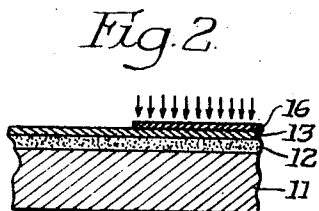
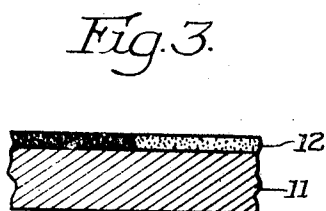
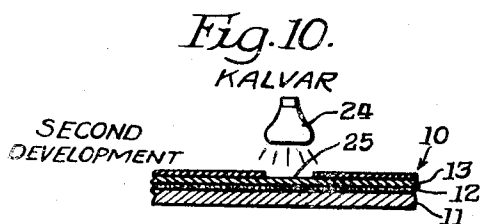
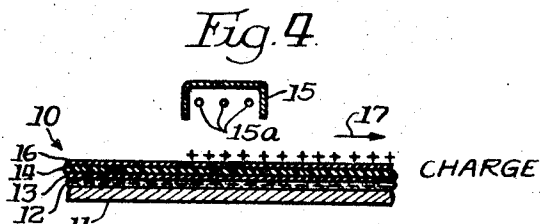
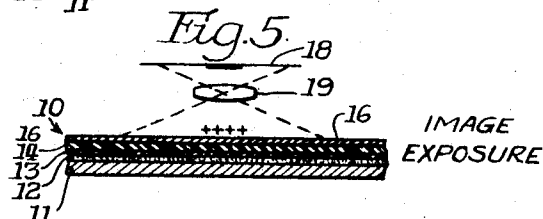
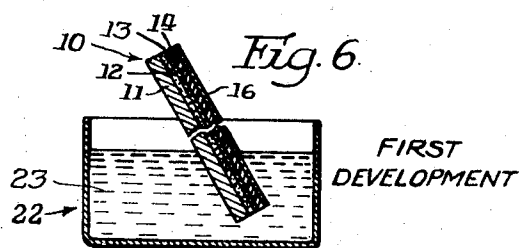
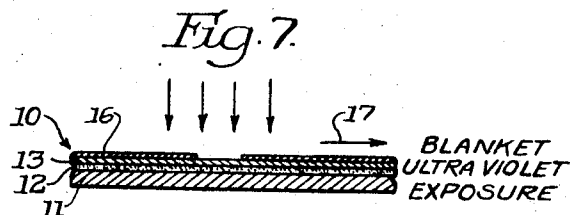
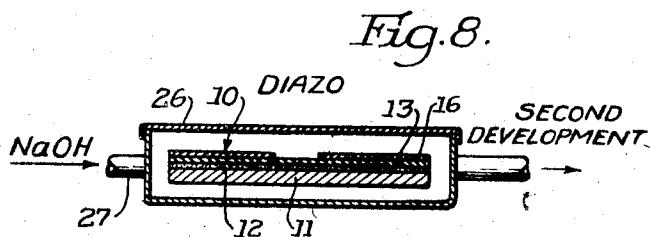
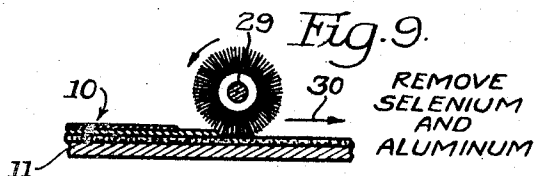


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PHOTOELECTROSOLOGRAPHIC ARTICLE AND METHOD
UTILIZING DIAZO MATERIAL
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PHOTOELECTROSOLOGRAPHIC ARTICLE AND METHOD UTILIZING DIAZO MATERIAL

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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 photoelectrosolography. 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 portions of the photoconductive layer are deposited on the aluminum layer during a first development step comprising dissolving the plastic layer. After a blanket ultraviolet exposure, the diazo material may be developed with an alkaline material, or if "Kalvar" material is used, the second development step is accomplished by heat. As a final step, the selenium and aluminum layers are removed.

This invention relates generally to the art of photoelectrosolography, sometimes referred to as PESO herein, and more particularly to a method and means of forming high resolution images such as microimages on a flexible film base such as film strip by interposing a layer of "Kalvar" or diazo material between a film base and a laminar disposition of an electrically conductive layer such as aluminum, a plastic layer such as thermoplastic and a photoconductive layer such as selenium.

In accordance with the present art of photoelectrosolography, a layer of aluminum is deposited by vacuum evaporation on a film base whereupon the layer of aluminum is successively coated with a layer of plastic and then a photoconductive layer such as selenium.

After charging and exposure to an image in accordance with electrostatographic procedures, the record media is dipped into a solvent of the plastic whereupon the plastic disappears and the selenium is deposited on the aluminum layer. In those areas not struck by light, the selenium is floated away leaving the photoconductive selenium in the exposed areas to form an image directly on the aluminum layer and film base.

With such an arrangement, the resulting image is very fragile since the selenium material rubs off readily. Moreover, selenium apparently displays some qualities of toxicity which is undesirable.

In accordance with the principles of the present invention, a layer of a diazo material containing a diazo compound is interposed between the film base and the aluminum layer. Following normal photoelectrosolography exposure and development, the record media is subjected to a blanket ultraviolet exposure. The image is developed by heating or by contacting with ammonia vapor, sodium hydroxide solution or the like. The image may be developed before or after the selenium and aluminum layers are completely removed, for example by abrasive means. If desired, the selenium and aluminum layers may be removed by the use of a weak solution 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 photoelectrosolography.

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 photoelectrosolographic film material.

Yet another object of the present invention is to provide an improved method and means of 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 photoelectrosolography which eliminates any risks of toxicity.

Yet another object of the present invention is to provide an improved method and means in the art of photoelectrosolography 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 photoelectrosolography 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 principle 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 ($-\text{N}=\text{N}-$) 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, i.e., 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 Staybelite, 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:

Staybelite—(rosin) Hercules Powder Company.

Piccotex—(styrene copolymer) Pennsylvania Industrial Chemical Company

RC-100—(co-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 photoelectrosology are not fully understood, one explanation is as follows. First of all, in accordance with the art of photoelectrosology, 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 electrostatic techniques, a uniform charge is first placed on the photoconductive layer. The photoconductive surface then 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 alumi-

num 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 corona charging unit herein 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 $10\times$ to $40\times$ and that a reduction of $18\times$ would 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 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 has deposited onto 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 where light struck and discharged the photoconductor coating during the imaging exposure. 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 so that the diazo material underneath is not affected. If an ordinary diazo material is used as the coating 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 density in the order to 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 photoelectrosolographic 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,

- a solvent-soluble thermoplastic resinous material on said conductive material, and
- a non-continuous layer of photoconductive material on said thermoplastic material,

whereby an image formed electrostatographically on said photoconductive layer may be made permanent in said diazo compound coating.

2. A photoelectrosolographic film material comprising a flexible film strip forming a film base,
- a coating on said base containing a light-sensitive diazo compound,
- a layer of aluminum of less than one micron thickness on said diazo compound coating,
- a layer of solvent-soluble thermoplastic resinous material of less than two microns thickness on said aluminum layer,
- and a layer of selenium in the order of 0.2 micron thickness on said thermoplastic material,

whereby an image formed electrostatographically on said selenium may be made permanent in said diazo compound coating.

3. For use in photoelectrosolography,

a composite film comprising

a film base having successive layers of

a layer containing a light-sensitive diazo compound,

a thin transparent layer of conductive material,

a solvent-soluble thermoplastic resinous material, and

a non-continuous layer of a photoconductive material,

whereby an image formed electrostatically in the photoconductive layer will be initially deposited on the conductive material when the thermoplastic layer is dissolved, thereby to form a filter for subsequently forming a visible image in said layer containing a diazo compound.

4. For use in photoelectrosolography, a composite film as defined in claim 3 wherein said diazo compound is capable of being developed by heat.

5. The composite film of claim 3,

wherein said layer containing a diazo compound comprises a diazo material capable of being developed by a coupling reaction.

6. The method of photoelectrosolography which includes the steps of

uniformly charging the photoconductive surface, comprising a non-continuous layer of photoconductive material, of a film base record medium,

optically exposing said surface to a light image to form an electrostatic image in the form of a charge pattern,

dissolving a thermoplastic resinous substrate interposed between said film base and said surface to deposit the exposed areas of photoconductor on a thin, transparent aluminum backing layer under said thermoplastic resinous substrate while washing away the unexposed areas,

thereby to form an image on the aluminum backing made of the photoconductor,

blanket exposing the aluminum backing with ultraviolet light to form a latent image corresponding to said photoconductor image in a layer containing a diazo compound under the aluminum layer,

developing the image in the diazo compound, and removing the aluminum and photoconductive material leaving a permanent image on the film base.

7. The method of claim 6

wherein the developing step comprises heating.

8. The method of claim 6

wherein the developing step comprises subjecting the record medium to ammonia vapor.

9. The method of claim 6

wherein the step of removing the aluminum and photoconductive material precedes the development step.

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10. The method of photoelectrosology 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

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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 12

wherein the step of forming the image comprises heating the film to form bubbles in said layer containing a diazo compound.

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