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METHOD OF ELECTROPHOTOGRAPHIC IMAGING EMPLOYING PHENAZINE AS THE SENSITIZER FOR THE PHOTOCONDUCTIVE MATERIAL

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ABSTRACT OF THE DISCLOSURE

A photosensitive electrophotographic material and photographic reproduction process using the same comprising an organic plastic material and a small amount of phenazine. The plastic may be one having inherent photoconductive properties in which case the properties are greatly enhanced or the phenazine can render plastics photoconductive which lack such inherent properties.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 491,833 filed Sept. 30, 1965 now abandoned.

SUMMARY OF THE INVENTION

This invention relates to photographic reproduction and more particularly relates to electrophotographic materials in which an electrostatic latent image is produced by utilizing the property of photoconduction wherein the conductivity of a layer of an organic material varies with the intensity of illumination.

There are two general processes of forming such electrostatic latent images; in one a transparent or translucent plastic having photoconductive properties per se is employed, and in the other a binder has an inorganic photosensitive compound such as zinc oxide dispersed therein. The present invention relates to the former category and more particularly relates to the employment of a novel sensitizer in an organic plastic material as the photoconductive substance.

In employing such photoconductive materials, the layer is first charged electrostatically in the dark such as with a corona discharge device and is then exposed to light under a master. This produces an electrostatic latent image which can then be developed by means of an electroscopic powder, such as a synthetic resin powder, whereupon the image becomes visible. Alternatively, the charged pattern can be offset onto an electrostatic paper and the offset image similarly developed by means of a resin toner. In either case, the image can be rendered permanent by heating the resin to soften it and make it adhere to the substrate. Although an electrostatic powder is normally used for this purpose, the developer can also be an electrostatic resin dispersed in a suitable inert liquid carrier.

The light sensitivity of the photoconductive layers heretofore known usually lies in the long-wave ultraviolet region of 3000 to 4000 A.U. Various sensitizers such as dyestuffs have been added to such conductive layers in an effort to make them sensitive to the visible portion of the spectrum and permit shorter exposure times. Since such dyestuffs are colored substances, a careful balance of the sensitizers has to be formulated in order to provide a neutral color.

In accordance with the present invention, it has been found that phenazine forms an effective sensitizer, which

permits short exposures and which add substantially no color to the photosensitive layer. Further, phenazine sensitizes the photoconductive layer in the visible portion of the spectrum so that it is no longer necessary to employ ultraviolet light; ordinary tungsten lamps may be employed in making the exposures.

The sensitizer of the present invention works in two different ways. In the first place, if one starts with an organic plastic material, such as a poly-N-carbazole, which has inherent photoconductive properties, these properties are greatly enhanced. Further the area of sensitivity is shifted so that such a plastic, which is normally most sensitive in the ultraviolet region, now becomes highly sensitive in the visible spectrum. In the second place, phenazine is capable of rendering plastics photoconductive having no inherent photoconductive properties. Thus, plastics such as the styrene, acrylic and vinyl families, which have no inherent photoconductive properties, can be rendered photoconductive by the employment of phenazine.

The sensitizers heretofore used have ordinarily been employed in relatively large quantities but phenazine need only be employed in extremely small quantities i.e. from about 0.1 to about 5% based on the plastic substrate in the preferred case of enhancing the photoconductive properties of materials having such inherent properties and up to 10 or 15% in the case of plastics having no such inherent properties.

Although sensitizers have been employed in the past wherein a complex dye which incorporates a phenazine nucleus is employed, these compounds essentially work as dyes and phenazine itself has not heretofore been known to impart photosensitivity. Phenazine is superior in effectiveness, stability and low cost to these previously used complex compounds. Even more important is the part that a white material is obtained since phenazine has little color and does not impart any color to the plastic in the minute quantities ordinarily employed.

In its preferred embodiment, the present invention contemplates employment of a poly-N-carbazole as a photoconductive substance which has been sensitized by addition of a small amount of phenazine. The poly-N-carbazole or other sensitive plastic can be either in the form of a self-supporting film or can be in the form of a thin coating on a suitable support material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following non-limiting examples illustrate preferred embodiments of the present invention:

Example 1

Ten g. of N-vinyl carbazole recrystallized twice from methanol was dissolved in 200 g. of toluene and poured in a vessel. To this solution 0.7 g. of n-butyl acrylate, .001 HQ inhibitor (Celanese Chemicals), and 1 cc. of a 10% solution of di-t-butyl peroxide in toluene was added.

Argon was passed in the solution for 15 minutes, the vessel closed and immersed in liquid nitrogen. When the solution was solidified the vessel was opened under vacuum and evacuated for 15 minutes. The vessel was closed again, the solution liquified at room temperature, frozen, evacuated and brought to room temperature again. The vessel was next immersed in a thermostatically controlled oil bath and the temperature was raised to 140° and lowered to room temperature over a period of hours.

The resulting solution was poured in 1500 cc. of methanol, filtered on a Buechner funnel and dried on the filter. The white polymer was dissolved in toluene and 5% of HB 40 (a high boiling oily hydrocarbon plasticizer) added. A film of .0001"–.0005" thickness was coated on

aluminum tickets and electrostatically charged in the dark with a 9000 kv. corona discharge device and this sensitized layer exposed to light under a master. Subsequently the image was developed with a toner.

The sensitivity of such a layer was measured with an exposure of 30 seconds to a 40 watt tungsten lamp at 30 cm. With the addition of 1% of bromophenol blue to the photoconductive insulating layer an exposure time of 5 seconds was obtained.

The same result was obtained when rhodamine B was substituted for the bromophenol blue. With the addition of 1% phenazine an exposure time of one second was obtained. When the same photoconductive insulating layer was contacted with an electrofax paper on which a latent image was formed and, next dusted with a toner, a very good image was obtained.

Example 2

Ten g. of N-vinyl carbazole recrystallized twice from methanol was mixed with acrylonitrile 2 g. and n-butyl acrylate 7 g. in 200 cc. of toluene, 2 cc. of 10% solution of di-t-butyl peroxide was added and the solution poured in a vessel, purified with argon and subjected at the freezing-vacuum cycle as in Example 1.

The vessel was next immersed in a thermostatically controlled oil bath and raised to 130° C. and lowered to room temperature over a period of hours. One hundred cc. of the solvent was stripped off in vacuum and substituted with 50 cc. of N,N′ dimethylformamide and 50 cc. of tetrahydrofuran (THF). The solution was poured in 1500 cc. of methanol, filtered on a Buechner funnel and dried on the filter. The white polymer was dissolved in 50 cc. toluene, 50 cc. THF and 50 cc. N,N′ dimethylformamide, 5% HB 40 plasticizers added and films of 0.0001–0.005 thickness cast by evaporation of the solvents on aluminum tickets. Next the samples were electrostatically charged in the dark with a 9000 kv. corona discharge device and the sensitized layers exposed to light under a master.

Subsequently the image was developed with a toner. The sensitivity of such a layer was measured with an exposure of 30 seconds to a 40 watt tungsten lamp at 30 cm. With the subsequent addition of

	Percent
Bromophenol blue	1
Rose rengala	1
Eosine Y (acid red 87)	1

to the photoconductive insulating layer, exposure times of 3–5 seconds were obtained. With the addition of 1% phenazine an exposure time of one second was sufficient to obtain, when developed with a toner, a very good reproduction of the master picture. When the same photoconductive insulating layer was contacted with an electrofax paper on which a latent image was formed, and next dusted with a toner a very good image was obtained.

Example 3

Twenty grams of polyvinyl carbazole obtained by bulk polymerization of n-vinyl carbazole was dissolved in 150 g. of toluene, 60 g. of tetrahydrofuran and 20 g. methyl ethyl ketone. Twenty grams of this solution was cast as a film on an aluminum ticket. The sample was charged in the dark with a 12 kv. corona discharge device and the sensitized layer exposed to light under a master.

The sensitivity of such a layer was measured with an exposure time of three minutes to a 40 watt tungsten lamp at 30 cm. When 0.01 g. of phenazine was added to the aforementioned solution (20 g.) an exposure time of 15 seconds was required to obtain the same quality picture. With the addition of 0.03 g. of phenazine to the same solution, an exposure time of 5 seconds was required.

Example 4

Eleven grams of polyvinyl carbazole, supplied by the Borden Chemical Company, Philadelphia, Pa., lot No. 700–18–2, was dissolved in 230 g. of benzene. Twenty gram portions of this solution were taken and each portion mixed with the number of grams of phenazine indicated in Table 1. Exposure times as indicated in the table were obtained. (Twenty grams of the solution corresponds to 0.914 g. of polyvinyl carbazole.)

TABLE 1

Phenazine, grams	Exposure time, sec.
0.01	30
0.02	7
0.03	3
0.04	1.5
0.045	1
0.050	1
0.06	1
0.07	1
0.08	2
0.09	1.5

Example 5

Ten grams of the same polyvinyl carbazole of Example 4 was dissolved in 175 cc. of benzene and 0.05 of phenazine added. With this solution an aluminized Mylar (polyethylene terephthalate) tape was coated so that the thickness of the dry film was 0.00015–0.0002 inch thick. The sample was charged with a 12 kv. corona discharge device and exposed to light under a master in the same manner as the preceding examples. An exposure time of 1 second provided a high resolution picture developed with liquid toner.

Example 6

Ten grams of resin PS–2 (a styrene polymer resin), marketed by the Dow Chemical Company, Midland, Mich., was dissolved in the following mixture of solvents:

	Percent
Xylene	42.5
Toluene	7.5
Methyl ethyl ketone	10.0
Methyl n-propyl ketone	10.0
Isopropyl alcohol	15.0
n-Butyl alcohol	15.0

and to this solution 0.35 g. of phenazine was added. A film of this solution was cast on an aluminum slide and the sample was charged in the dark with a 12 kv. corona discharge device and the sensitized layer exposed under a master to the light of a lamp marketed by General Electric as DWA type (650 w., 120 v. home movie lamp) at a distance of 30 cm. An exposure time of 8 seconds was sufficient to obtain a picture.

Example 7

Five grams of an acrylic resin marketed by E. I. du Pont de Nemours and Company as Lucite 2045 was dissolved in 30 cc. of acetone, 10 cc. of toluene and 10 cc. butyl acetate. To this solution 0.45 g. of phenazine was added and a film cast on an aluminum ticket. The sample was processed as in Example 6 and an exposure time of 10 seconds was obtained.

Example 8

About 0.10 gram of phenazine was added to 10.03 g. of a solution of 9% solids of polyvinyl toluene in the solvents of Example 6, and the film was cast on aluminum slides. The sample was processed as in Example 6 and an exposure time of 5 seconds was obtained.

Note: For exposure time is understood the time necessary to obtain on the developed pictures a resolution of 0.0010 inch/line. The compositions indicated in the Examples 1, 2, 3, and 4, are also sensitive to long wave ultraviolet (3000–4000 A.U.) as well as visible light.

I claim:

1. In a photographic reproduction process which comprises exposing an electrostatically charged photoconduc-

tive layer to a light image, whereby the light struck area is discharged and developing the resulting image with an electroscopic material, the improvement comprising employing poly-n-vinyl carbazole contained from 0.1 to 5% phenazine sensitizer as the photoconductive layer.

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