ABSTRACT OF THE DISCLOSURE

A method and article used therein for forming high resolution images, such as micro images, by the technique referred to as photoelectroslography. The article is made by interposing a layer of "Kalvar" or other diazo material between a film base and a successive laminar disposition of a conductive layer, a soluble plastic layer, and a surface layer comprising a photoconductive material. In the method, the film base record medium is first charged and exposed to a light image and then the exposed portion is treated with a coating of sodium hydroxide which, further, will develop the diazo layer simultaneously if ordinary diazo material is used.

The resulting article is a film base with an image formed thereon displaying excellent qualities of resolution, image density, and abrasion resistance. Moreover, all potentially toxic material is completely eliminated and no undesirable qualities such as background density from the aluminum layer or the like interfere with the subsequent use of the image.

It is an object of the present invention, therefore, to provide an improvement in the art of photoelectroslography.

Yet another object of the present invention is to provide an improved method of making a photoconductive record media.

A still further object of the present invention is to provide an improved method and means for forming high quality images of improved resolution and image density.

A still further object of the present invention is to provide improved method and means in the art of photoelectroslography which eliminates any risks of toxicity.

A still further object of the present invention is to provide an improved method and means in the art of photoelectroslography which eliminates any interferences with the use of the image.

A still further object of the invention is to provide an improved method and means for obtaining images on a final support which have improved resistance to abrasion of the imaging material.

Many other features, advantages and additional objects of the present invention will become manifest to those versed in the art upon making reference to the detailed description which follows and the accompanying sheet of drawings in which the method and means of practicing the improvements disclosed herein in connection with the art of photoelectroslography are illustrated by way of exemplification.

On the drawings:

FIG. 1 is a schematic cross-section showing in exaggerated enlarged form a composite film or image record media provided in accordance with the principles of the present invention;

FIG. 2 is a view similar to FIG. 1 but showing the composite film after charging, exposure and development;

FIG. 3 is a view similar to FIGS. 1 and 2 but showing the composite film following blanket light exposure, a second development and removal of aluminum and selenium layers;

FIGS. 4, 5, 6, 7, 8 and 9 show one sequence of steps of a method which may be practiced in accordance with the principles of the present invention by means of which an image is formed on an image record media provided in accordance with the principles of the present invention; and

FIG. 10 illustrates an alternative development step which would be substituted for the second development step of FIG. 8 in the method of FIGS. 4-9 if a "Kalvar" film were used instead of conventional diazo materials in the image record media.

As shown on the drawings:

Referring, first of all, to FIG. 1, there is shown a film base which may be made of Mylar or other suitable flexible plastic material and the film base is indicated as comprising the thickest portion 11 of an image record media shown generally at 10.

In accordance with the principles of the present invention, the film base is provided with a coating of a diazo material, which coating is shown at 12.

One article generally available is sometimes identified
as "Kalvar" and constitutes an emulsion carried on a film base. It is understood that "Kalvar" may consist of a diazo compound held or dispersed in vinylidene chloride. As is generally understood, the term "diazo compound" as used herein refers to those light-sensitive compositions belonging to the class of aromatic compounds having an azo linkage (\(-N=N-\)) directly attached to one of the aromatic carbon atoms. Some are capable of being developed by a coupling reaction, initiated by an alkaline material, such as ammonia, or heat, as in conventional diazo practice; others, as is the case in "Kalvar" films, are "developed" by the entrapment, when heated, of expanded gaseous bubbles formed during an imaging exposure.

Coated over the diazo material 12 is a very thin transparent layer of aluminum 13. The aluminum layer may be vacuum-evaporated onto the diazo layer and it is contemplated that the aluminum layer 13 will be less than one micron in thickness, it is sufficiently thin to afford 75% light transmission therethrough. Over the aluminum layer is coated a thermoplastic layer of a thickness in the order of about two microns and shown at 14. Suitable materials for the thermoplastic layer include Staybellite, Piccotex, RC-100, Araldite and others which can be dissolved by solvents as mentioned below. Such materials are more particularly identified as follows in terms of their commercial availability:

- Staybellite—(resin) Hercules Powder Company
- Piccotex—(styrene copolymer) Pennsylvania Industrial Chemical Company
- RC-100—(methacrylate monomer plasticizer) Rubber Corporation of America
- Araldite—(epoxy resin-adhesive) Ciba Products Company

Finally, a thin layer of a photoconductive material 16 is coated over the thermoplastic layer and such photoconductive material preferably takes the form of a layer of selenium which may be vacuum-evaporated and which is in the order of thickness of about 0.2 micron. Other photoconductor materials may be used, e.g. selenium-tellurium, poly-N-vinyl carbazole, etc.

While the phenomena involved in the art of photoelectrosography are not fully understood, one explanation is as follows. First of all in accordance with the art of photoelectrosography, a sandwich of aluminum, thermoplastic and selenium is carried on a film made of Mylar and having a thickness of approximately 0.005 inch to 0.007 inch. The 0.2 micron selenium layer consists of discrete spherical particles almost in contact with each other, but not forming a continuous film. The following steps (illustrated in FIGS. 4-6) are conducted in darkness. With the aluminum layer grounded in accordance with accepted electrostaticographic techniques, a uniform charge is first placed on the photoconductive layer. The photoconductive surface is exposed by optical projection or contact in order to form a latent image in the form of an electrostatic charge pattern. The sandwich is then dipped into a solvent for the thermoplastic material and apparently the solvent penetrates between the selenium particles dissolving all of the thermoplastic layer beneath the selenium. The selenium particles no longer having a physical support are subject to movement by any electrostatic forces present. These forces cause the selenium particles that have been exposed to a light image to move directly to the aluminum underlayer and become deposited there forming a selenium image. Particles of selenium in the unexposed area just wash away as particles in the solvent.

Because of the small particulate nature of the particles and the short distance they move, the resulting resolution of the images produced is of good quality and the image is of high density. However, the image lacks abrasion-resistance and the residual presence of the aluminum layer may cause some interference with the subsequent usage of the image. Moreover, the potential toxicity of the selenium presents an additional problem.

In accordance with the principles of the present invention, the layer 12 of diazo materials is interposed as a part of the sandwich as shown in FIGS. 1-3.

Thus, the method of usage contemplated by the present invention is shown in FIG. 4 wherein the composite film is initially charged in darkness by the entrapment therein shown schematically as including a shield 15 and a plurality of charging wires 15a. An arrow is shown at 17 to depict a traversing movement of the composite film 10 under the charging unit.

In FIG. 5, the composite film 10 has been moved on to an image exposure station. Thus, the original having imaged areas to be copied is shown at 18 and there is provided an optical lens system 19 so that the image may be projected onto the photoconductive layer 16. In accordance with known principles of electrostatic image formation on photoconductors, a latent electrostatic charge pattern is formed on the photoconductor, as shown, the charges in the unexposed areas remain on the photoconductor. If the method is being practiced in connection with the formation of microimages, it will be understood that the optical system 19 will result in an image reduction of approximately 10X to 40X and that a reduction of 18X could be an exemplary reduction in connection with the formation of microimages on 16 mm. film.

In FIG. 6 there is shown a first development station and for purposes of illustration a development tank is shown diagrammatically at 22 containing a charge of solvent 23 selected to have a solvent relationship with respect to the thermoplastic layer 14. A solvent for the above listed thermoplastic materials may be selected from the following: Freon 113 (a fluorinated hydrocarbon sold by Du Pont), trichloroethylene, cyclohexane, toluene, pentane, etc. The particular material in the thermoplastic layer and the solvent therefore used in the process forms no part of the present invention and those skilled in the art may select combinations from the above and others.

In accordance with the present invention, it is contemplated that the same phenomena described above occur in that when dipped into the solvent, as shown in FIG. 6, it is believed that the solvent penetrates between the selenium particles dissolving all of the thermoplastic layer beneath the selenium layer, whereupon the selenium particles which have been exposed to light move directly to the aluminum underlayer and become deposited there to form a selenium image. In the composite shown in FIG. 7, the portion of the layer of selenium exposed to light is illustrated and the aluminum layer while the unexposed area of the selenium layer corresponding to the original image has been washed away with the thermoplastic layer. Thus, a negative image of the original 18 is formed by the deposited selenium coating.

The composite film after charging, exposure and development is depicted in FIG. 2 of the drawings wherein it will be noted the thermoplastic layer 14 is washed away and the photoconductive layer 16 is directly on the aluminum 13. The arrows graphically indicate those areas of the original composite which have been light struck and discharged the photoconductor coating during the development stage. In accordance with the principles of the present invention, after the first development station, the composite film is subjected to a blanket exposure to ultraviolet light as shown in FIG. 7. In this exposure, the deposited selenium has the effect of filtering the ultraviolet light so that the diazo material underneath is not affected. If an ordinary diazo material is used as the coating 12, the blanket ultraviolet exposure of the composite 10, as shown in FIG. 7, will destroy the coupling capability of the diazo compound in the areas where selenium has been washed away. The second development which follows, in the case of ordinary diazo compounds, may be carried out using so-
dium hydroxide solution which simultaneously removes the selenium deposit and the aluminum layer and develops the diazo material, in the ordinary manner. That is, in the areas under the selenium deposit, which have not been exposed to ultraviolet, and, consequently, the diazo material is still capable of undergoing a coupling reaction, there is formed a colored dye image. In this case, the image is a negative image of the original 18.

This step is shown diagrammatically in FIG. 8 in which the developing material such as a weak solution of sodium hydroxide is introduced into an enclosure 26 through an inlet 27 and exits through an outlet 28.

FIG. 3 shows the composite film following blanket light exposure, a second development and removal of the aluminum layer 13 and the photoconductive layer 16. The figure illustrates positive development as is readily obtained using "Kalvar" materials, but it is understood that negative development is also possible using the invention, e.g., using ordinary diazo materials.

It is also contemplated that the selenium and aluminum layers may be chemically removed by solutions such as sodium hydroxide or mechanically removed, e.g., by abrasion followed by development with ammonia vapor.

In some cases, it may be possible to develop the diazo material directly by use of ammonia vapor without first removing the selenium and aluminum layers. To fulfill the objectives of the invention, these layers would subsequently be removed as by dissolving with sodium hydroxide or mechanically by abrasion.

Thus, there is shown for illustrative schematic purposes in FIG. 9, a brush 29 for removing the selenium and aluminum layers and means for removing the composite film in the direction of the arrow 30. By virtue of the removal of the selenium and the aluminum, the toxic material is completely eliminated and the aluminum layer is no longer present, thereby avoiding any possible interference with the subsequent utilitarian usage of the image.

As shown in the alternative second developing step of FIG. 10 which may also be accomplished before or after removal of the selenium and aluminum layers, if a so-called "Kalvar" material is utilized in the layer 12, then the exposed, image areas 25 when heated, form bubbles, thereby producing a visible utilitarian image. Accordingly, in FIG. 10 there is shown a thermal unit 24 for exposing the composite film 10 to thermal energy.

Whichever alternative is used, the development of the image on the film permits the selenium and aluminum to be removed from the final permanently imaged composite 10, eliminating the undesirable effects mentioned previously.

The final image record medium resembles a conventional diazo or "Kalvar" film and displays all of the permanence and durability generally associated with such an article. However, since the imaging exposure was made using the high sensitivity of the selenium photoconductor material, the resulting image formed by the combinative technique contemplated by the present invention, affords resolution characteristics greater than 225 lines/mm. and a diffuse transmission intensity in the order of 1.3. The clear areas have a density of approximately 0.12 or less. Moreover, the image can be effectively utilized without any risk of toxicity.

Although minor modifications might be suggested by those versed in the art, it should be understood that I wish to embody within the scope of the patent warranted hereon all such modifications as reasonably and properly come within the scope of my contribution to the art.

I claim as my invention:

1. A photoelectroerosographic film material comprising a flexible film strip forming a film base, a coating on said base containing a light-sensitive diazo compound, a thin, transparent layer of electrically conductive material on said coating,
10. The method of photoelectrosography which includes the steps of uniformly charging the photoconductive surface of a composite film having layers of film base, a layer containing a light-sensitive diazo compound, a thin, transparent conductive material, solvent-soluble thermoplastic resin and a photoconductor, optically exposing the charged surface of the composite film to a light image to form an electrostatic image in the form of a charge pattern, dissolving said thermoplastic resin substrate in the composite film to deposit the exposed areas of photoconductor on the conductive substrate of the composite film, thereby forming a negative image, blanket exposing the composite film to ultraviolet light, whereby the negative image has the effect of filtering the ultraviolet light, and developing the composite film by removing the conductive and photoconductive materials and forming an image in said layer containing said diazo compound corresponding to the negative image.

11. The method of claim 10 wherein the step of removing the conductive and photoconductive materials consists of mechanical abrasion.

12. The method of claim 10 wherein the step of developing the composite film comprises simultaneously removing the conductive and photoconductive materials and forming an image in said layer containing a diazo compound.

13. The method of claim 12 wherein the step of removing the conductive and photoconductive materials consists of chemical dissolution.

14. The method of claim 11 wherein the developing step comprises forming a colored dye image by treating with ammonia vapor.

15. The method of claim 13 wherein the step of forming the image comprises heating the film to form bubbles in said layer containing the diazo compound.

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