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[54] **REMOVAL OF PROTECTIVE RESIN LAYER BY LIQUID DEVELOPER IN ELECTROPHOTOGRAPHIC IMAGING**

[75] Inventor: **Satoru Honjo**, Asaki-shi, Saitama, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.**, Kanagawa, Japan

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[51] **Int. Cl.** **G03g 13/22**

[58] **Field of Search** ...117/37 LY; 96/1 R, 1 LY, 1.4; 252/62.1

[56] **References Cited**

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Primary Examiner—John C. Cooper, III
Attorney—Addams & Ferguson

[57] **ABSTRACT**

Such susceptibility is reduced REMOVAL OF PROTECTIVE RESIN LAYER BY LIQUID DEVELOPER IN ELECTROPHOTOGRAPHIC IMAGING forming overlying the photoconductive coating a protective top coating which can be removed by dissolving away into an insulating liquid prior to or during liquid development. An electrophotographic process wherein an electrostatic latent image is formed on an electrophotographic member, the member comprising a flexible support bearing thereon a photoconductive insulative layer insoluble or only sparingly soluble in a non-polar, electrically insulating liquid. Disposed on the photoconductive insulative layer is an insulative protective layer consisting mainly of a non-polar resin. The protective layer may be dissolved with the non-polar electrically insulating liquid either prior to or during the development of the latent image with the non-polar electrically insulating liquid. If the protective layer is dissolved during the development step, the carrier liquid of the liquid developer is the non-polar, electrically insulating liquid.

An electrophotographic coating is generally susceptible to mechanical damage in the course of manufacture storage and processing.

Such susceptibility is reduced by forming overlying the photoconductive coating a protective top coating which can be removed by dissolving away into an insulating liquid prior to or during liquid development.

6 Claims, No Drawings

REMOVAL OF PROTECTIVE RESIN LAYER BY LIQUID DEVELOPER IN ELECTROPHOTOGRAPHIC IMAGING

This invention relates to an electrophotographic process, more particularly to an electrophotographic process employing liquid development.

The electrophotographic sensitive material to which the present invention is directed is produced by coating a flexible base with a photoconductive insulative layer made of a mixture comprising a resinous binder and a photoconductive substance. While the flexibility of base offers many advantages, and this sensitive materials of such type are now used abundantly in copying documents, flexible sensitive materials are defective in that the surface is highly susceptible to mechanical damage because of extremely high volume content of photoconductive substance in the sensitive layer.

Such damages do not throw any serious obstacle in the way of using these materials for document copying. However, when photographic continuous tone images are to be produced on electrophotographic paper, this damage poses a very serious problem. When such sensitive papers are so handled in the course of production or storage as to suffer the sensitive layers thereof to be rubbed against or brought into contact with other articles, pressure and other external forces may cause areas of such sensitive layers to sustain physical damage or undergo deterioration of properties. On exposure to corona discharge, for example, such affected areas may acquire lower initial potential than in other areas or, on exposure to light, the potential in these areas may be attenuated by light at an accelerated or a retarded rate than in unaffected areas.

When the sensitive paper having such defects is subjected to liquid development which can accomplish toner deposition accurately in accordance with the charge distribution of a latent electrostatic image, such areas appear conspicuous as mottles or scars in the continuous tone image.

The object of the present invention, therefore, is to provide an electrophotographic process which makes such shortcomings difficult to occur.

This invention relates to an electrophotographic process characterized by forming an electrostatic latent image on an electrophotographic light sensitive material obtained by providing a photoconductive insulative layer on a flexible base and further forming thereon an insulative protective layer consisting mainly of resin and dissolving said protective layer prior to or during the step of developing operation using a liquid developer which is prepared by having electrically charged particles dispersed in an insulating liquid.

Since the aforementioned insulative protective layer is intended to provide mechanical protection for the sensitive layer, it is formed on the sensitive layer subsequently to or, where a special coating method is used, simultaneously with the formation of the sensitive layer on the base. For practical purpose, the thickness of this layer should be above 0.2μ but should not exceed 5μ. Resins for use in this layer have only to satisfy the requirement that they should be soluble in a carrier liquid used for the liquid developer or in an insulative prebath which is applied to the sensitive material prior to the step of liquid development and that they should own a suitable degree of electric insulation. Practical examples are styrene-modified alkyd resin, non-drying oil-modified alkyd resin, long oil type epoxyester resin, polybutylmethacrylete, homopolymer of alkyl ester of acrylic acid or methacrylic acid containing more than 5 carbon atoms in its alkyl group and copolymer mainly consisting of said ester styrene-butylmetyacrylate copolymer, styrene-butadiene copolymer, silicone resins and compatible combinations thereof. Since treating baths are generally made mainly of liquids which are nonpolar and have low dissolving power, the resins to be used in the protective layer are naturally limited to those of nonpolar type.

Although all the conventionally known photoconductive insulative layers (sensitive layers) can be used for this invention they are required to be insoluble in the treating bath to be used for dissolving the protective layer. Therefore, the binding agent to be used in the sensitive layer must be of the type which has so strong polarity or which is so cured as to be sparingly soluble in the treating bath.

Examples of the binder for use in the sensitive layer are alkyd resins cured with isocyanate compounds, epoxyester resin, vinyl chloride-vinyl acetate copolymer, polyvinyl acetate and ethyl acrylate methyl methacrylate copolymer. For the purpose of this invention, it is unacceptable to use formulations which permit a hardening catalyst or a hardening agent to diffuse into the protective layer after the step of coating and also cure the protective layer.

Generally, successful over-coating of a protective layer can be accomplished without affecting the sensitive layer by a resin solution for the protective layer by use of a solvent having the composition similar to that of a bath which is later used for dissolving the protective layer.

The process of this invention can be modified in numerous ways, including those given below.

a. The sensitive layer with the protective layer coated thereon is subjected to corona charging and image exposure. Then the sensitive material is placed in a prebath capable of dissolving the protective layer immediately before the developing procedure. The electrostatic charge given by corona charging is considered to have penetrated through the thin thickness of the protective layer and reached the upper surface of the photoconductive layer, for a satisfactory image is obtained by subjecting the latent image to ordinary liquid development method after such treatment.

b. Prior to electrostatic charging, the protective layer is dissolved with an insulative treating bath and the sensitive material which is still wet to image exposure and then development.

It has been confirmed that an image of extremely high quality can be obtained so far as the treating bath has sufficiently high electric insulation.

c. The sensitive material is electrically charged by an ordinary method and then it is subjected to image development with a liquid developer which comprises electrically charged particles in a carrier liquid capable of dissolving the protective layer.

In this case, the resin which forms the protective layer dissolves into the carrier liquid. Consequently, the electrophoretic characteristics are affected gradually by the dissolved resin and the viscosity of the developer increases in particular.

This modified process can be exercised within the range in which the viscosity of the liquid is tolerable for the treatment.

When any of the aforementioned processes is employed, the presence of the protective layer serves to reduce markedly the chance of the sensitive layer being directly damaged by external forces. Thus, the possibility of the finally produced image suffering from defects can be reduced to a great extent.

As a supplemental explanation from the processes, a) and b), the resin which is one component of the protective layer gradually undergoes dissolution and is contaminated into the bath used for dissolving it. Consequently, the viscosity of the bath increases and electric insulation will be affected. If the bath has its electric resistance degraded excessively, the latent image is destroyed or attenuated rapidly in the case of a) or a sufficiently high potential cannot be achieved in the subsequent charging. Therefore, the resin for use in the protective layer must be of such type that, when dissolved in the bath, it will not lower the resistivity of the treating bath. Among alkyd resins, those of long oil length are preferable in this sense. Since a small portion of the resin for the protective layer contaminates via the dissolving bath into the liquid developer the resin is desired to exert no adverse affect upon the developing agent.

The resins cited preciously all satisfy these requirements.

It may be clear from the spirit of the present invention that this invention can also be applied to any electrophotographic processes utilizing electrostatic latent images other than Carlson Process, such as Kalman process, processes based on photovoltaic effect and Thermo-xerographic Process.

Now, the present invention is desribed in more detail by referring to preferred embodiments.

EXAMPLE 1

With a suitable quantity of butyl acetate, 100 parts of photoconductive zinc oxide, 20 parts of styrene-modified aklyd resin varnish (nonvolatile content 50 percent) and 14 parts of polyisocyanate compound (nonvolatile content 75 percent) were mixed. The mixture was spread to a dry thickness of 7 μ on an art paper which had been treated to possess a suitable electroconductivity. This sensitive material was allowed to stand overnight in a thermostated drying vessel kept at 50°C. Then the material had its surface coated with toluene solution of polybutyl methacrylate to form a protective layer. The coated amount was 1.2 g/m^2 on dry base.

The sensitive paper thus prepared was subjected to dark adaptation. One sheet of this sensitive paper was negatively charged and exposed to light from an optically positive image and immersed in a liquid developer comprising black toner particles of positive polarity dispersed in kerosene as carrier liquid. As a result, polybutyl methacrylate on the surface was dissolved into the liquid developing agent to give rise to a clear positive image.

Another sheet of the same paper was treated in the following sequence. The sensitive paper was first submerged in cyclohexane so as to allow polybutyl methacrylate layer to be removed by dissolution. This treatment could be accomplished by manual operation or by using an automatic device provided with means to direct a strong flow of liquid against the surface of the sensitive paper and to squeeze the liquid.

After removal of the polybutyl methacrylate layer, excessive liquid was removed by means of squeeze. Then the sensitive paper was electrically charged through exposure to negative corona, exposed to light from an image in the same manner as before and subjected to development. Again a clear image was obtained.

EXAMPLE 2

With toluene, 100 parts of photoconductive zinc oxide, 40 parts of varnish made from epoxyester of dehydrated castor oil fatty acid (nonvolatile component 50 percent) and 0.1 part of cobalt naphthenate were blended. The mixture was spread to a dry thickness of 10 μ on a sheet of bond paper which had been with an electroconductive polymer. The sheet of paper thus obtained was allowed to harden in a thermostat kept at 40° C. for 15 hours.

On the surface thereof, Pliolite S–7 (styrene-butadiene copolymer made by Goodyear Tire & Rubber Co. in the U.S.) was spread in different coating weights; the coating weights are shown in the following table. Prior to electrostatic charging, the sensitive paper was wetted on its surface with kerosene to swell the surface layer. It was immediately charged electrically through the exposure to negative corona. After the subsequent image exposure the paper was subjected to development in a liquid developer using kerosene as the carrier liquid. Better results were obtained on areas coated with Pliolite of smaller film thicknesses. In the area of the greatest film thickness of Pliolite, the saturated density was low and the edge effect was observed in the reproduction of images of continuous tone, the sensitive paper was wetted on the surface with kerosene, thereafter charged negatively and then subjected to surface potential measurement. The results are given in Table 1.

In this example, it has been found that excessive thickness of the surface layer is rather harmful and that satisfactory results are obtained with the protective coating thinner than 1 μ.

Table 1

No.	Thickness of surface layer	Initial potential	Residual potential ratio after one minute dark decay
1	0.6μ	260 V	75%
2	0.8μ	220 V	70%
3	1.5μ	110 V	42%

EXAMPLE 3

The procedure of Example 2 was followed, except Pliolite S–7 was substituted by polybutyl methacrylate. In this case, there was obtained on image of high density free from the edge effect even with the sensitive paper using a protective layer as thick as 1.5 μ.

The same test was conducted as in Example 2. Consequently, it was found that increase in the surface layer thickness did not result in any appreciable change in properties. (Table 2).

Table 2

No.	Thickness of surface layer	Initial potential	Residual potential ratio after one minute dark decay
4	0.6 μ	280 V	86%
5	0.8 μ	310 V	83%
6	1.5 μ	320 V	81%

EXAMPLE 4

The procedure of Example 1 was followed, except the component of the protective layer was substituted by a styrene-modified alkyd resin. Consequently, there were obtained satisfactory results similar to those of in Example 1.

What is claimed is:

1. An electrophotographic process which comprises forming an electrostatic latent image on an electrophotographic sensitive member comprising a flexible support bearing thereon a photoconductive insulating layer insoluble or only sparingly soluble in a non-polar treatment bath and further thereon an insulative protective layer consisting mainly of a non-polar resin, and dissolving said protective layer with said treatment bath; and developing said latent image with a liquid developer which comprises an electrically insulating carrier liquid and an electrically charged toner dispersed in said carrier liquid.

2. An electrophotographic process as claimed in claim 1, wherein said insulative protective layer consisting mainly of styrene-modified alkyd resin, non-drying oil-modified alkyd resin, long oil type epoxyester resin, polybutyl methacrylate, homopolymers of alkyl

ester of acrylic acid or methacrylic acid containing more than 5 carbon atoms in its alkyl group and copolymer mainly consisting of said ester, styrene-butylmethacrylate copolymer, styrene-butadiene copolymer or silicone resin.

3. An electrophotographic process as claimed in claim 1 wherein said insulative protective layer is 0.2 – 5 μ in thickness.

4. An electrophotographic process which comprises forming an electrostatic latent image on an electrophotographic sensitive member comprising a flexible support bearing thereon a photoconductive insulative layer insoluble or only sparingly soluble in a non-polar, electrically insulating carrier liquid and further thereon an insulative protective layer consisting mainly of a non-polar resin, and dissolving said protective layer during the step of development of said latent image with a liquid developer which comprises said non-polar, electrically insulating carrier liquid and an electrically charged toner dispersed in said carrier liquid.

5. An electrophotographic process as claimed in claim 4, wherein said insulative protective layer is selected from the group consisting mainly of styrene-modified alkyd resin, non-drying oil-modified alkyd resin, long oil type epoxyester resin, polybutyl methacrylate, homopolymers of alkyl ester of acrylic acid or methacrylic acid containing more than 5 carbon atoms in its alkyl group and copolymer mainly consisting of said ester, styrene-butylmethacrylate copolymer, styrene-butadiene copolymer and silicone resin.

6. An electrophotographic process as claimed in claim 4 wherein said insulative protective layer is 0.2 – 5 μ in thickness.

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