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3,525,613

THERMOPLASTIC DEFORMATION IMAGING PROCESS

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5 Claims

ABSTRACT OF THE DISCLOSURE

A thermoplastic deformation imaging process using a recording member comprising a layer of thermoplastic photoconductive insulating material having a surface provided with an overall, substantially uniform, light-scattering pattern. This pattern may be produced by subjecting the surface of said layer, while soft, to electronic bombardment.

This invention relates to electrophotography and more specifically to improved electrophotographic recording members and methods.

In the art of electrostatic printing, electrostatic images are produced on an insulating surface and may then be rendered visible. Electrostatic images may be directly produced on an insulating surface by scanning thereover, in vacuum, with an electron beam. When the insulating surface comprises the surface of a thermoplastic layer, heat development can be employed to produce a surface-modulated or rippled image which can thereafter be viewed by means of a schlieren optical system. A method for preparing surface modulated tape is described in Thermoplastic Recording by W. E. Glenn, Journal of Applied Physics, vol. 30, No. 12, December 1959.

In the thermoplastic recording method described by W. E. Glenn, the thermoplastic layer must be maintained in a vacuum during the time the electrostatic image is created thereupon by the electron beam. In addition, for all practical purposes, the heat developed rippled image requires a special optical system such as a schlieren system for viewing.

It is a general object of this invention to provide improved materials for and methods of electrostatic printing for producing visible images.

It is another object to provide improved transparent photoconductive members which can be processed into projection slides and films.

A still further object of this invention is to provide improved electrostatic printing methods for producing projection slides and films.

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A further object of this invention is to provide improved recording members for and methods of electrophotography which obviate the need for applying developer materials to an electrostatic image.

Yet another object of this invention is to provide improved recording members for and methods of electrophotographically preparing projection slides and films without the need of recording in a vacuum or the need for special viewing apparatus.

These and other objects and advantages are accomplished in accordance with this invention, generally speaking, by providing a recording member which comprises a layer of thermoplastic photoconductive insulating material having a surface provided with an overall, substantially uniform, light-scattering pattern. This light-scattering surface may have much the same appearance as does frosted glass. Such recording members may be prepared, for example, by forming a layer comprising a solid solu-

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tion of a dye intermediate in an organic resinous thermoplastic material. A surface of the layer is then heated to at least the softening temperature of the solid solution. Thereafter the surface of the layer is subjected to electronic bombardment, while soft whereupon minute depressions are formed in the layer and are so closely spaced as to provide a light-scattering, frosted appearance. Upon cooling, the minute depressions are frozen in the layer surface. By "electronic" bombardment is meant bombarding with electrified particles such as ions or electrons.

In the methods of this invention, electrostatic latent images are produced on layers of thermoplastic photoconductive insulating material by electrophotographic techniques. By using such methods on the previously described recording members or in various combinations with the techniques employed in preparing such recording members, visible images can be produced which include smooth surface areas and light-scattering areas. Smooth surface areas are produced on portions of the photoconductive surface which have been exposed to light while light-scattering areas are produced or left unchanged in portions which have not been exposed to light.

RECORDING MEMBERS

As mentioned heretofore, the recording members of this invention include a layer of organic thermoplastic photoconductive insulating material. It is preferred that material be employed which has a narrow temperature range over which transition occurs from the solid to the softened state and vice versa. By way of illustration, such a layer may be prepared from the following materials:

Example I

- 27.8 parts by weight of a 36% solution of polystyrene in toluene such as, for example, a solution of "Styron" PS-2
- 7 parts by weight of the leuco base of malachite green, bis-(4,4'-dimethylaminophenyl) phenyl methane
- 4 parts by weight of a chlorinated paraffin such as, for example, Chlorowax 70
- 20 parts by weight methyl ethyl ketone

The leuco base of malachite green is dissolved in the polystyrene solution. The chlorinated paraffin is dissolved in the methyl ethyl ketone to make a second solution. The two solutions are then mixed together to form a final solution. The final solution is coated on a suitable substrate such as, for example, conductive glass or metallized transparent film.

A preferred substrate comprises high quality glass such as lantern slide glass having on one surface thereof a vacuum-deposited metallic conductive film, or a tin oxide film made by spraying tin chloride solution on hot glass. The final solution is applied to the conductive film by well known techniques such as, for example, flow coating, dip coating or spin coating. The solvent is then evaporated from the coating on the slide to produce thereon a thin uniform photoconductive layer. When preparing a transparent slide with this coating, it is preferred that a small area of the conductive film be bared of photoconductive coating to provide means for electrically contacting or grounding the conductive film.

Another preferred substrate comprises high-melting film such as, for example, one sold under the trademark "Mylar" or "Cronar." A conductive surface can be readily produced on such a film by vacuum deposition of a metal such as, for example, copper or aluminum. A thermoplastic photoconductive layer can be readily produced on the metallized film by applying the final solution described above by well known methods such as, for example, roll coating, flow coating or dip coating. Once

the coating on the film is dried, a highly flexible photoconductive film is provided.

Heat may be applied to the thermoplastic photoconductive layer on the metallized glass or film substrate to accelerate the drying thereof. Once dried, continued heating for from two to three minutes at a temperature of about 180° C. will produce a faint green tint in the clear coating. After being heated in this manner, the layer on the substrate has maximum photoconductive response to visible light of about 6300 Å. and has another response peak at about 4200 Å. It also has a relatively sharp thermoplastic transition point at about 50° C.

A thermoplastic photoconductive layer, prepared as described above, has a smooth surface with a glossy or specularly reflecting appearance. This surface is converted into a light-scattering surface by means of the combined effect of electronic bombardment and heat. The surface of the layer is heated to a temperature of 50° centigrade, or above, to make the surface soft and malleable. While the surface is still soft it is subjected to electronic bombardment, as by a discharge of ions from a corona generating device, to convert the smooth surface into the desired light-scattering surface.

When the thermoplastic photoconductive layer comprises a coating on a lantern slide or other heat resistant substrate, heating can be readily accomplished on an ordinary hot plate. For example, with the substrate positioned on a hot plate at 140° C., the temperature of the layer can be raised to 50° C. or more in a few seconds. Time and temperature are not important so long as the surface of the layer is made soft and malleable. Overheating presents no problem since the purpose of softening the surface is also achieved when the layer is liquified. In the alternative, heating may be accomplished by any other convenient technique such as infra-red exposure or radio-frequency heating.

A convenient device for electronic bombardment of the layer surface comprises a fine wire corona generating device. Such a device may comprise one or more fine wires at a corona generating potential of 5,000 or more volts, such as is commonly employed in electrophotography. A coated slide, heated as described before, is removed from the hot plate and positioned on a grounded metal plate, coated side up. The fine wire corona generating device is then passed over the coating two or more times to bombard the coating surface with ions. Uniform coverage of the coating surface can be insured by employing a somewhat circular motion of the corona generating device. During bombardment, the coating surface cools sufficiently to freeze the bombardment-formed light-scattering deformations. The grounded plate, mentioned above, can and probably does function as a heat sink to accelerate cooling. This, while convenient, is not necessary. An ambient cooling may be sufficient. Bombardment of the coating surface with electrons or other electronic particles also produces the desired results but may require more elaborate equipment.

A thermoplastic photoconductive layer can also be provided with a built-in half tone screen pattern to enhance the grey scale rendition of reproduction of continuous tone images. Such a pattern can be produced by subjecting a heat-softened layer to ion bombardment with an appropriate screen imposed between the ion source and the smooth surface of the thermoplastic photoconductive layer. For example, a grid of fine parallel wires can be positioned just above the smooth, heat-softened surface. Ions passing through the grid produce a pattern of fine light-scattering bars on the layer surface which are frozen by cooling the layer. Electrical bias applied to the grid provides means for controlling the width of the light-scattering bars and also means for producing a graded light scattering bar pattern corresponding to a graded half tone screen such as those employed in silver halide photography. A light-scattering dot pattern can be produced in a like manner using an interposed mask similar to the type of aperture mask employed in producing color

kinescopes. Ions passing through the apertures (holes) in the mask produce light-scattering dot areas on the surface of the thermoplastic photoconductive layer. Light scattering screen patterns can also be produced by scanning the softened surface of the layer with an electron beam, beam scanning and modulation being controlled to produce either a line or dot pattern as desired.

IMAGE REPRODUCTION

Several methods of image reproduction may be practiced using the above-described recording elements. In some of the methods a recording element having a light scattering (frosted) surface (prepared as in Example I) is employed. For example, a light-scattering image can be produced in a matter of seconds on a coated lantern slide by a simple three step process as follows:

(1) With the slide positioned on a grounded plate, a corona generating device, described above, is passed over the coating on the slide to produce a substantially uniform electrostatic charge of either negative or positive polarity on the coating surface. This step is carried out in darkness or in safe light to which the layer is insensitive.

(2) With a photographic transparency resting on the coating, it is exposed for about one second to about 200 foot-candles of light from a tungsten lamp to produce an electrostatic latent image on the layer which includes light discharged areas and other areas where the charge is substantially unaffected because masked from the light. Exposure time can be substantially decreased by increasing light intensity. Projection exposure techniques can be employed with equal facility.

(3) A visible image is produced on the coating by heating, on a hot plate, for a few seconds. Formation of the image can be observed during heating under safe-light conditions. As soon as areas on the coating are seen to smooth out and become glossy, the slide is removed from the hot plate and allowed to cool, whereupon the visible image made up of both smooth and frosted areas is frozen in the coating surface.

The sequence of the above steps may be varied from that indicated without detracting from the results achieved. For example, all three steps may be carried out simultaneously. The exposure step (2) may precede both the charging step (1) and the heating step (3) the latter steps being carried out in sequence or simultaneously.

Reproduction methods may also be employed wherein one starts with a smooth surfaced recording member such as can be prepared with the materials specified in Example I. These methods combine, as mentioned heretofore, techniques for producing frosted surfaces (as in Example I) with electrophotographic techniques. For example, in a continuous process, one can start with a smooth surfaced coated slide, convert the smooth surface into a light-scattering surface, electrophotographically produce an electrostatic image on the light-scattering surface and then convert exposed areas thereof, with heat, to smooth areas and form the desired image. Or, a smooth-surfaced slide can be exposed to a light image to produce a conductivity pattern therein and thereafter be subjected to ion bombardment and heat to produce a frost image on the coating.

When recording elements are prepared and processed as described herein many important advantages become readily apparent. The frosted images which are produced have excellent contrast with a good range of gray scale rendition. When transparent coatings and substrates are employed, slides or films can be produced for viewing in ordinary slide or film projectors obviating (although they are useful in) schlieren projection systems. When the processed slide is used in ordinary projectors, the dark areas of the projected image correspond to the light-scattering areas on the slide. With schlieren projection, the sense of the projected image is reversed i.e. the

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bright areas of the projected image correspond to the light-scattering areas on the slide.

The photoconductive layer of Example I and the examples which follow include at least one dye intermediate dissolved in an organic resinous material. The resinous material not only acts as a binder for the system but includes or comprises a material which reacts, in the solid state, with the dye intermediate to form a third material which acts as a sensitizer for the photo-conductive system. The formation of this sensitizer can be brought about by exposure of the solid solution to incident radiation such as visible or ultra-violet light or with heat as in Example I. The sensitizer is a dye formed from the dye intermediate. In most cases, less than one percent of the dye intermediate need be converted to the sensitizer to provide maximum photoconductive sensitivity, formation of more sensitizer merely increases the amount of color in the layer. With only trace amounts of sensitizer needed, photoconductive layers are prepared which are substantially transparent to light within the visible spectrum. Such layers have a resistivity of at least 10^9 ohm-centimeters in darkness and at least two orders of magnitude (10^2) less when irradiated.

In lieu of the combination of resinous binder materials, polystyrene and chlorinated paraffin, set forth in Example I, many other resinous materials or combinations thereof may be employed as binders in the thermoplastic photoconductive layers described herein. Suitable resinous materials include the following:

(1) Chlorinated paraffins, such as Chlorowax 70, Diamond Alkali Co., Cleveland, Ohio.

(2) Polyvinyl chloride.

(3) Polyvinyl chloride copolymers, such as Vinylite VAGH, 91% vinyl chloride, 3% vinyl acetate, and 6% vinyl alcohol

VYCM 91% vinyl chloride and 9% vinyl acetate

VMCH 86% vinyl chloride, 13% vinyl acetate, and 1% dibasic acid

(4) Polystyrene.

(5) Styrene butadiene copolymers such as Pliolite S-5, the Goodyear Tire and Rubber Co., Akron, Ohio; Piccotex 120, Pennsylvania Industrial Chemical Co., Clairton, Pa.

(6) Hydrocarbon resins such as Piccotex 120, Pennsylvania Industrial Chemical Co., Clairton, Pa.

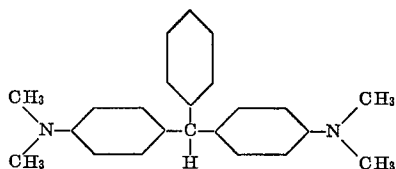
(7) Acrylates and acrylic copolymers, such as Acryloid A-101, Rohm and Haas Co., Philadelphia, Pa.

(8) Epoxy resins, such as Epon 1002, Shell Chemical Co., Houston, Tex.

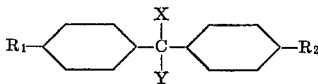
(9) Thermoplastic hydrocarbon terpene resins, such as Piccolyte S-135, Pennsylvania Industrial Chemical Co.

Various combinations of resinous materials can be employed to provide enhanced flexibility in the thermoplastic layers. For example, mixtures of polyvinyl chloride with chlorinated paraffins or hydrocarbon terpene resins will provide highly flexible layers.

To provide a substantially transparent photoconductive layer a dye-intermediate is selected which is soluble in the selected resin. The leuco base of malachite green set forth in Example I is only one of a large class of suitable dye intermediates. It has the formula:

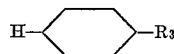


In general, the suitable dye intermediates have the basic formula:

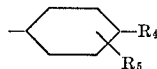


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wherein R_1 and R_2 are selected from the class consisting of monoalkylamino, di-alkylamino, mono-arylamino, and alkylarylamino; X is selected from the class consisting of



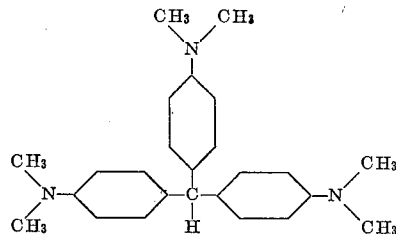
wherein R_3 is selected from the class consisting of H, OH, CH_3 , OCH_3 , R_1 and



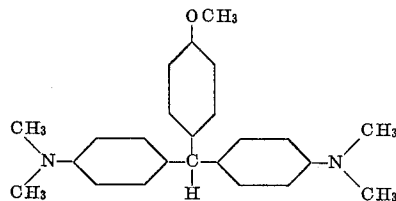
wherein R_4 and R_5 are selected from the class consisting of H, OH, CH_3 and OCH_3 ; and Y is H except when $X+Y$ is double bonded oxygen.

Other suitable dye intermediates which conform to the above basic formula include the following:

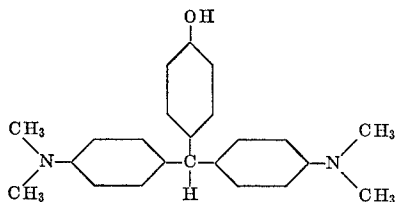
(1) The leuco base of crystal violet, tris-(4,4',4''-dimethylaminophenyl) methane.



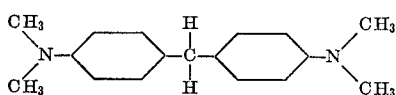
(2) Bis-(4,4'-dimethylaminophenyl)-4''-methoxyphenyl methane.



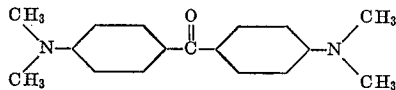
(3) Bis-(4,4'-dimethylaminophenyl)-4''-hydroxyphenyl methane.



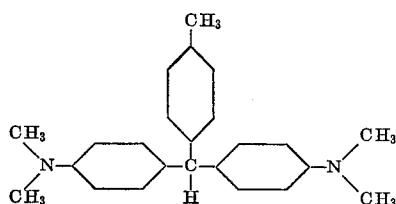
(4) Bis-(4,4'-dimethylaminophenyl) methane.



(5) 4,4'-bis-(dimethylamino) benzophenone (Michler's ketone).

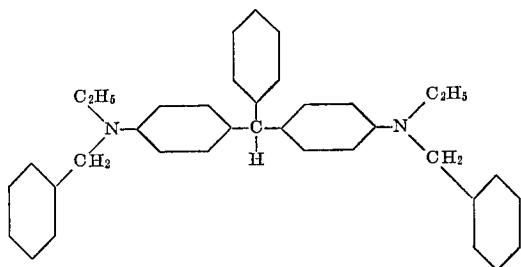


(6) Bis (4,4'-dimethylaminophenyl) 4''-tolyl methane.

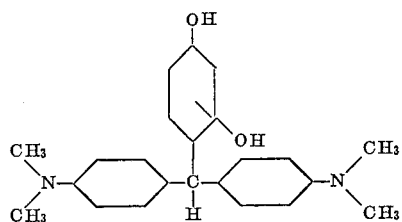


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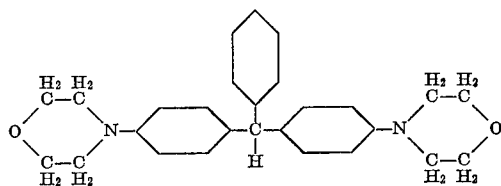
(7) Bis-(4,4'-ethyl-benzylaminophenyl) phenyl methane.



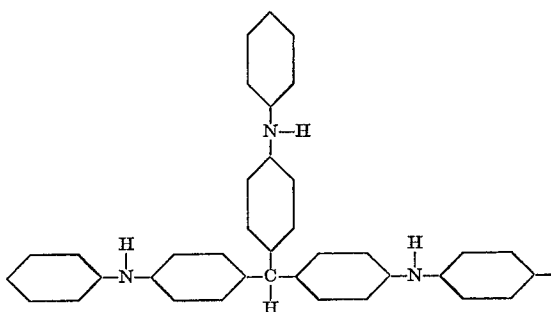
(8) Bis-(4,4'-dimethylaminophenyl) 2'',4''-dihydroxyphenyl methane.



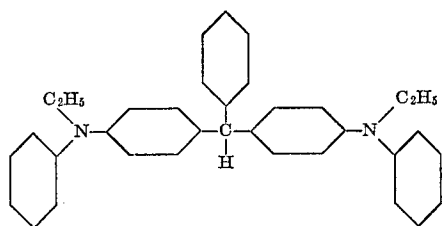
(9) Bis (4,4'-morpholinophenyl) phenyl methane.



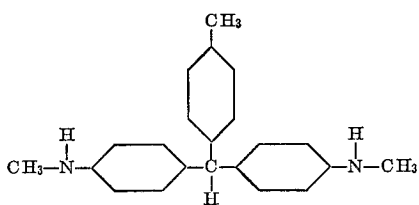
(10) Tris-(4,4',4''-phenylaminophenyl) methane.



(11) Bis-(4,4'-ethylphenylamino phenyl) phenyl methane.

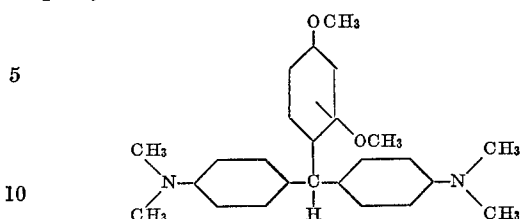


(12) Bis-(4,4'-methylaminophenyl) 4''-tolyl methane.

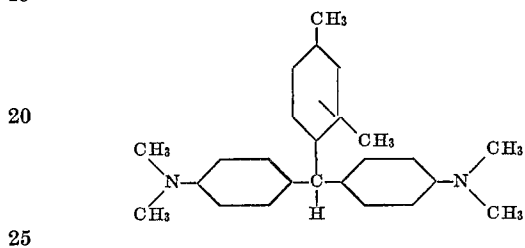


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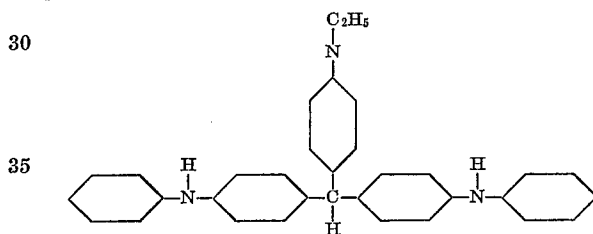
(13) Bis-(4,4'-dimethylaminophenyl)-2'',4''-dimethoxyphenyl methane.



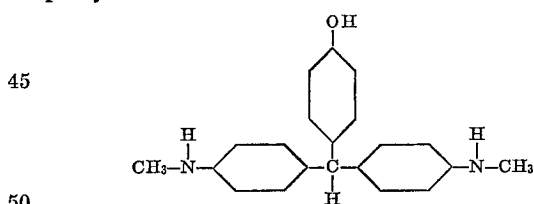
(14) Bis - (4,4' - dimethylaminophenyl) - 2'',4'' - xylyl methane.



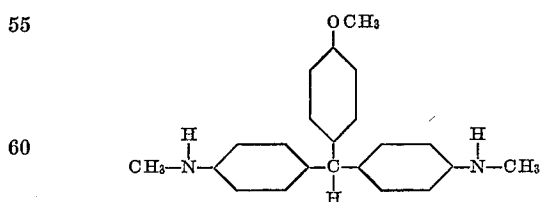
(15) Bis-(4,4' - phenylaminophenyl) - 4'' - ethylamino-phenyl methane.



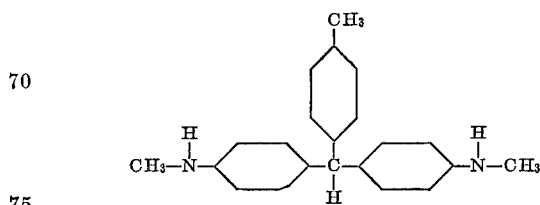
(16) Bis - (4,4' - methylaminophenyl) - 4'' - hydroxyphenyl methane.



(17) Bis - (4,4'-methylaminophenyl)-4''-methoxyphenyl methane.

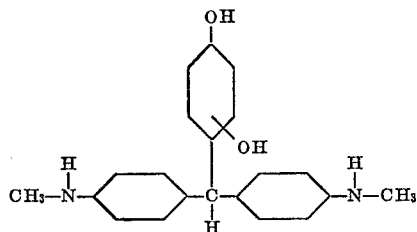


(18) Bis - (4,4'-methylaminophenyl) - 4''-tolyl methane.

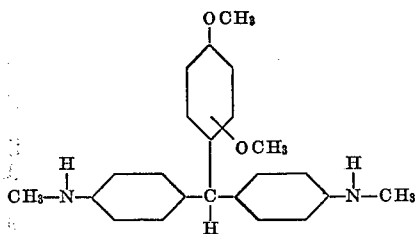


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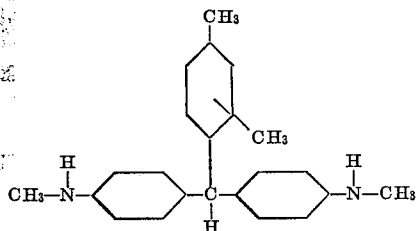
(19) Bis - (4,4'-methylaminophenyl - 2'',4''-dihydroxyphenyl methane.



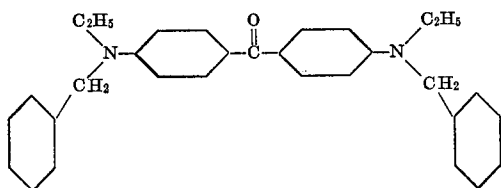
(20) Bis - (4,4'-methylaminophenyl) - 2'',4''-dimethoxyphenyl methane.



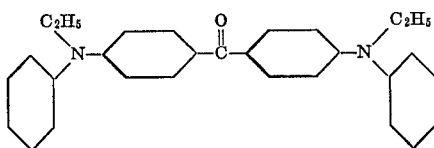
(21) Bis - (4,4'-methylaminophenyl) - 2'',4'' - xylyl methane.



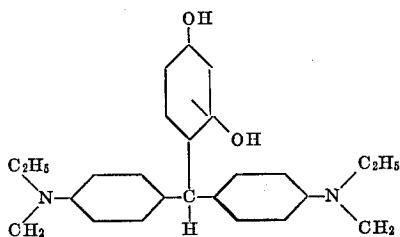
(22) 4,4'-bis-(ethyl-benzylamino) benzophenone.



(23) 4,4'-bis(ethyl-phenylamino) benzophenone.

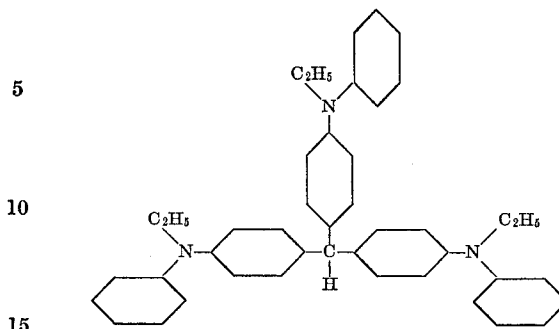


(24) Bis - (4,4'-ethyl-benzylaminophenyl) - 2'',4''-dihydroxyphenyl methane.



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(25) Tris - (4,4',4''-ethylphenylaminophenyl) methane.



Photoconductive compositions are conveniently prepared, for example, by dissolving a quantity of the resinous material in a suitable solvent such as, for example, methyl ethyl ketone, toluene or mixtures thereof and, when the resinous material is completely dissolved, adding to the solution a quantity of the dye intermediate. The proportion of dye intermediate to resinous material may vary over a wide range. The choice of resinous material as well as the dye intermediate can change the optimum ratio for a given use. In many instances, it is desirable that a photoconductive layer or coating be as transparent as possible. For such purposes 0.2 part by weight or less of dye intermediate for each part by weight of resinous material can be employed. For some purposes, the color of a photoconductive film or coating may not be of major concern. For such purposes, up to 1.4 parts by weight or more of dye intermediate for each part by weight of resinous material may be employed. The solubility of a particular dye intermediate in a particular resin should also be taken into consideration. In some instances, if a solution is prepared containing too much dye intermediate the excess thereof will, upon drying, crystallize out of solution which generally is undesirable.

Further illustrations of compositions which can be used to form transparent photoconductive layers exhibiting thermoplastic properties which are useful in the same manner as described in connection with Example I include the following solutions:

Example II

2.5 parts by weight bis-(4,4'-dimethyl-aminophenyl) phenyl methane

and

5.0 parts by weight of a styrene-butadiene copolymer such as, for example, Pliolite S-5B by the Goodyear Tire and Rubber Co., Akron, Ohio.

dissolved in

42.0 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening temperature of about 55 to 57° C.

Example III

2.5 parts by weight of bis-(4,4'-dimethyl-aminophenyl) phenyl methane

and

5.0 parts by weight of styrene-butadiene copolymer (Pliolite S-5D)

dissolved in

42.0 parts by weight of methyl ethyl ketone.

A layer from this solution has a softening temperature of about 56 to 58° C.

Example IV

1.5 parts by weight of bis-(4,4'-dimethyl-aminophenyl) phenyl methane

and

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5.0 parts by weight of styrene-butadiene copolymer (Pliolite S-5)
dissolved in

42.0 parts by weight of methyl ethyl ketone.

A layer from this solution has a softening point of about 54 to 56° C.

Example V

1.0 part by weight of tris-(4,4',4''-dimethylaminophenyl) methane

and

5.0 parts by weight of styrene-butadiene copolymer (Pliolite S-5)
dissolved in

42.0 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening point of about 85 to 87° C.

Example VI

1.0 part by weight of tris-(4,4',4''-dimethylaminophenyl) methane

and

5.0 parts by weight of a hydrocarbon resin such as, for example, Piccotex P-120, Pennsylvania Industrial Chemical Corp., Clairton, Pa.

and

1.6 parts by weight of a polyvinyl chloride copolymer such as, for example, GEON 400X-110, B. F. Goodrich Chemical Co., Akron, Ohio

dissolved in

50.6 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening point of about 50 to 52° C.

Example VII

2.5 parts by weight of bis-(4,4'-dimethyl-aminophenyl) methane

and

5.0 parts by weight of a high styrene copolymer such as, for example, Marbon-9200 LLV, Marbon Chemical Co., a division of Borg-Warner Corp., Gary, Ind.

and

1.2 parts by weight of a vinyl chloride copolymer such as, for example, Vinylite VYCM, Union Carbide Plastics Co., a division of Union Carbide Corp., New York, N.Y.

dissolved in

72.0 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening point of about 50° C.

Example VIII

2.5 parts by weight of bis-(4,4'-dimethyl-aminophenyl) methane

and

5.0 parts by weight of a high styrene copolymer (Marbon M-1100 TMV)

1.6 parts by weight of a polyvinyl chloride copolymer GEON 400X-110)

dissolved in

50.0 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening point of about 48 to 50° C.

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Example IX

1.0 part by weight of bis-(4,4'-dimethyl-aminophenyl) phenyl methane

and

5.0 parts by weight of a hydrocarbon resin (Piccotex P-100)

and

1.6 parts by weight of a vinyl chloride copolymer (Vinylite VMCH)

dissolved in

50.0 parts by weight of methyl ethyl ketone.

15 A layer made from this solution has a softening point of about 40° C.

Example X

1.0 part by weight of tris-(4,4',4''-dimethyl-aminophenyl) methane

and

5.0 parts by weight of a polystyrene resin such as for example, Styron PS-2, The Dow Chemical Co., Midland, Mich.

and

1.6 parts by weight of a vinyl chloride copolymer (Vinylite VMCH)

30 dissolved in

50.0 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening point of about 52° C.

Example XI

35 1.0 part by weight of tris-(4,4',4''-dimethyl-aminophenyl) methane

and

40 5.0 parts by weight of polystyrene resin (Styron PS-2)

and

1.6 parts by weight of polyvinyl chloride copolymer (GEON 400X-110)

45 dissolved in

50.0 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening point of about 47° C.

Example XII

50 1.0 part by weight of tris-(4,4',4''-dimethyl aminophenyl) methane

and

55 5.0 parts by weight of hydrocarbon resin (Piccotex P-120)

and

1.6 parts by weight of a vinyl chloride copolymer (Vinylite VMCH)

60 dissolved in

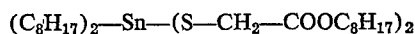
50.0 parts by weight of methyl ethyl ketone.

A layer made from this solution has a softening point of about 63 to 65° C.

Various modifying agents may be added to the foregoing compositions to vary the physical properties or appearance thereof provided they do not interfere with the electrical properties. Flexibility can be enhanced, for example, by including in a composition, such as that of Example I, a small amount of a plasticizer, such as, for example, tricresyl phosphate, butyl phthalylbutyl-glycolate, tris-2,3-dibromo-propyl)phosphate, or di-(2-ethyl-hexyl) phthalate. Such a composition can be coated on a flexible substrate or can be formed into self-supporting

flexible films. A self-supporting film may be produced by flow-coating a mirror-finish metal plate with the composition to form a photoconductive coating on the plate. The coating is then physically stripped from the plate and thus provides a self-supporting photoconductive film. Additional solvents can also be added, such as, for example, toluene to produce the desired coating thickness of the dry finished thermoplastic photoconductive layer.

When a composition is prepared wherein a dye intermediate is dissolved in a non-halogenated resin, enhanced photoconductive response can often be obtained or at least ensured by including in the composition at least a trace amount of a compatible non-volatile halogenated compound such as, for example, tris-(2,3-dibromopropyl) phosphate or any compatible chlorinated hydrocarbon. Many of the compositions contemplated herein, when coated on a substrate or formed into a film, may have a tendency to form color which may be undesirable under some circumstances. Color formation in a film or coating can be substantially retarded by including in the compositions a small amount of stabilizer for the dye intermediate thereof. A specific example of a suitable stabilizer is one having the formula



(Thermolite 20, Metal and Thermit Corp., Rahway, N.J.). Other materials such as procatechol, 2-hydroxy-4-methoxy benzophenone, and 2,2'-dihydroxy-4-methoxy benzophenone may also be used. Some compositions including such a stabilizer will remain substantially colorless for a considerable time unless subjected to intense ultraviolet radiation.

What is claimed is:

1. A method of recording on a smooth surface of a layer of thermoplastic photoconductive insulating organic material comprising the steps of:

heating said surface to a temperature at least equal to the softening temperature of said material;

before the temperature of said surface is reduced below said softening temperature, subjecting said surface to electronic bombardment to convert said smooth surface into a light-scattering surface;

exposing said light-scattering surface to a light image to form an electrostatic latent image thereon and

again heating said surface to at least said softening temperature to cause light discharged areas of said light-scattering surface to be reconverted into substantially smooth areas.

2. A method of recording on a layer of thermoplastic photoconductive insulating organic material comprising the steps of:

shielding said layer from activating illumination to maintain the resistivity of said material at a high value;

exposing a smooth surface of said layer to a light image to produce a latent conductivity pattern in said layer;

heating said surface to at least the softening temperature of said material; and,

before the temperature of said surface is reduced to less than said softening temperature, subjecting said smooth surface to electronic bombardment to convert unexposed areas of said surface into light-scattering areas.

3. A method of recording on a layer of thermoplastic photoconductive insulating organic material comprising the steps of:

simultaneously heating a smooth surface of said layer to a temperature at least equal to the softening tempera-

ture of said material and exposing said surface to a light image; and,

before the temperature of said surface is reduced to less than said softening temperature subjecting said surface to ion bombardment to convert unexposed smooth areas on said surface into light-scattering areas.

4. A method of recording on a layer of thermoplastic photoconductive insulating organic material, having a light-scattering surface formed by bombarding said layer with ions or electrons, said method comprising the steps of:

applying a substantially uniform electrostatic charge to said surface;

exposing said surface to a light image to form an electrostatic image thereon; and

heating said surface to a temperature at least equal to the softening temperature of said thermoplastic material to cause light discharged areas of said surface to be converted from light-scattering areas to substantially smooth areas.

5. A method of recording on a layer of thermoplastic photoconductive insulating material, having an exposed light-scattering surface formed by bombarding said layer with ions or electrons,, said method comprising the steps of:

exposing said surface to a light image to form a conductivity pattern in said layer; thereafter,

applying substantially uniform electrostatic charge to said surface to produce thereon an electrostatic image in conformity with said pattern; and

heating said surface to a temperature at least equal to the softening temperature of said thermoplastic material to convert selected areas of said surface from light-scattering areas to substantially smooth areas in conformity with said electrostatic image.

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U.S. Cl. X.R.

96—1.5; 340—173

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,525,613 Dated August 25, 1970

Inventor(s) Frederick Hermes Nicoll

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11, lines 60 and 61, reading "2.5 parts by weight of bis-(4,4'-dimethyl-aminophenyl) methane" should read -- 1.0 parts by weight of tris-(4,4',4''-dimethylaminophenyl) methane --

SIGNED AND
SEALED
NOV 1 1970

NOV. 17, 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents