produced by Daicel Co.) was dissolved in 100 cc. of dioxane. The resulting solution was coated onto a 40 μ thick photosensitive CdS plate to a thickness of about 0.5 μ, whereby the photosensitive plate showed the same characteristics as in Example 1.

What we claim is:

1. An electrophotographic photosensitive plate, comprising an electroconductive layer, a photoconductive layer thereon, and a protective polymer coating layer on the opposite surface of said photoconductive layer, said protective coating having a thickness not greater than one micron and comprising polyvinyl butyral having a butyralation degree of 57 to 65 mole percent and a cellulose derivative selected from the group consisting of cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose acetobutyrate, and cellulose nitrate, said polyvinyl butyral being present in said coating in an amount varying from 50 to 90 percent by weight, and said cellulose derivative being present in said coating in an amount ranging from 10 to 50 percent, by weight, said protective polymer coating layer having a volume resistivity no greater than 10^{15} ohm-cm.

2. An electrophotographic photosensitive plate as claimed in claim **1**, wherein the protective polymer coating layer is composed of 50 to 80 percent by weight of polyvinyl butyral and 20 to 50 percent by weight of cellulose nitrate.

3. An electrophotographic photosensitive plate as claimed in claim **1**, wherein the protective polymer coating layer is composed of 70 to 90 percent by weight of polyvinyl butyral and 10 to 30 percent by weight of cellulose diacetate.

4. An electrophotographic photosensitive plate as claimed in claim **1**, wherein the protective polymer coating layer is composed of 72 to 80 percent by weight of polvinyl butyral and 20 to 28 percent by weight of cellulose triacetate.

5. An electrophotographic photosensitive plate which comprises, on a support of an inorganic material selected from the group consisting of aluminum, zinc, brass, copper, and electroconductive glass, a photoconductive layer made of a substance selected from the group consisting of selenium, selenium-tellurium, zinc oxide, lead oxide and cadmium sulfide and a protective polymer coating layer coated on the opposite surface of said photoconductive layer, said protective coating having a thickness not greater than one micron and comprising a polyvinyl butyral having a butyralation degree of 57 to 65 mole percent and a cellulose derivative compatible with said polyvinyl butyral, said polyvinyl butyral being present in said coating in an amount varying from 50 to 90 percent, by weight, and said cellulose derivative being present in said coating in an amount ranging from 10 to 50 percent, by weight, said protective polymer coating layer having a volume resistivity no greater than 10^{15} ohm - cm.

6. An electrophtographic photosensitive plate, as claimed in claim **1** wherein said protective polymer coating layer also contains 3 to 8 percent of ethyl cellulose.

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