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Saklikar

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[54] **LAMINATED ELECTROPHOTOGRAPHIC UNIT AND PROCESS**

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[52] **U.S. Cl.** ..... **96/1 R,** 96/1 C, 96/1.5, 96/1.8, 355/17

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

[58] **Field of Search** ..... 96/1 R, 1 C, 1.5–1.8; 250/49.5; 317/262 A; 355/17

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Primary Examiner—Charles E. Van Horn

[57] **ABSTRACT**

A unit adapted for use in electrophotographic cameras and an electrophotographic process are disclosed where the unit has electrostatic charges and comprises a photosensitive member consisting of a photoconductive layer and an electroconductive layer electrostatically attached to an insulating layer. If the unit is to be used as a film and stored for later exposure, it is sealed in an encasing sheet of the insulating material. If the unit is to be exposed directly, the insulating layer can comprise a master containing an image. During formation of the unit, the photoconductive layer is given a charge of a first polarity and the insulating layer is given a charge of an opposite polarity prior to contacting the two and prior to exposure to radiation. A preferred embodiment utilizes a clear plastic insulating layer with a resistivity of 10^{14} to 10^{18} ohms-meters and a dielectric constant of about 2 which in the form of a film contains no image and in the form of a printing element contains an image.

5 Claims, 3 Drawing Figures

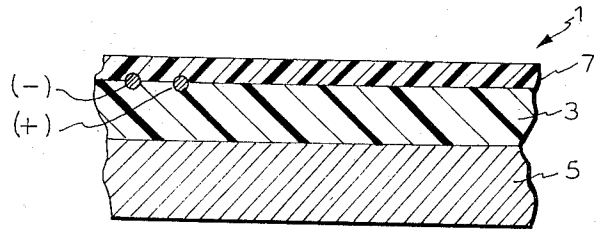


FIG.1

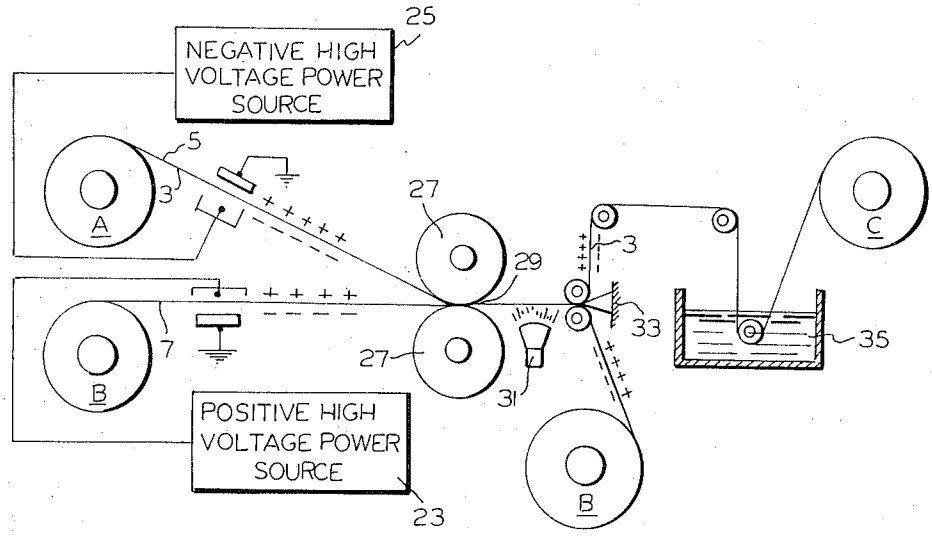


FIG.2

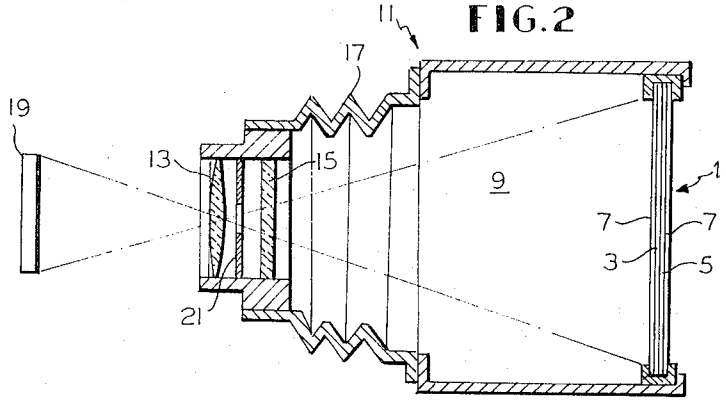


FIG.3

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LAMINATED ELECTROPHOTOGRAPHIC UNIT AND PROCESS

The present invention provides a method and means for electrophotographic copying wherein the principles of the electrophotographic reproduction are improved and are applied in one embodiment to conventional cameras and in another to engineering template production.

In its broadest aspect, this invention comprises positively applying an electrostatic charge to a photoconductive surface, as is typical in electrostatic printing, and laminating this surface prior to exposure to an oppositely charged transparent insulating layer. One specific application of the invention provides a film adapted for long-term storage which can be exposed to a projected image far from corona or like charging apparatus. Another specific application provides an improved template for the construction industry produced by contact imaging without arc spots thereon.

Although it is recognized in electrophotography that oppositely charged photoconductive and insulating surfaces are held together by electrostatic attraction, all known processes rely on charges on one or both the layers applied or induced at the time of exposure. This means exposures must be made in the vicinity of charging means. This practice is caused by the tendency of charges to decay.

The use of electrophotographic principles in photography is also known and it has been proposed to use film in such cameras which receives an electrostatic image which then can be developed according to electrophotographic methods. Such prior proposals are illustrated by U.S. Pat. No. 3,237,197; however, such proposals have suffered from the deficiency of requiring complex mechanisms associated with the camera with which to electrostatically charge the photosensitive film member prior to imaging. Moreover, it is also found that the imaged film does not retain the image and must be developed and printed shortly after exposure, in order to prevent charge decay resulting in faint prints from the film.

In the field of reproducing engineering drawings on conductive templates, the use of electrophotographic principles is also known; however, conventional methods of electrophotographic contact printing are used therein and the templates are frequently ruined or marred by sparking which results when the master is pulled away from the exposed conductive template. Moreover, it is discovered that a master used in such electrophotographic reproductions tends to develop induced electrostatic charges of a polarity like that on the charged printing element and upon separation after a few uses, arcing is so heavy that a new master must be used.

It is, accordingly, an object of this invention to provide a film adapted for use in all electrophotographic imaging systems which does not require complex charging means contained in or associated with the imaging device and which will produce a high clarity print during exposure.

This invention is particularly adapted for use in those electrophotographic systems wherein the photosensitive elements, prior to use, are provided with an electrostatic charge which is dissipated on exposure to irradiation in selected areas leaving a charge image on the paper.

According to this invention, a photosensitive member is given a charge and then contacted with an oppositely charged insulating layer prior to exposure. The charges do not decay, since decay is strongly dependent upon the dielectric constant and resistivity of the atmosphere and the charged material. It is known in certain humidity conditions decay is greater than it is in other conditions and this is in conformity with theoretical expectations. Charge patterns usually decay in an exponential fashion with the characteristic decay time being given by the equation $\tau = \rho\epsilon$ where ρ is the time constant, ρ is the resistivity of the image bearing member and ϵ is the dielectric constant of the member, all quantities being expressed in MKS units. The available resistivities in suitable image bearing members have heretofore limited the length of time during which it has been possible to retain an electrostatic image. This has been particularly true with photoconductive insulating materials where it has generally been necessary to develop the charge pattern very soon after its formation. Ordinary insulating materials can be obtained with resistivities higher than those of most photoconductive insulators, but here also the resistivity is often inadequate to support the charge for the desired length of time.

By contacting the charged photoconductor with an oppositely charged insulating layer, according to this invention, the initial charges are retained and the charges do not migrate through the respective layers because each is in contact with an attracting charge of an opposite polarity. When used (e.g. exposed to light) portions of the charge on the photoconductive surface are dissipated leaving an electrostatic image pattern thereon but the remaining charges are protected from dissipation by the insulating layer until developed. Thus, the unit of this invention will retain an initial charge prior to use and will retain a sharp image after exposure for months during storage, if desired. When it is desired to develop the image and the insulating layer is peeled off, it tries to induce a charge opposite to its own on the photoconductor and the photoconductor acts likewise. This results in a decrease of electrical field between the two layers, so that no arcing results and a clear unspotted image is reproduced on the photoconductive surface.

The invention generally improves electrophotographic processes over those wherein electrostatic attraction of an original and a copy sheet was induced during exposure by increasing the speed and efficiency of the charging and exposing steps. Positive charging allows faster and more uniform development of electrostatic charges. Moreover, it is found that the unit of this invention produces an electrostatic image faster during exposure because the electrostatic charge built upon the photoconductor can dissipate in two directions whereas an uncharged master allows dissipation of the contacted photoconductor in only one direction. This is of particular advantage when using the unit in a camera with short shutter opening times.

The invention will be better understood by reference to the following Figures and specific Examples.

In the Figures, like numerals represent like elements and

FIG. I represents a cross-section of an electrophotographic unit according to this invention.

FIG. II diagrammatically represents steps in the use and formation of a unit of FIG. I.

FIG. III represents projection imaging of a unit of FIG. I.

Referring more specifically to FIG. I, the electrophotographic unit is generally designated **1** and is seen to comprise a photosensitive member comprising a photoconductive layer **3** with a first charge, shown as negative (−), and electroconductive layer **5** which is covered by an insulating layer **7** having an opposite charge, shown as positive (+).

The photoconductive layer **3** may be any organic or inorganic photosensitive or photoconductive substance typically used in electrophotography. Typical systems used for this purpose in the art are selenium, zinc oxide (alone or dispersed in a binder) and certain organic non-polymeric materials, such as anthracene and anthraquinone, as well as organic polymeric materials found to be photoconductive. These materials are normally not electrically conductive but are activated on exposure to incident radiation to an electroconductive state. In the art, inorganic materials, such as selenium and cadmium sulfide, are often vacuum deposited on a base. Other inorganic materials, such as zinc oxide, and organic materials, such as oxadizoles, pyrazolines, imidazoles, triazoles, etc., are applied with binders, such as polystyrene. Still other photoconductive organic polymers are directly coated on the base from solutions, such as poly-N-vinylcarbazole, polyacenaphthylene, and polyvinyl triphenylpyrazoline. Any of these and other systems can be utilized; however, the preferred element of this invention utilizes a zinc oxide coating dispersed in a suitable insulating polymeric binder. This material is coated on a base material **5** which is also any of the conventionally used materials, such as paper, plastic or metal. If the material is paper or plastic, which are normally not electroconductive, it is typically provided with a sizing or coating (not shown) to render it electroconductive. To improve adhesion of layer **3**, it may be desirable to provide a primer coat (not shown) on base **5** before depositing layer **3**.

The backing material **5** may be either a flexible composition or may be a rigid inflexible material, depending in part on the intended manner of use of the element. Examples of rigid materials which can be employed are, for instance, glass, unsaturated polyester resins; metals, such as aluminum, nickel, chromium, etc. (all in the form of plates, slides, disks, etc.). Metals are generally desired when the invention is to be used to produce engineering templates by contact imaging, as discussed below. Examples of flexible materials, which can advantageously be employed as the backing material, are, for instance, polyethylene terephthalate film sold by E. I. duPont de Nemours and Company of Wilmington, Delaware, under the name Mylar. A more refined grade of polyester terephthalic acid tape or film found highly appropriate as the base for recording images is sold under the name of "Cronar." Another flexible backing material which can be used advantageously because of its good heat resistance, strength, inertness and resistance to radiation is polycarbonate resin film. Flexible backings are generally preferred when the unit is to be used as camera film for projection imaging, as discussed below.

The insulating layer **7** provided according to this invention should be transparent to the activating radiation. It is generally a sheet or film, preferably plastic, of any suitable thickness, preferably 0.5–15 mils. The selection of a film is not based on the chemical nature of the film, but on the physical properties of the film. Thus, for use in this invention, the film should have a resistivity of from about 10^{14} to 10^{18} ohm-meters and a dielectric constant of at least about 1.5. Specific films having suitable properties are found to include 7 mil thicknesses of Mylar film and polyamide films, such as Nylon 66, as well as Teflon, polyacrylonitrile, and films from copolymers of vinylchloride and vinyl acetate. Other materials, such as glass or metals, treated to have the required insulating properties can be used.

Layer **7** may be applied as a temporary or permanent layer, again depending primarily on the intended use. If a camera film is to be prepared, this film must generally withstand long storage times both before and after exposure, so it is desirable to "permanently" apply layer **7** to thereby seal and prevent atmospheric decay. In this case, the layer **7** can be wrapped around the base containing the photoconductor or can be applied only onto surface **3** and hermetically sealed in known manner. For example, a heated wire may be drawn across the overlapped ends or edges of the film preferably while in a vacuum chamber to improve contact of layers **7** and **3.** The method of sealing the film forms no part of this invention. If a temporary layer is desired, for example, in a continuous type process, such as shown in FIG. II, no sealing is required and the electrostatic attraction of surfaces **3** and **7** will alone prevent charge decay.

Whereas visible light is the preferred radiation used to form an electrostatic image on the unit of this invention, other radiation capable of activating layer (**3**) to an electroconductive state is contemplated.

As one example of the scope of the invention, reference is made to its application to the recording of X-ray patterns. In the case of X-rays, it will be recognized that metal layers are substantially transparent to such activating radiation, and thus the transpartent layer **7** may be a metal sheet or the like. Thus, specifically, it may be desired to form an electrical image from X-ray activation in which case both backing member **5** and layer **7,** or either of them, may be metal, and exposure to the X-ray pattern may be accomplished at the desired stage in the operations by exposure through such metal layer. In known manner, X-ray activation is effective for forming a charge pattern on layer **3.** It is to be understood, furthermore, that operation of the invention with X-rays or other penetrating radiation can be improved with a heavy metal, such as lead or the like, as a simulated intensifying screen either as a nontransparent conductive electrode or backing member, or as a thin layer on the surface of the transparent insulating member **7** through which the radiation sensitive layer is activated. Likewise, in view of the suitability of the invention for X-rays or penetrating radiation, the term "photoconductive" as applied to layer **3** should be interpreted in its broader sense to denote a layer that is an insulator in the absence of activating radiation and is rendered conductive by the action of such radiation. It is already noted that the possibility of X-ray activators also requires that the term "transparent" as applied to layer **7** should be interpreted broadly to correspond to the intended radiation.

According to this invention, the charge can be provided during formation of the films and it will not decay by reason of the protective insulating layer. As shown in FIG. II, a previously prepared photosensitive mem-

ber supply A and an insulating layer supply B are oppositely charged, for example, by exposure to corona discharge means **23** and **25** and then contacted with the oppositely charged surfaces of the two laminae facing together. Illustrative contact means is shown as rollers **27.** It is immaterial whether means **23** and **25** are positive or negative respectively, so long as they supply opposite charges. Then at point **29** optional steps can be effected, depending on the intended use, e.g. the edges of the encasing film can be hermetically sealed by means not shown and e.g. the unit can be severed by means not shown. The system illustrated in FIG. II is a continuous system where exposure occurs immediately by radiation lamp **31.** In this system, adapted for making engineering templates, the insulating layer **7** will have been provided with an image. So long as the electrostatically attracted unit at point **29** is not contacted by activating radiation, it will retain its initial electrostatic charge for periods of up to six months.

As further shown in the continuous process of FIG. II, the unit is separated after exposure by separating means **33,** so that the electrostatic image in layer **3** can be developed at developing station **35** and fixed by suitable means (not shown) prior to storage at C. The insulating layer **7** is recovered as supply B for reuse. It is apparent that layer **7** could be directly returned to supply B for recharging by corona **23.** Immediate separation **33** is not essential, as the image can be retained for months prior to developing.

If a non-continuous use is desired exposing means **31** and separating means **33** can be by-passed and replaced at **29** by sealing and severing means to form a camera film.

When it is desired to use such a film, it can be placed in any conventional camera, such as that shown as **9** in FIG. III and exposed to an image **19** through lens (**13** and **15**) and shutter **21** with focusing means **17** and housing **11** provided as is typical in cameras. As already noted, the film may be exposed in use to light or X-ray or other activation to produce an image **19.**

The exposed film from FIG. III can be stored, out of contact with activating radiation, and it can be developed by conventional electrostatic developing techniques by returning it to separating means **33** and developer **35** of FIG. II. In developer **35** dry toner particles or liquid toner is applied to the surface **3** containing the electrostatic image and the toner will be attracted and held to the surface **3** whereupon the toner can be fused by conventional methods.

The liquid developers which can be employed can be of the type as commonly known in the prior art. In addition, the following developers can be used.

Positive developer. This developer is one containing developer material which is attractable by negative electrostatic charges forming a latent electrostatic image and thus this developer can be used to produce a facsimile or positive reproduction of an original on a charged and exposed electrophotographic sheet containing zinc oxide as the photoconductor. The developer comprises a concentrate which is dispersed in the developer liquid to produce the liquid developer. The concentrate is prepared by grinding or milling

Isol Ruby BKS red pigment	20 grams
Bodied linseed oil	20 grams
Lithographic varnish	20 grams

The concentrate thus prepared can be dispersed in any developer liquid possessing the required electrical properties, that is, a volume resistivity of at least 10^9 ohm-cm. and a dielectric constant of preferably less than 3. The following liquids are suitable: n-hexane, n-heptane, Shell X55, Shell X4, Shellsol T, Mineral Turpentine, cyclohexane, Solvesso 100, Freon 113, perchloroethylene and the like.

Negative developer. This developer contains developing material which is repelled by negative electrostatic charges forming a latent electrostatic image and which deposits onto areas free from such charges or containing the minimum of such charges and thus, this developer can be used to produce a negative or reversal reproduction of an original on a charged and exposed electrophotographic sheet containing zinc oxide as the photoconductor. This developer is also sufficiently sensitive to develop conductivity patterns on the photoconductive surface as hereinbefore referred to. The developer comprises a concentrate which is dispersed in the developer liquid to form the liquid developer. The concentrate is prepared by grinding or milling

	Grams
Carbon black pigment	10
Automotive oil SAE 40	100

This concentrate can be dispersed in the developer liquids as described in connection with the positive developer.

Both of the above developers can be used in a concentration of approximately 5 grams of the concentrate to from 100 to 1,000 ml. of the developer liquid.

The invention can be understood by reference to the following preferred embodiments:

EXAMPLE I

A photoconductive coating comprising

	Grams
Zinc Oxide (Durham Special Z)	600
Binder (Rhodene M8/50)	600
Solvent (Toluol)	250
Activators (4% Manganese Naphthenate and 3% Cobalt Naphthenate)	2.5
	2.5

is prepared by milling the ingredients together, diluting and depositing on a relatively conducting support consisting of Bartya paper containing conductive carbon particles to produce a coating of about 1 mil thickness.

This coated member and a 7 mil thickness of Mylar film were charged to about 280 and 1200 volts respectively in a positive and negative Corona charger by placing the respective members on grounded metal plates and subjecting the exposed surfaces to about 6,000–10,000 volts at low amperage; (a negative charge was placed on the photoconductor and a positive charge on the Mylar).

The Mylar was then wrapped longitudinally around the electrophotographic member and the edges overlapped while in a vacuum chamber with pressure reduced to about 1 mm Hg. Next, a heated tungsten filament was drawn across the overlapped edges to seal the

film and sever excess film. A suitable length of film is cut, also in the vacuum chamber, by a "hot knife" which severs and seals the cut edges of the film.

This film was kept in the dark for about 6 months until placed in a "box" camera and exposed in normal manner. The exposed film was then removed and kept in the dark about 2 months until developed with the positive developer listed above. The developer was fixed in normal manner and yielded a clear high quality positive reproduction.

EXAMPLE II

A sheet of aluminum, five feet by ten feet and three-eighths inch thick, was coated with about 0.5 mil epoxy resin primer.

This was then coated with a photosensitive composition comprising a solvent solution of zinc oxide particles, epoxy resin, and acrylic binder (commercially known as CA 9251 of the Sherwin-Williams Company). This sheet was then passed under a corona and a negative electrostatic charge of about 1,200 volts was produced on the photosensitive coating.

A Mylar sheet of like dimensions which contained an inked engineering drawing was passed under a corona and a positive electrostatic charge of about 280 volts was produced thereon. The oppositely charged surfaces of the sheets were placed in contact by passing through driven rollers and then exposed, separated, and developed, as in the prior Example, to yield a metal template free of spotting. The Mylar master was reused continuously without development of spotting on the templates produced.

I claim:

1. An unexposed electrophotographic unit comprising a photosensitive member comprising a photoconductive surface with an electroconductive backing said photoconductive surface being sufficiently insulating to accept and hold an electrostatic charge and said photoconductive surface having an electrostatic charge of a first polarity by which it is electrostatically attracted to an insulating transparent layer having an electrostatic charge of the opposite polarity said insulating layer having a resistivity of from about 10^{14} to about 10^{18} ohm-meters and a dielectric constant of at least about 1.5, wherein said insulating layer is free of conductive backing and external electrical connection.

2. The unit of claim **1** wherein the insulating layer is a plastic sheet having a resistivity of about 10^{18} ohm-m and a dielectric constant of about 2.

3. The unit of claim **1** wherein the insulating layer is hermetically sealed about the photosensitive member.

4. In the method of electrophotographic reproduction wherein a photoconductive surface is charged prior to exposure; the improvement which consists of charging a photoconductive layer, comprising a photoconductive surface being sufficiently insulating to accept and hold an electrostatic charge, to a first polarity; charging a separate transparent insulating member, having a resistivity of from about 10^{14} to about 10^{18} ohm-meters and a dielectric constant of at least about 1.5 to the opposite polarity; contacting the oppositely charged surfaces of said members without substantial charge transfer; and then exposing the unit so formed to activating radiation.

5. The method of claim **4** wherein the insulating layer is a plastic sheet having a volume conductivity of about 10^{18} ohm-m and a dielectric constant of about **2.**

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