United States Patent

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[15] 3,637,433

[45] Jan. 25, 1972

[54] **PROCESS FOR IMPROVING PHOTOCONDUCTIVE ELEMENTS**

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[22] Filed: **Aug. 21, 1969**

[21] Appl. No.: **852,018**

[52] **U.S. Cl.** **117/201,** 117/34, 117/62, 96/1.5, 96/1.8

[51] **Int. Cl.** **B44d 1/18**

[58] **Field of Search** 117/201, 34, 62; 96/1.5

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

The surface properties of a solvent coated photoconductive element comprising a heat softenable photoconductive insulating layer on an electrically conductive substrate are improved by quickly heating the photoconductive insulating layer above its softening point such as by placing the element in contact with a heated member for a short period of time.

10 Claims, 2 Drawing Figures

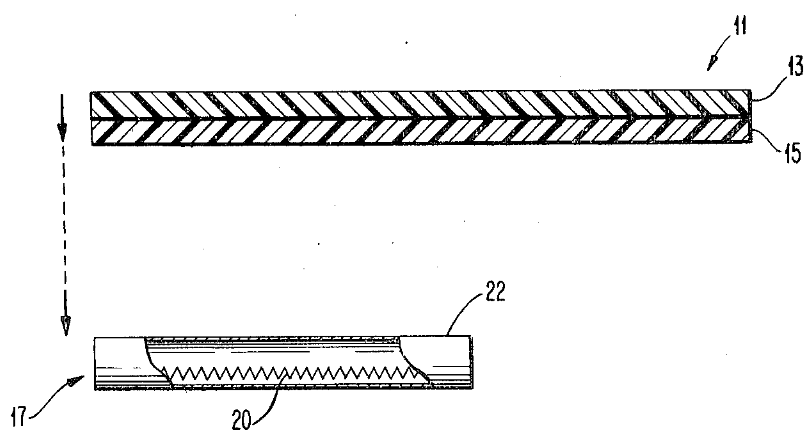

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FIG. 1

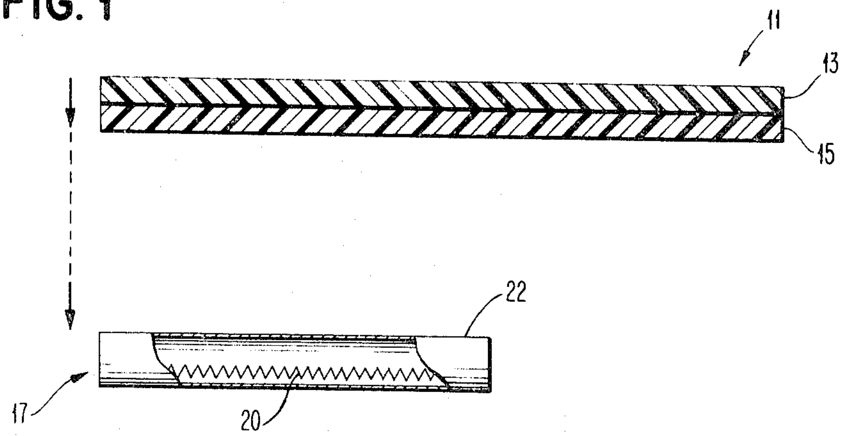
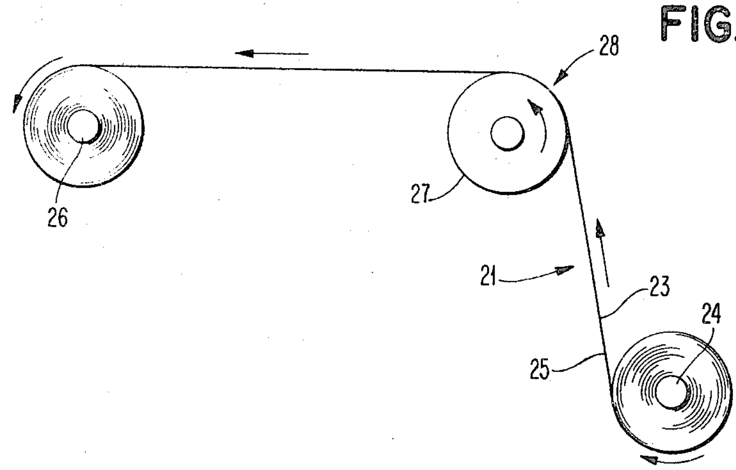


FIG. 2



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PROCESS FOR IMPROVING PHOTOCONDUCTIVE ELEMENTS

BACKGROUND OF THE INVENTION

This invention relates to electrophotography and particularly to the preparation of electrophotographic elements.

Electrophotography utilizes the change in conductivity of photoconductive materials upon exposure to light. A charge is placed on the surface of a photoconductive insulating layer and the surface is exposed imagewise to light. The light discharges the surface areas which are struck by light with the charge usually being removed through an electrically conductive backing layer which may also serve as a support for the photoconductive insulating layer. The areas which are not illuminated retain the charge and are developed, for example, by charged marking particles which are attracted to the image areas.

The quality of the developed image depends upon a number of factors. One factor is the uniformity of the photoconductive insulating layer. Impurities in the layer can cause uneven charging of the layer and minute discontinuities in the layer can cause a shorting out of the charge to the conductive layer. The result is an imperfect electrical image and when the image is developed, parts of the image are missing and parts of the background areas which should remain blank are developed.

The nonuniformity of the surface of the photoconductive layer has been found to be a problem particularly with layers prepared by solvent coating techniques. Even when precise coating techniques are employed, discontinuities in the layer may occur. Another problem is the presence of traces of solvent which are difficult to remove by heating at times and temperatures at which the layer is stable. The residual solvent effects can be present either on the surface (blushing) and/or within the bulk of the film (solvent pockets) these effects cause nonuniform charging characteristics to the extent that unwanted development occurs around the areas of solvent concentration.

BRIEF DESCRIPTION OF THE INVENTION

A method has now been found for improving the structure of photoconductive insulating layers and removing residual solvent.

In accordance with this invention, the properties of a photoconductive insulating layer are improved by heating the layer for a short time at a temperature above the softening point of the layer.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic elevational side view with parts broken away of a system or apparatus for carrying out the process of the invention with the dimensions somewhat exaggerated for the purpose of illustration.

FIG. 2 is a schematic elevational side view of a system or apparatus for carrying out another embodiment of the process of the invention.

DETAILED DESCRIPTION

Suitable photoconductive materials for use in photoconductive insulating layers include, for example, both inorganic and organic compounds and various combinations thereof. Representative compounds include, for example, selenium; cadmium sulfide, zinc sulfide; cadmium selenide; zinc oxide; anthracene, benzidine, oxazoles, triazines, pyrazolines, azomethines, anthraquinone, and polymers such as polyindene, polyacenaphthene polyvinylquinoline and polymers of n-vinyl carbazole and its lower alkyl and halogen derivatives. Mixtures of photoconductive compounds and polymers can be used. Electron acceptors to increase the sensitivity or exposure speed can be added such as, for example, 2,4,7-trinitro-9-fluorenone; 9-(dicyanomethylene) 2,4,7-tri-nitrofluorene; phthalic anhydride; 1,3,5-tricyanobenzine; 1,5-diphenoxy anthraquinone; 2,3-dichloronaphthaquinone 1–4; and 3-nitro-N-butyl carbazole.

Where the materials themselves are film forming they may be coated from a solvent to form the photoconductive insulating layer. Where additional strength is desired or in the case of nonfilm forming materials, the materials can be mixed with film forming insulating resins such as, for example, polyethylene, polystyrene, ethyl cellulose, polyacrylics and methacrylic acid esters, formaldehyde resins, polyethylene glycol esters, alkyd resins, polyurethane resins, silicon polymers and epoxy resins.

Various additives such as dyes which extend the spectral response of the photoconductor, or plasticizers and lubricants can be employed as is known in the art.

Conveniently, the materials making up the photoconductive layer are dissolved or dispersed in a volatile liquid carrier and then coated on a substrate, using conventional coating techniques, to a cured coating thickness usually of from about 5 to 50 microns. Suitable solvents include, for example, toluene, xylene, petroleum ether, chlorobenzene, methyl ethyl ketone, tetrahydrofuran, benzene, 1,2-dichloro-ethene, ethanol, etc.

Generally, conductive substrates are used such as, for example, steel, aluminum, or plastic sheets such as, for example, as polyethylene and polyesters which have deposited thereon a conductive coating of aluminum, gold, or conductive particles dispersed in a binder.

The bulk of the liquid carrier is then removed by conventional techniques, for example, by passing the coated substrate into an air-circulating oven to dry the coating.

The last traces of solvent are difficult to remove from the coating even on prolonged heating. These traces of solvent concentrate in certain areas close to the surface (blushing) or in pockets within the bulk of the film which makes the coating nonuniform. Even where prolonged heating is used to successfully remove the solvent, it has been found that such treatment often results in an impairment of the properties of the photoconductive insulating coating by causing physical or chemical changes in the structure, for example, crystallization of the materials or separation of the components of the layer.

These difficulties have been overcome by a short heat treatment conveniently accomplished by placing the back surface of the substrate, which carries the layer, in intimate contact with a heated surface for a short period of time. The heating is accomplished in this manner because contact with the photoconductive layer surface by the heating member would mar the surface. The treatment effectively solves the problem caused by concentrations of residual solvent. Surprisingly, the structure of the layer is also improved by the treatment. Whereas longer heating at relatively low temperatures of the photoconductor element in an effort to solve the residual solvent problem caused crystallization and other undesirable results, the short heating at a higher temperature not only does not impair the properties of the photoconductive layer but restores the original smoothness and gloss to layers which have a partially crystallized surface. The treatment also eliminates discontinuities or "pin holes" in the layer caused by improper coating or curing. The heating can be of any convenient means to provide efficient heat transfer to the photoconductive layer. It can be, for example, an infrared source, a heated surface such as a plate in stationary contact with the photoconductive element or it can be a moving surface such as a heated rotating cylindrical roll which is a convenient way to continuously treat long webs of material. The element should be heated to a temperature sufficient to soften the photoconductive layer to the point where the solvent can rapidly migrate through the layer to the atmosphere without causing damage to the substrate. Usually temperatures of from about 10° to 70° C. above the softening point of the layers are adequate. The heat source temperature required will vary depending upon the softening point of the binder phase of the photoconductive layer, the nature of the substrate, and the thickness of the photoconductive element. The time of contact is short and usually less than 1 minute. Preferably, heating times of from about 1 to 10 seconds are employed depending upon the amount of solvent to be removed and the efficiency of heat transfer to the photoconductive layer.

The invention is further illustrated, but is not intended to be limited by the following examples.

EXAMPLE I

Turning now to FIG. 1 a suitable system for carrying out the process of the invention is shown. Electrophotographic element **11** comprises a photoconductive insulating layer **13** which is about 18 microns in thickness and which comprises a 1:1 molar ratio of poly-N-vinylcarbazole and 2,4,7-trinitro-9-fluorenone. The layer was prepared by roll coating a solvent solution of the two components of the layer onto a 3 mil aluminized Mylar polyester backing sheet **15** from the solvent, tetrahydrofuran. The layer was dried in an air-circulating oven at 100° C. for 2 minutes. After about 2 days observable solvent blemishes appeared on the surface of the layer. The back surface **18** of sheet **15** of the left half of element **11** was placed in contact for about 2 seconds with an electrically heated platen **17** containing resistance wires **20** to heat stainless steel contacting plate **22** to a temperature of about 170° C. In this time, the photoconductive insulating layer became heated to about 165° C. (The softening point of the continuous polyvinyl carbazole resin phase of the layer was about 100° C.) After the plate was removed, the treated portion of element **11** quickly resolidified and had a surface which was smooth and glossy without any observable solvent defects.

The element **11** was secured to the surface of the cylindrical drum of a conventional electrophotographic copy apparatus and charged with a corona discharge to a negative polarity of about 600 volts, exposed imagewise to a line copy original for about 10 seconds, and cascade contacted with commercially available carrier and toner particles. The toner particles were transferred and heat fused to a copy sheet. The copy produced by the untreated portion of element **11** was relatively light with broken characters and background spots of toner. In contrast, the copy produced by the treated portion had darker images with sharp outlines and excellent character fill.

EXAMPLE II

A portion of untreated photoconductive element prepared in the same manner as described in example I was placed in an air-circulating oven at an air temperature of 130° C. for 20 hours in an attempt to remove the residual solvent. Not only did the solvent defects persist, but the surface of the photoconductive layer became dull which was caused by crystallization of portions of the trinitrofluorenone. A portion of the surface of the backing sheet was placed in contact with plate **17** at a temperature of 165° C. for 3 seconds. The treated surface portion became smooth and glossy. The photoconductive layer when used in accordance with the procedure described in example I generated excellent copy for the treated portion and poor copy for the untreated portion.

EXAMPLE III

FIG. **2** schematically shows another suitable system for treating the photoconductive insulating layer. Element **21** has a photoconductive insulating layer **23** of 1 part by weight of copolymer of N-vinylcarbazole and ethylacrylate (41 mole percent N-vinylcarbazole) and 1.5 part by weight of 2,4,7-trinitro-9-fluorenone which layer was coated on a web of aluminized Mylar polyester **25** from a 1:1 volume ratio of methylene chloride and tetrachloroethane carrier liquid. The surface of the moving element was transported from supply spool **24** to a driven takeup spool **26** past treating station **28** where sheet **25** was contacted by a driven rotating steel roll **27** whose surface was heated at a temperature of about 160°C. The speed of the roll was adjusted to approximately equal the speed of the element to maximize the heat transfer to element **21**. The speed was adjusted so that the residence time of each portion of element **21** in contact with the surface of the roll **27** was about 5 seconds. The layer **23** quickly cooled and solidified under ambient conditions after leaving roll **27** without need to provide any special cooling means. Portions of the heated web were used in an electrophotographic copy machine to produce images which when transferred and fused to plain paper showed sharp outlines, with good character fill, and no background toner caused by residual solvent effects.

While the invention has been particularly shown and described with reference for preferred embodiments thereby it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without department from the spirit and scope of the invention.

What is claimed is:

1. A method of improving the properties of a photoconductive insulating layer comprising heating said layer from about 10° to about 70° C. above the softening point for a short time, sufficient to evaporate residual solvent from said insulating layer.

2. A method of improving the properties of a photoconductive element comprising a photoconductive insulating layer supported on a conductive substrate which method comprises heating said element from about 10° to about 70° C. above the softening point of said photoconductive insulating layer for a short period of time, sufficient to evaporate residual solvent from said insulating layer.

3. The method of claim **2** wherein said layer is heated for from 1 to 60 seconds.

4. The method of claim **2** wherein said heating is accomplished by placing said substrate in intimate contact with a heated member.

5. The method of claim **3** wherein heating is accomplished by placing said substrate in contact with a plate.

6. The method of claim **3** wherein said heating is accomplished by contacting said substrate with a moving heated roll.

7. A process for improving the properties of a photoconductive element comprising a heat softenable photoconductive insulating layer supported on a substrate, said element having been prepared by coating said substrate with a solvent mixture of the material comprising said layer and evaporating the bulk of said solvent, said process comprising the steps of applying heat to the surface of said substrate opposite said photoconductive insulating layer at a temperature less than about 70° C. above the softening point of said photoconductive insulating layer so as to permit rapid escape of solvent from said layer, continuing said heating for a time sufficient to evaporate the residual solvent from said photoconductive insulating layer, and then cooling said element to resolidify said photoconductive insulating layer.

8. The process of claim **7** wherein said heating time is from 1–60 seconds.

9. A process for improving the properties of a photoconductive element comprising a heat softenable photoconductive insulating layer supported on an electrically conductive substrate, said element having been prepared by coating said substrate with a solvent mixture comprising poly-N-vinyl carbazole and 2,4,7-trinitro-9-fluorenone in tetrahydrofuran and evaporating the bulk of said tetrahydrofuran, said method comprising the steps of applying heat to the surface of said substrate opposite said photoconductive insulating layer to heat said insulating layer to a temperature of from about 160° to 170° C. to soften said photoconductive insulating layer so as to permit rapid escape of solvent from said layer, continuing said heating for from 1 to 10 seconds to evaporate the residual solvent from said photoconductive insulating layer, and then cooling said element to resolidify said photoconductive insulating layer.

10. A process for improving the properties of a photoconductive element comprising a heat softenable photoconductive insulating layer supported on an electrically conductive substrate, said element having been prepared by coating said substrate with a solvent mixture comprising a copolymer of N-vinyl carbazole and ethylacrylate and 2,4,7-trinitro-9-fluorenone in methylene chloride and tetrachloroethane and evaporating the bulk of said methylene chloride and tetrachloroethane, said method comprising the steps of applying heat to the surface of said substrate opposite said photoconductive insulating layer to a temperature of about

160° C. to soften said photoconductive insulating layer so as to permit rapid escape of solvent from said layer, continuing said heating for from 1 to 10 seconds to evaporate the residual solvent from said photoconductive insulating layer and then cooling said element to resolidify said photoconductive insulating layer.

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