

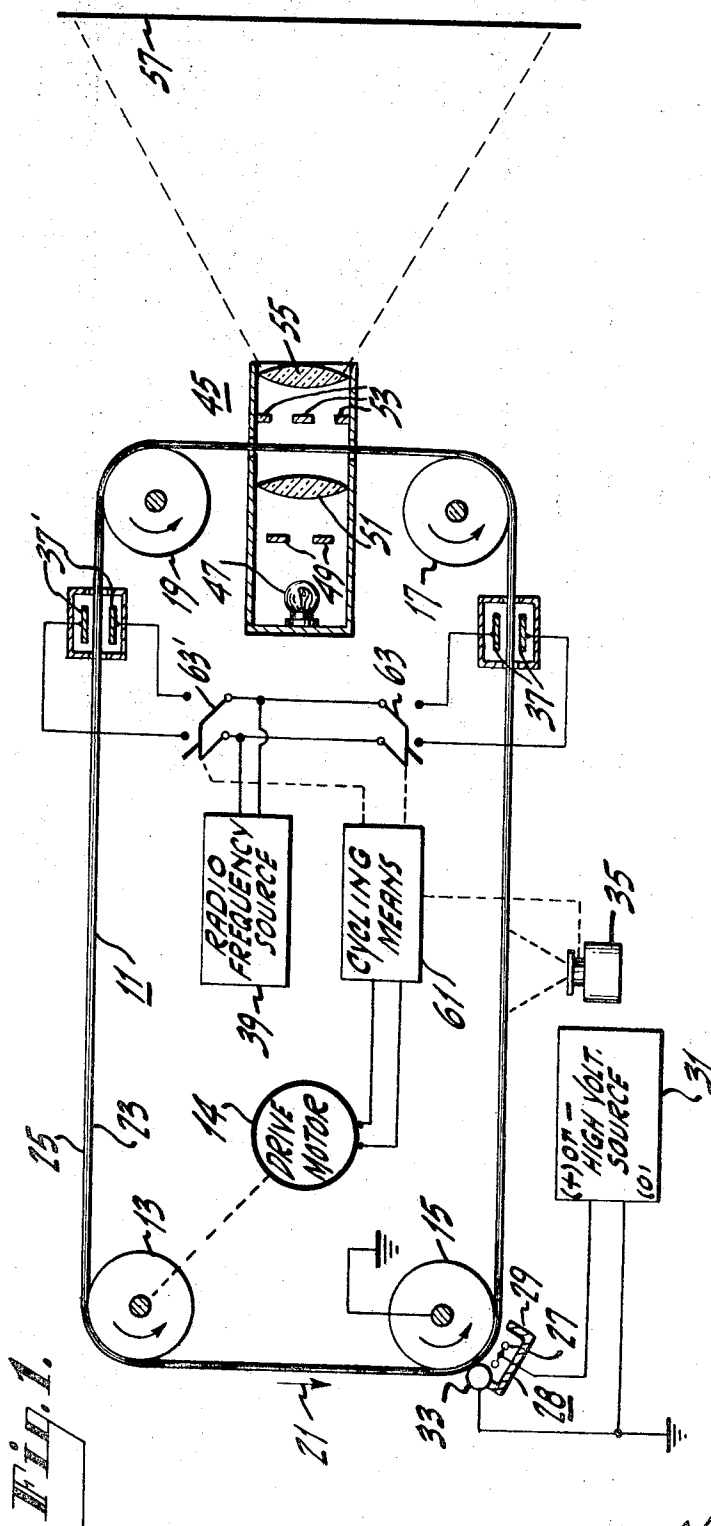
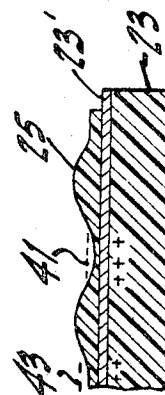
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3,547,628

PROCESS OF THERMOPLASTIC DEFORMATION IMAGING

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PROCESS OF THERMOPLASTIC DEFORMATION IMAGING

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Continuation of application Ser. No. 106,702, May 1, 1961. This application Mar. 28, 1966, Ser. No. 544,643
Int. Cl. B41m 5/18, 5/20; G03g 5/06
U.S. Cl. 96—1.1

6 Claims

ABSTRACT OF THE DISCLOSURE

In a method of storing information in the form of surface modulations on a deformable layer which is both photoconductive and thermoplastic, the information is applied by electrophotographically producing a latent electrostatic image on the surface of said layer and then softened by heating to produce the surface modulations.

This application is a continuation of application Ser. No. 106,702, filed May 1, 1961 and now abandoned.

This invention relates to improved methods of electrostatic recording and more specifically to improved methods of and means for preparing and utilizing surface modulations on a thermoplastic photoconductive layer.

In some methods of reproducing images such as, for example, by means of schlieren optics, surface modulations on a transparent slide or film can be projected onto a viewing screen as a visible image. One method for preparing surface modulated tape is described in *Thermoplastic Recording* by W. E. Glenn, *Journal of Applied Physics*, volume 30, Number 12, December 1959. Briefly this method includes writing with an electron beam onto a high-melting base film coated with a transparent conductive coating and overcoated with a thin film of low-melting insulating thermoplastic. Writing with the electron beam lays down a charge pattern on the thermoplastic in accordance with the information to be stored. The film is then heated to the softening point of the thermoplastic. Electrostatic forces between the charges on the film and a ground plane depress the surface where the charges occur. The film is then cooled below the softening point of the thermoplastic to freeze the surface modulations. A major disadvantage of this method resides in the fact that the recording steps have to be carried out in vacuum. Usually the recording film is stored on reels in a vacuum chamber and must be demounted from the vacuum before being used in a schlieren projection system. The complexity of this method of recording also makes it difficult to use the surface modulated film immediately after the record has been made.

Accordingly, it is a general object of this invention to provide improved methods of producing surface-modulated films.

It is another object of this invention to eliminate the need for recording within a vacuum chambers in producing surface-modulated films.

Yet another object is to provide improved methods of thermoplastic recording on thermoplastic photoconductive layers.

A still further object is to provide improved methods of image reproduction wherein surface modulations are continuously projected as light images on a viewing screen.

These and other objects and advantages are accomplished in accordance with this invention by producing surface modulations on a thermoplastic photoconductive layer. This layer comprises a transparent thermoplastic photoconductive material. It is well known that the resistivity of a photoconductive layer will decrease with increasing temperature. The layer has a resistivity in

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darkness at its softening or melting temperature of at least 10^9 ohm-centimeters. In light it has a resistivity at least two orders of magnitude less than the dark resistivity.

An electrostatic charge image is electrophotographically produced on the surface of the layer. This may be accomplished, for example, by producing an overall electrostatic charge on the surface and then exposing the surface to incident radiation. Because of the difference in the resistivity of the layer in darkness and in light the incident radiation substantially reduces or removes completely the charge in irradiated areas, thereby forming the electrostatic image. The layer is then heated to at least its softening point, whereupon surface modulations corresponding to the charge image form on the surface.

Once the surface modulations are so formed the layer is allowed to cool, thereby freezing the modulations. In continuous reproducing systems, the surface modulated layer may immediately pass to a projection station, which may comprise a schlieren optical arrangement, where the surface modulation image is converted into a visible light image. Subsequent to projection, the surface modulation image can be erased by heat whereupon the layer is ready for reuse.

This invention also includes apparatus for producing the aforementioned surface modulations. In general, the apparatus includes means for producing a substantially uniform electrostatic charge on the surface of the thermoplastic photoconductive layer, means for producing a light image incident upon the surface of the layer, and means for heating the layer at least to its softening point. In a continuous reproducing apparatus, an optical projection station is provided for converting the surface modulations into a projected light image.

Other objects and advantages appear from the following detailed description and the accompanying drawings wherein:

FIG. 1 is a schematic diagram in elevation of apparatus for recording and projecting surface modulation images on a thermoplastic photoconductive layer in accordance with this invention.

FIG. 2 is an enlarged fragmentary schematic view in cross section illustrating the formation of the surface modulation image on the layer of FIG. 1.

In practicing this invention, a thermoplastic photoconductive insulating layer is employed which preferably has a high degree of light transmissivity and which has a narrow temperature range over which transition occurs from the solid to a softened state and vice versa. By way of illustration, such a layer may be prepared from the following material.

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 produced by the Dow Chemical Co., Midland, Mich.

7 parts by weight of the leuco base of malachite green, bis-(4,4'-dimethyl-aminophenyl) phenyl methane.

4 parts by weight of a chlorinated paraffin such as, for example, Chlorowax 70, manufactured by the Diamond Alkali Co., Cleveland, Ohio.

20 parts by weight methyl ethyl ketone.

The 7 parts of the leuco base of malachite green are dissolved in the polystyrene solution. The remaining materials are made into a second solution comprising chlorinated paraffin dissolved in the methyl ethyl ketone. The two solutions are then mixed together and 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 vac-

um deposited conductive film such as, for example, tin chloride. The solution of Example I 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 for use in the methods of this invention, 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 photoconductive layer can be readily produced on the metallized film 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 a photoconductive layer on a 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. When prepared in this manner, the layer on the substrate will have maximum photoconductive response to visible light of about 6300 Å. and will have another response peak at about 4200 Å. It will also have a relatively sharp thermoplastic transition point at about 50° centigrade.

Surface modulations can be produced on the layer of Example I by employing electrostatic printing techniques. One specific method includes the following steps:

(1) Electrostatic charging.—With the substrate of example I grounded or on a grounded plate, a substantially uniform electrostatic charge is applied to the layer by passing thereover a corona generating device which includes at least one fine wire to which is applied a potential of about $\pm 5,600$ volts. Some photoconductive layers are more efficiently charged with negative polarity, others with positive polarity. However, with respect to the photoconductive layers specifically described herein either polarity of charge may be employed with about equal efficiency. This step is carried out in darkness or in safe light to which the layer is insensitive.

(2) Exposing.—With a photographic transparency resting on the layer, it is exposed for about one second to about 200 foot candles of light from a tungsten lamp to produce an electrostatic image consisting of charged areas on the layer which correspond to the dark areas of the transparency. Exposure time can be substantially decreased by increasing the light intensity. Projection exposure techniques can be employed with equal facility.

(3) Developing.—A visible surface modulated image is produced on the layer by heating it and its substrate for about 3 to 15 seconds at a temperature of about 140° centigrade which will raise the temperature of the layer to at least 50° centigrade. Time and temperature are not critical in this step so long as temperature and/or time are not sufficient to discharge the layer before surface modulations are produced. Surface modulations can be simply produced by placing the layer and its substrate on a hot plate (140° C.) and observing the layer while it is illuminated with low-angle safe-light (yellow). As soon as ripples are seen to form on the surface of the layer it is removed from the hot plate and allowed to cool whereby a surface modulation image freezes in the layer. If desired, the layer and substrate may be removed from the hot plate and contacted to a metal plate which will function as a heat sink to accelerate freezing of the surface modulated image. The freezing step will require only about one-half the time required to develop the surface modulation image. Once the surface modulation image is produced as described in this step there is no longer any

need to maintain the photoconductive layer in darkness or under safe-light illumination. The foregoing surface modulated layer can be prepared for re-use by simply heating the layer at a temperature above its softening or melting point until the surface modulations disappear.

An alternative method for producing surface modulations includes the charging step and combines the exposing step and developing steps described heretofore. The exposure light source in this method is one chosen to produce sufficient light of a wavelength to which the photoconductive layer is sensitive while at the same time producing sufficient infra red to heat the layer to at least its softening temperature. Some light sources for this purpose may require more time for properly heating the layer than for producing the latent electrostatic image, thus resulting in overexposure. In such a case, exposure time can be lengthened by using appropriate filters to cut out a portion of the light to which the layer is sensitive. In this way, exposure time and heating time can be appropriately balanced to provide for producing the latent electrostatic image and the surface modulation image in a single step. In the alternative, the layer can be exposed to a light source for a time sufficient to produce an electrostatic image thereon and simultaneously exposed to a separate infra red source for a time sufficient to produce the surface modulation image thereon.

With the foregoing method and employing a conductive glass slide coated with a thermoplastic photoconductive layer an excellent transparency can be prepared in a few seconds for use in a schlieren optic slide projector. For use in a continuous reproduction apparatus it is preferred to employ a flexible transparent metallized film instead of the glass slide.

The methods of this invention may be embodied in an apparatus such as that illustrated in FIG. 1. As shown in the figure, an endless belt 11 is carried on four rollers 13, 15, 17 and 19. One or more of these rollers, such as roller 13, may be driven by any suitable means, such as motor 14, to transport the belt 11 in the direction of the arrow 21. The endless belt 11 preferably comprises a suitable substrate such as, for example, a copper coated, or aluminized transparent film 23 on which a photoconductive thermoplastic layer 25 such as that described in Example I has been laid down.

A substantially uniform electrostatic charge is produced on the photoconductive layer 25 as it passes under a corona generating source 28. This source 28 may comprise an array of fine parallel wires 27 supported in a shield 29. The wires 27 are connected to a high voltage source 31 and a $\pm 5,000$ or more volts are applied to the wires 27 to generate thereby corona for charging the photoconductive layer 25. Charging will be enhanced if, during generation of corona, the metallized film 23 is at ground potential. This can be easily accomplished by maintaining in contact with the exposed surface of the photoconductive layer 25 a grounded conductive roller 33. For best results, the conductive roller should be close to the wires 27. A spacing of $\frac{3}{4}$ inch or less from the nearest wires 27 will provide good results. If desired, the conductive roller 33 and the shield 27 can comprise an integrated structure both being maintained at ground potential. In the alternative, a strip along one edge of the transparent film 23 can be bare of the photoconductive layer 25. In this instance a grounded conductive wheel replaces the conductive roller 33 and is maintained in conductive contact with the bared strip of the transparent film 23.

The photoconductive layer 25 next passes to an exposure station where it is exposed to a light image from an ordinary projector 35. The electrostatic charge in all areas of the photoconductive layer struck by light is substantially reduced or dissipated. In this way, a latent electrostatic image is formed on the photoconductive layer 25.

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In the next step, the photoconductive layer is passed through a heating zone. In a preferred embodiment, this zone includes dielectric heating elements 37 connected to a suitable radio frequency source 39. In the alternative, heating could be accomplished by other means such as a hot filament, radiant heat or hot air. When the photoconductive layer is heated at least up to its softening point, the surface thereof becomes modulated as depicted in much exaggerated form in FIG. 2. In areas where charges remain after exposure to the light image, the charges cause depressions to form in the surface of the layer. Such depressions are illustrated at 41 and 43. FIG. 2 also shows in detail how a strip 23' of the metallized surface of the transparent film 23 can be left bare so that a conductive wheel can be contacted thereto.

When the endless belt 11 passes out of the heating zone formed by the dielectric heating elements 37, it quickly becomes cooled to ambient temperature and the surface modulations on the photoconductive layer 25 are frozen in place. Cooling of the belt 11 can be accelerated if the roller 17 is formed of heat conductive material such as, for example, copper so that it can function as a heat sink for the belt 11.

Once the surface modulations are frozen on the endless belt 11, it is passed to a schlieren optic projector 45. This projector will include, for example, a point light source 47, a slotted baffle 49, a condensing lens 51, a grid of bars 53 in registry with the slots in the baffle 49 and a projection lens 55. There are several well known schlieren optic systems which could be employed in the apparatus of FIG. 1. For a more complete description of schlieren optic projection, reference is made to U.S. Pat. 2,644,938 to M. Hetzel et al. In the projector 45, the surface modulations on the photoconductive layer 25 cause a visible light image to be projected onto a viewing screen 57.

When the surface modulated photoconductive layer 25 has served its purpose in the projector 45, it may again be heated to a temperature above its softening point to erase the surface modulations therefrom. To this end, additional dielectric heating elements 37' connected to the source 39 are provided. Complete erasure of the surface modulations from the photoconductive layer may require a higher temperature or a longer heating cycle than that produced by heating element 37.

Once the surface modulations have been erased, the endless belt is ready to be recycled to produce another schlieren projected image.

In operating the device of FIG. 1, movement of the endless belt 11 is desirably controlled by a start-stop cycling means 61. Such control is desirable in the case where images projected on to the screen 57 are viewed for different periods of time than required for exposure of the electrostatic images. In addition, such control can provide for regulation of exposure from projector 35, and for regulation of heating with the RF heating elements 37 and 37'. The drive motor 14 thus provides frame by frame movement of the endless belt 11. During such movement, the endless belt 11 passes under the charging wires 27 and the photoconductive layer 25 becomes electrostatically charged. Since this layer 25 is a good insulator in darkness, it will retain its charge until struck by light from the projector 35.

Under control of the cycling means 61 the endless belt 11 is stopped during exposure to a light image from the projector 35. During this exposure, an image being viewed on the screen 57 may be retained for a time in excess of that required for complete exposure of the frame which is at rest under the projector 35. To prevent over-exposure, the cycling means 61 is coupled to the shutter or light source of the projector to provide an exposure time within a range of from about 0.1 to 10 seconds depending on the intensity of the light source in the projector 35. Again, due to the high dark resistivity of the photoconductive layer 25, the electrostatic image produced

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thereon by exposure will be retained for a considerable length of time.

The exposed frame of the photoconductive layer next passes between the RF heating elements 37 and comes to rest therebetween. The elements 37 are preferably of a size to heat one complete frame at a time. Excessive heating at this time would dissipate the charge image on the photoconductive layer 25. To prevent excessive heating, switching means 63 is provided in the RF heating circuit controlled by the cycling means 61. RF energy may be applied to the heating elements 37 for only a fraction of a second and then cut off whereby the photoconductive layer 25 is quickly heated and cooled to produce and freeze, *in situ*, a surface modulated image on the photoconductive layer. This surface modulated image is then cycled to move into the schlieren projector 45 for viewing on the screen 57.

In order to erase the surface modulated image from the photoconductive layer 25, the image frame is next cycled to pass from the schlieren projector 45 into the space between the RF heating elements 37'. At this station, heat will generally be applied to the photoconductive layer 25 for a time in excess of that employed to produce the surface modulated image in order that complete erasure thereof may be ensured. Control for this purpose is provided by switching means 63' in the RF heating circuit controlled by the cycling means 61. Upon erasure of the surface modulated image from the frame of the photoconductive layer 25 by means of the heating elements 37' that frame is ready for recycling to produce another schlieren image.

Under some circumstances, it may be desirable to produce a permanent surface modulated record. This can be easily accomplished with only minor modifications to the apparatus of FIG. 1. For this purpose, the endless belt 11 would be replaced by an elongated web, the roller 15 would become a supply roller for the web and the roller 13 a take up roller for the web. With such a structure there would be no need for erasing the surface modulations on the web and the heating elements 37' could be dispensed with.

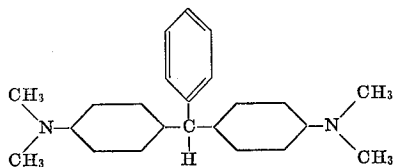
In lieu of the combination of resinous materials, polystyrene and chlorinated paraffin, set forth in Example I, many other resinous materials or combinations thereof may be employed in the thermoplastic photoconductive layers described herein. Suitable resinous materials include the following:

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

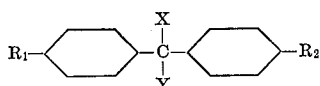
Various combinations of resinous materials can be employed to provide enhanced flexibility in the thermoplastic layers. For example, mixtures of polyvinyl chloride with chlorinated paraffins or hydrocarbon terpene resins will provide highly flexible layers.

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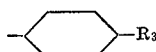
To provide a substantially transparent photoconductive layer, a dye-intermediate is selected which is soluble in the selected resin. The leuco base of malachite green set forth in Example I is only one of a large class of suitable dye intermediates. It has the formula:



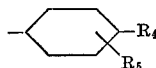
In general, the suitable dye intermediates have the basic formula:



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 H,



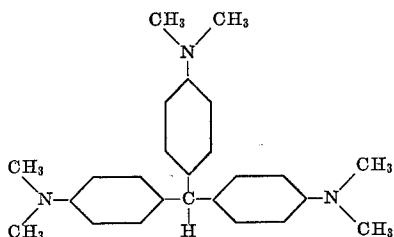
wherein R_3 is selected from the class consisting of H, OH, CH_3 , OCH_3 , R_1 and



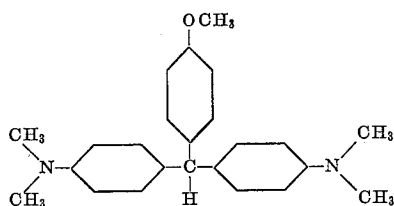
wherein R_4 and R_5 are selected from the class consisting of H, OH, CH_3 and OCH_3 ; and Y is H except when $X+Y$ is double bonded oxygen.

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

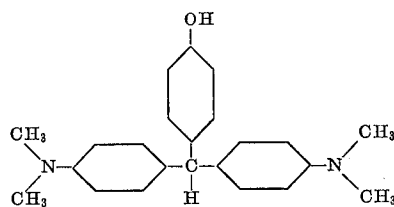
(1) The leuco base of chrystal violet, tris-(4,4',4''-dimethylaminophenyl) methane



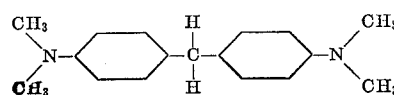
(2) Bis - (4,4' - eimethylaminophenyl) - 4'' - methylphenyl methane



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

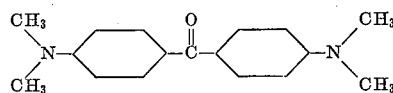


(4) Bis-(4,4'-dimethylaminophenyl)methane

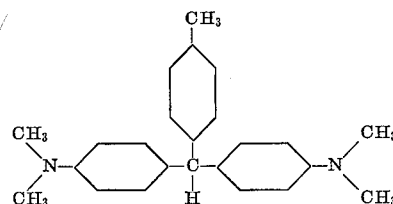


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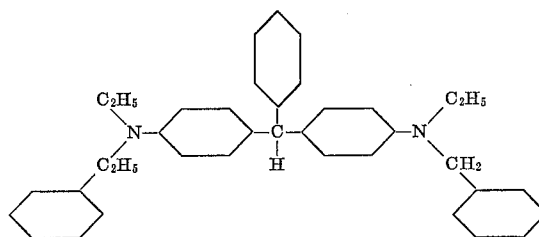
(5) 4,4'-bis-(dimethylamino)benzophenone (Michler's ketone)



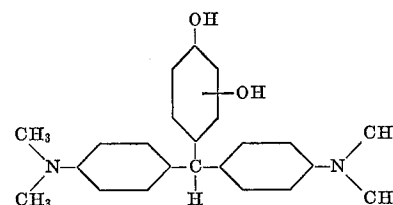
(6) Bis-(4,4'-dimethylaminophenyl)-4''-tolyl methane



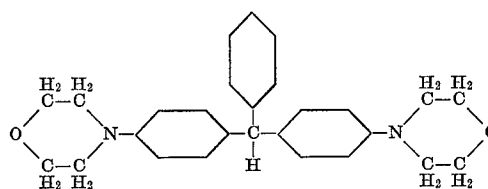
(7) Bis - (4,4'-ethyl-benzylaminophenyl)phenyl methane



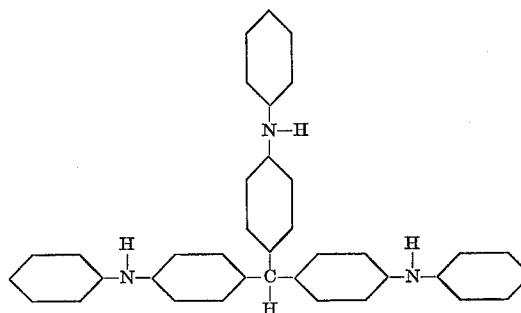
(8) Bis - (4,4' - dimethylaminophenyl) - 2'',4'' - dihydroxyphenyl methane



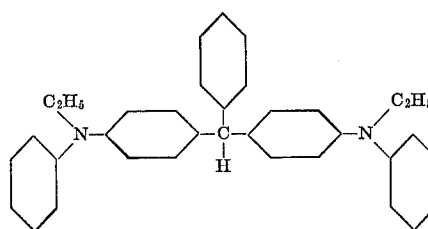
(9) Bis-(4,4'-morpholinophenyl)phenyl methane



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

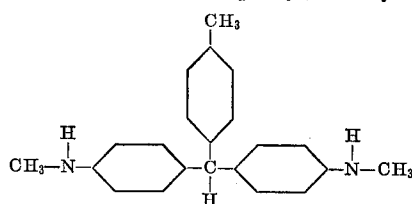


(11) Bis - (4,4'-ethylphenylaminophenyl)phenyl methane

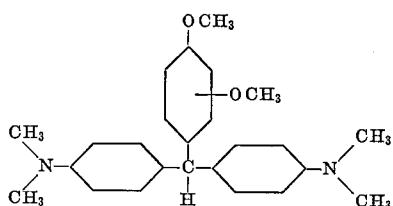


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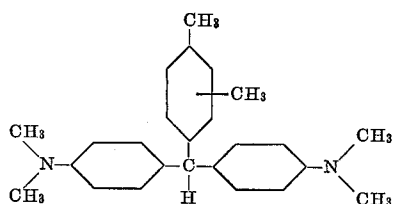
(12) Bis - (4,4'-methylaminophenyl)-4''-tolyl methane



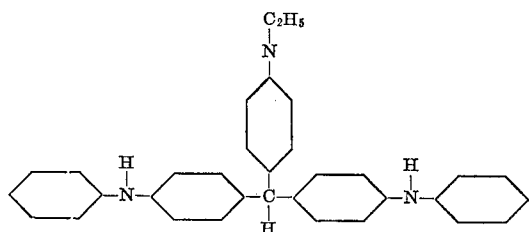
(13) Bis - (4,4' - dimethylaminophenyl) - 2'',4'' - di-methoxyphenyl methane



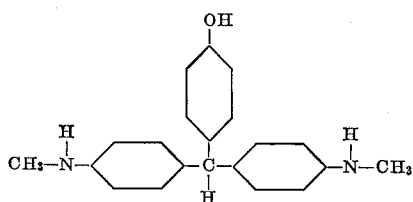
(14) Bis - (4,4' - dimethylaminophenyl) - 2'',4'' - xylyl methane



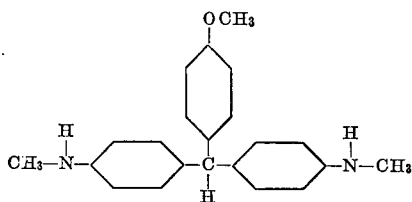
(15) Bis - (4,4' - phenylaminophenyl) - 4'' - ethylaminophenyl methane



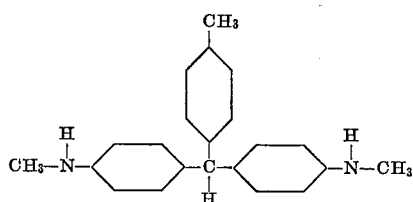
(16) Bis - (4,4' - methylaminophenyl) - 4'' - hydroxyphenyl methane



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

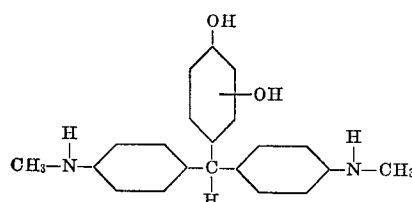


(18) Bis - (4,4' - methylaminophenyl) - 4'' - tolyl methane

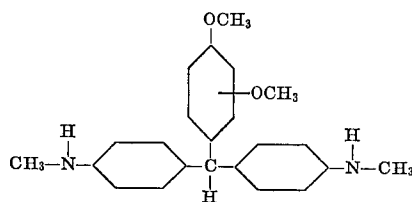


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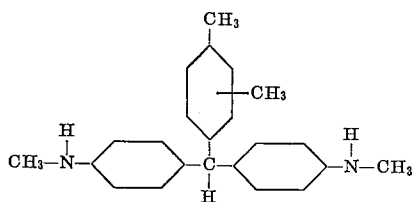
(19) Bis - (4,4' - methylaminophenyl) - 2'',4'' - dihydroxyphenyl methane



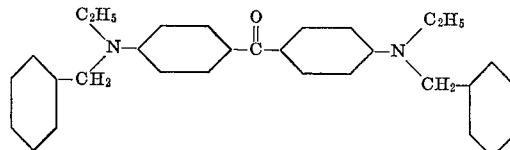
(20) Bis - (4,4' - methylaminophenyl) - 2'',4'' - di-methoxyphenyl methane



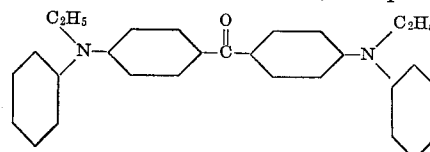
(21) Bis - (4,4' - methylaminophenyl) - 2'',4'' - xylyl methane



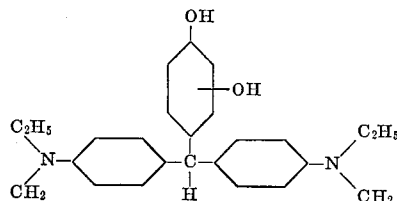
(22) 4,4' - bis - (ethyl-benzylamino) benzophenone



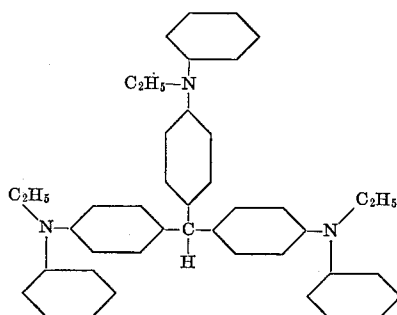
(23) 4,4' - bis - (ethyl-phenylamino) benzophenone



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



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



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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 of 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 0.8 parts 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 made 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

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 54 to 56° C.

EXAMPLE V

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

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

and

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

and

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.

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

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50.0 parts by weight of methyl ethyl ketone.

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'-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)

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

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

and

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

and

1.6 parts by weight of 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 47° C.

EXAMPLE XII

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

and

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

and

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

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.

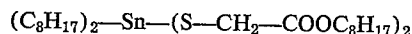
Various modifying agents may be added to the foregoing compositions to vary the physical properties or appearance thereof provided they do not interfere with the electrical properties. Flexibility can be enhanced, for example, by including in a composition, such as that of Example I, a small amount of a plasticizer, such as, for example, tricresyl phosphate, butyl phthalylbutylglycolate, tris-(2,3-dibromopropyl)phosphate, or di-(2-ethylhexyl)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

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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 pyrocatechol, 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 ultra-violet radiation.

I claim:

1. A method of strong information comprising providing a recording element consisting essentially of a single layer of a transparent material that is both thermoplastic and photoconductive and having a resistivity in darkness at its softening temperature of at least 10^9 ohm cm. and in light a resistivity of at least 2 orders of magnitude less than said resistivity in darkness, electrophotographically producing a latent electrostatic image on a surface of said layer by the combination of steps of providing said layer with an electrostatic charge and exposing said layer to an image of light and shadow, thereby neutralizing the charges in the light struck areas of said image by the action of the light on said layer, heating said layer to at least said softening temperature to produce surface modulations in the form of ripples thereon in conformity with said electrostatic image, wherein the depressed portions of said ripples correspond to charge-retaining areas of said image and raised portions of said ripples correspond to image areas where the charge has drained off, and cooling said layer to freeze said ripples in place.

2. A method according to claim 1 in which said latent electrostatic image is formed by first providing a surface of said layer with a substantially uniform electrostatic charge and then exposing said layer to said image of light and shadow.

3. A method of reproducing visible images of light and shadow comprising a transparent layer of material that is both thermoplastic and photoconductive and which has a resistivity in darkness of at least 10^9 ohm cm. at the softening temperature of said layer and a resistivity in light of at least 2 orders of magnitude less than said resistivity in darkness, electrophotographically forming a latent electrostatic image on a surface of said layer by the combined steps of providing said layer with an electrostatic charge and exposing said layer to an image of light and shadow, thereby neutralizing the charges on the light-struck areas of said images by the action of the light on said layer, heating said layer to at least said softening temperature to produce surface modulations in the form of ripples thereon in conformity with said electrostatic image, wherein the depressed portions of said ripples correspond to charge-retaining areas of said image and raised portions of said ripples correspond to image areas where the charge has drained off, cooling said layer to freeze said ripples, and converting said ripples into a visible projected image by projecting light through said layer.

4. The method for storing information on a deformable medium in an image pattern which comprises electrostatically charging a thermoplastically deformable photoconductive medium to establish a uniform charge pattern on its surface, selectively discharging portions of the uniform pattern by activating radiation to yield a latent electric charge image pattern, and heating the deformable

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medium to reduce the viscosity thereof and produce physical deformations corresponding to the latent electric charge image pattern by forces resulting from said latent electric charge image pattern.

5 5. The method for storing information on a deformable medium in an image pattern which comprises electrostatically charging a thermoplastically deformable photoconductive medium to establish a uniform charge pattern on its surface, selectively discharging portions of the uniform pattern by exposure to a light image in accordance with the light intensity variations of an image to yield a latent electric charge image pattern, and heating the deformable medium to reduce the viscosity thereof and produce physical deformations corresponding to the latent electric charge image pattern by forces resulting from said latent electric charge image pattern.

6. The method for storing information on a deformable medium in an image pattern which comprises electrostatically charging a composite recording member comprising a thermoplastic film having a photoconductive material incorporated therein to establish a uniform charge pattern on the surface of the thermoplastic film, selectively discharging portions of the uniform pattern by ac-

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tivating radiation to yield a latent electric charge image pattern, and heating the thermoplastic film to reduce the viscosity thereof and produce physical deformations corresponding to the latent electric charge image pattern by forces resulting from said latent electric charge image pattern.

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