Dec. 13, 1966 F. H. NICOLL 3,291,600

ELECTROPHOTOGRAPHIC RECORDING ELEMENT AND METHOD OF MAKING

Filed Jan. 14, 1963

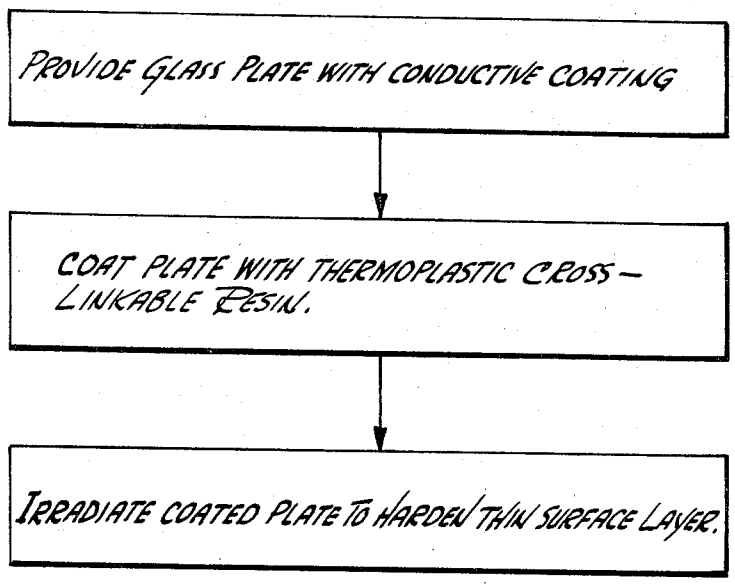


Fig. 1.

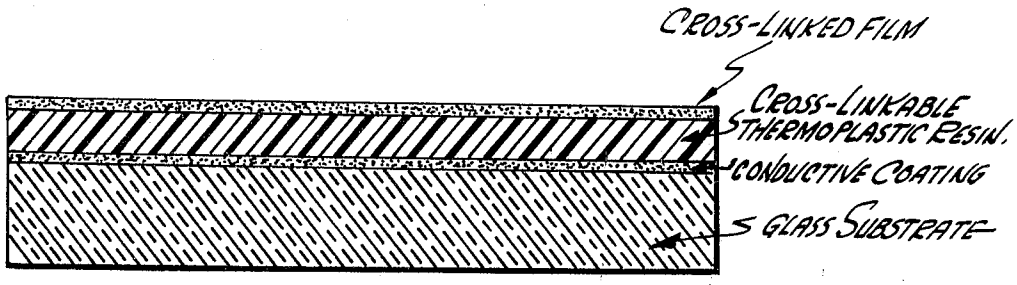


Fig. 2.

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United States Patent Office 3,291,600 Patented Dec. 13, 1966

3,291,600

ELECTROPHOTOGRAPHIC RECORDING ELEMENT AND METHOD OF MAKING

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Filed Jan. 14, 1963, Ser. No. 251,062
10 Claims. (Cl. 96—1)

This invention relates to electrostatic printing and more specifically to improved methods of producing electrostatic recording members and the products of those methods as well as improved electrostatic printing and electrophotographic methods of producing visible images.

In the art of electrostatic printing, electrostatic images are produced on an insulating surface and are then rendered visible. The electrostatic images may be produced by direct charge deposition as by selectively energizing pin electrodes to deposit charges on an insulating surface in a dot pattern. Images so produced are generally rendered visible by applying thereto electroscopic developer particles which are held on the surface by electrostatic forces. This technique of producing and developing electrostatic images is described in greater detail in U.S. Patent 2,919,170 to H. Epstein, issued December 29, 1959, and also in U.S. Patent 2,928,973 to R. W. Crews, issued March 15, 1960. Electrostatic images may also be directly produced on an insulating surface by scanning an electron beam thereover in a vacuum. 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, volume 30, No. 12, December 1959. Electrostatic images on a photoconductive insulating layer may also be produced by electrophotographic techniques as described in "Electrofax" Direct Electrophotographic Printing on Paper by C. J. Young and H. G. Greig, RCA Review, December 1954, volume XV, No. 4.

The foregoing methods of recording are well suited for many practical applications. However, except for the aforementioned thermoplastic recording method, development is generally accomplished with a toner or developer powder. This requires not only means for applying the toner but also means for fixing the toner in place if a permanent image is to be provided. 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 election beam. In addition, the heat developed rippled image often requires a special optical system such as a schlieren system for viewing. With respect to photoconductive layers, selenium and zinc oxide-binder layers, both of which are opaque, have been used. The opacity of such layers has lead to complicated procedures for electrophotographically producing transparent slides and films such as, for example, the electrophotographically producing a loose powder image on a photoconductive layer and thereafter electrostatically transfering the powder image to a transparent insulating layer.

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

Another object of this invention is to provide improved photoconductive members which are essentially self developing as well as methods of producing such members.

It is another object to provide improved transparent photoconductive members which can be processed into projection slides and films as well as methods of producing such members.

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

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

It is another object of this invention to provide improved methods of producing heat-developed images on an electrostatic printing medium among those which do not require schlieren optics for viewing.

Yet another object of this invention is to provide improved methods of producing heat-developed images on an electrostatic printing medium without the need for vacuum chambers.

In the drawing:

FIGURE 1 is a flow sheet illustrating method steps in making a recording element in accordance with the invention, and

FIGURE 2 is a cross-section view of a recording element of the invention.

In accordance with a first embodiment of this invention, many of the foregoing and other objects and advantages are achieved by producing an improved recording member. Such a member may be prepared by forming a polymeric insulating or photoconductive insulating material into a layer. This material is one which is normally heat-deformable or thermoplastic and which includes molecular chains which can be cross-linked when subjected to actinic radiation to render the material substantially non-heat-deformable and insoluble in the polymeric material which has not been so irradiated. Once the layer is formed, an entire recording surface thereon is exposed to actinic radiation to cross-link the polymeric material near the surface of the layer to a depth of up to about 500 Angstrom units to thereby form a thin layer, which film is substantially non-thermoplastic and insoluble in the underlying thermoplastic polymeric material.

A second embodiment of this invention constitutes a method of recording in which one starts with a layer of polymeric insulating material as described above. In this method, a film of cross-linked polymeric material is formed on the layer as described in the first embodiment of this invention. Thereafter, an electrostatic charge pattern is created on the film and it is heated to at least the softening temperature of the thermoplastic polymeric material. Such heating results in a selective break-up of the cross-linked polymeric film coincident with deformation of the underlying thermoplastic material near the interface between it and the film on it. Break-up of the film occurs only in charged areas on the layer and produces a light-scattering image conforming to the charge pattern and having an appearance much like that of frosted glass. Upon cooling, this light-scattering image is frozen on the layer of polymeric material.

In accordance with a third embodiment of this invention, also constituting a method of recording, one again starts with a layer of polymeric insulating material and produces a thin cross-linked film thereon as described heretofore. In this case, however, the polymeric insulating material is one having photoconductive insulating properties and an electrostatic charge pattern or image is produced thereon by electrophotographic techniques. In other respects, the procedures here involved are the same as in the method comprising the second embodiment of this invention.

Another recording method, comprising a fourth embodiment of this invention, again involves the use of a layer of polymeric insulating material. In this method, the entire recording surface of the layer is not irradiated as before. Instead, the layer is exposed to an image pat-

tern of actinic radiation. When so exposed, a film of cross-linked polymeric material is formed but, instead of covering all the layer, the film is formed only in exposed areas, leaving a thermoplastic surface in all unexposed or masked areas on the layer. After exposure, the entire recording surface is provided with a substantially uniform electrostatic charge. Upon heating to the softening temperature of the non-irradiated polymeric material, the cross-linked film in irradiated areas breaks up to again form a light scattering image.

A fifth embodiment of this invention comprises yet another recording method. In this method, one starts with a special recording member comprising a layer of thermoplastic polymeric insulating material having bonded to one surface thereof a film of relatively non-thermoplastic material which is substantially insoluble in the polymeric material. This film having a thickness of up to about 500 angstrom units, may comprise cross-linked polymeric material produced as described in the first embodiment of this invention or it may comprise an entirely different material which has been coated on the surface of the layer. In the instant method, the recording member is exposed to actinic radiation capable of transpiercing the insoluble film on the layer of polymeric material. Exposure is made to a radiation pattern or image and so controlled as to cross-link the irradiated polymeric material underlying the insoluble film to a depth of at least 500 angstrom units. The irradiated polymeric material is thus converted into a high-melting substantially non-thermoplastic material. Thereafter an overall electrostatic charge is applied to the insoluble film and the layer heated to at least the softening temperature of the non-irradiated polymeric material until the insoluble film covering this material breaks up to produce a light scattering image. Wherever the polymeric material has been actinically cross-linked, formation of light scattering areas is prevented.

RECORDING MEMBERS

As mentioned heretofore, recording members used or made in accordance with this invention include an electrically insulating layer of heat-deformable or thermoplastic material. The layer preferably comprises an organic resinous material capable of undergoing cross-linking between molecular chains when subjected to actinic radiation. Among the many such materials having desirable properties, one may cite the following:

(1) Polystyrene.

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

(3) Polyvinyl chloride.

(4) Polyvinyl chloride copolymers, such as Vinylite VAGH, VYCM or VMCH.

(5) Styrene-butadiene copolymers, such as Pliolite S–5, The Goodyear Tire and Rubber Co., Akron, Ohio.

(6) Hyrocarbon resins, such as Piccotex 120, Pennsylvania Industrial Chemical Co.

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

(8) Epoxy base resin which is solid at room temperature 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 modify the physical properties of the insulating layers such as the softening point or flexibility thereof. Other materials may be added to modify the physical properties of the layers, provided they do not interfere with the electrical properties thereof. For example, various plasticizers may be added to enhance flexibility of the layers or to enhance formation of a thermoplastic material into a layer.

The recording members preferably also include a suitable support element for a thermoplastic layer. These include metal plates, glass plates, glass slides coated with conductive tin oxide, high melting films such as "Mylar" or "Cronar" which have been coated with copper or aluminum ,and high-melting conductive plastics.

Example I

A solution is prepared comprising 20% by weight of polystyrene dissolved in toluene. This solution is poured onto a lantern slide coated with conductive tin oxide. The slide is allowed to drain for about one minute and is dried on a hot plate in about ½ minute at 140° C.

The entire exposed surface of the polystyrene layer, so produced on the slide, is then subjected to actinic radiation to cross-link the polystyrene to a depth of up to about 500 angstrom units, the cross-linked polystyrene thus comprising an insoluble thin film adhering to a layer of thermoplastic non-cross-linked polystyrene.

A thin cross-linked film can be produced on a polystyrene layer by subjecting it to many kinds of actinic radiation. For example, the layer can be exposed to short wave length ultra violet light. Specifically, an excellent film can be produced with an exposure of about 5 seconds ⅛ inch from a source emitting ultra violet a portion of which has a wavelength about 2000 angstrom units. An article made by this process is shown in FIGURE 2.

Electron bombardment will also produce an appropriate cross-linked film. It has been found that best results are achieved by electron bombardment with a voltage of about 2000 volts and about 10^{-4} coulombs per square centimeter. If the voltage is too high excessive penetration of the beam will result in cross-linking the polystyrene to too great a depth i.e. more than about 500 angstrom units. An adequate film of cross-linked polystyrene having the desired thickness can also be produced by exposure for less than 30 minutes, 10 inches from a 20 milliamp, 45,000 volt tungsten-target X-ray source through a beryllium window. Here again, if the X-rays penetrate too deeply or are too hard, too deep a film of the polystyrene will be cross-linked.

A lantern slide prepared as above has a surface film of cross-linked polystyrene, less than 500 angstrom units in thickness, overlying and adhering to a heat-deformable layer of polystyrene, 19 microns or less in thickness, on the conductive coating on the glass slide.

ELECTROSTATIC RECORDING

Some embodiments of this invention envisage including the step of producting a thin cross-linked film on a polymeric layer as part of continuous recording or printing processes. For example, having been provided with a lantern slide coated with a thermoplastic polystyrene, such as that of Example I, the first step in such a process constitutes the production of a thin cross-linked film on the slide in the same manner as described in connection with Example I. Thereafter a suitable mask or stencil is superimposed on the coated surface of the slide and it is subjected to a corona discharge to produce an electrostatic image on the coated surface in those areas which are not masked by the stencil. Having produced a charge pattern on the coated slide, it is then heated to a temperature sufficient to soften the polystyrene layer under the cross-linked polystyrene film whereupon a surface deformation results in the areas of the charge pattern to form a clearly visible light scattering image which, upon cooling, is frozen in place.

In the method of the immediately preceeding paragraph, the charge pattern can be readily produced by passing over the masked slide 2 or 3 times a corona generating unit consisting of 1 or more fine wires, 2 to 3 mils in diameter, maintained at a potential of from 4,000 to 7,000 volts while supplying a ground connection to the tin oxide coating on the slide. Heat development can be easily accomplished by contacting the uncoated side of the slide to a hot plate maintained at about 140° C. until the surface deformations are seen to form. These deformations,

which have the appearance of frosted glass, will form in about 9 seconds or less. With the hot plate at 215° C., heat development can be accomplished in about one second.

In this method and in others to be described hereinafter, the thicknesses of the polystyrene layer and of the cross-linked film play important roles. If a polystyrene layer of about 11 microns or less is employed, an interference pattern may be heat developed on the coated slide. For example, an image produced on a slide which has a polystyrene layer about 1 micron thick will result in surface deformations which scatter light which is predominantly blue in color. Slightly thicker layers will result in scattering of green and red light.

For best results in the instant invention, the cross-linked film on the polystyrene should not exceed about 100 A. in thickness. Light scattering patterns can be produced with cross-linked films as thick as 500–1000 A. but only with a corresponding decrease in surface deformation and image contrast. Accordingly, it is generally preferred that the cross-linked film have a thickness of from 50 to 100 A.

In lieu of the stenciling method for producing electrostatic charge patterns on a coated slide, as described heretofore, such charge patterns may be produced by direct deposition of charges in patterns as described in either U.S. Patent 2,919,170 to Epstein or 2,928,973 to Crews mentioned above, or by electron beam scanning as described in the W. E. Glenn publication or in the W. E. Glenn Patent 3,008,006. However, the charge pattern may be produced, heat development will form a visible light scattering image on the coated surface of the slide.

ELECTROPHOTOGRAPHY

A visible light scattering image may also be produced on the coated slide of Example I by a method which is based on the photoconductivity of polystyrene. Although polystyrene is not normally considered as a photoconductive material, when employed in thin layers as are specified herein, it exhibits a photoconductive response when exposed to intense ultra-violet light. Thus, in this method, the first step again comprises actinic irradiation of the polystyrene to produce a thin cross-linked film thereon. A substantially uniform electrostatic charge is then applied to the entire coated surface of the slide as by means of a corona generating unit. It is then exposed to an intense pattern of ultra violet light. Such exposure can be accomplished in a few minutes with light from an arc lamp passing through a suitable mask. Whenever light has struck the coating, the electrostatic charge is dissipated leaving a charge image thereon corresponding to the masked areas. This charge image is then heat-developed as described heretofore to produce a positive light-scattering image.

Slides prepared as described herein may be viewed in an ordinary slide projector. The dark areas of the projected image correspond to the developed or light scattering areas produced on the slide. Such slides may also be viewed by schlieren projection in which case the bright areas of the projected image will correspond to the light-scattering areas on the slide.

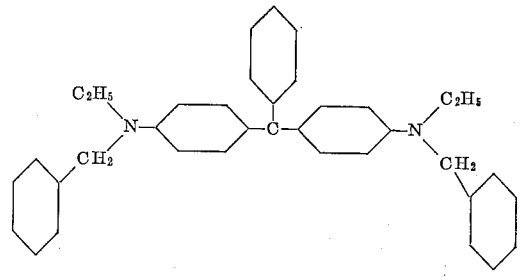
The foregoing electrophotographic method, while satisfactory for many purposes, has limited applicability because the photoconductive response of the polystyrene layer is essentially limited to relatively short wave-length ultra violet light. Response to ultra violet of longer wave-lengths can be enhanced with a polymeric layer produced as follows:

Example II

A coating solution is prepared which consists of:

13.9 grams polystyrene solution (36% by weight solids in toluene)

3.0 grams of the dye intermediate bis-(4,4'-ethylbenzylamino-phenyl) phenyl methane, having this formula:



The latter material is dissolved in the polystyrene solution diluted with about 17 grams of toluene and a conductively coated slide is overcoated therewith to provide thereon a photoconductive layer.

A cross-linked film is produced on the slide by actinic radiation as in Example I. The coated slide is then subjected to corona discharge to provide a substantially uniform electrostatic charge on the coating thereon. It is then exposed to light passing through a photographic transparency. Exposure using two 4 watt black lamps (ultra-violet) held at about 4" from the slide for about 10 seconds or less will produce a latent electrostatic image on the slide. A visible light-scattering image is produced thereon in about one second by contacting the uncoated side of the slide to a hot plate at 215° C.

Preferred recording members include photoconductive layers sensitive to light well above the wavelength of ultra violet. Such layers may be prepared using resins such as those listed heretofore or combinations of such resins and dissolving a suitable dye intermediate therein. The resin not only acts as a binder for but also reacts with the dye intermediate to form a third material which acts as a photoconductive sensitizer. The sensitizer may be a dye formed from the dye intermediate. In many cases, less than one percent of the dye intermediate need be converted to the sensitizer to provide maximum sensitivity to photoconductive layer. Formation of more sensitizer merely increases the amount of color in the layer without any appreciable increase in photoconductive sensitivity. With only trace amounts of sensitizer needed and with dye intermediates and resinous materials, photoconductive layers can be prepared which are substantially transparent to light within the visible spectrum, which have a resistivity in darkness of at least 10^9 ohm centimeters, and which have a resistivity of at least two orders of magnitude (10^2) less when irradiated.

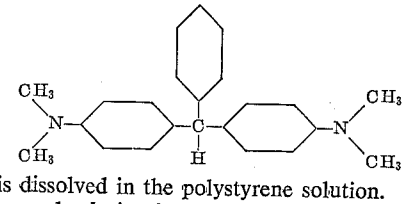
A substantially transparent recording element which includes a photoconductive layer having a high value of photoconductive sensitivity may be prepared as follows:

Example III

A coating solution is prepared which consists of:

(a) 139 grams of polystyrene dissolved in toluene (36% by weight solids) and

25 grams of the dye intermediate bis-(4,4'-dimethylamino-phenyl) phenyl methane, having this formula:



which is dissolved in the polystyrene solution.

(b) a second solution is prepared by dissolving:

4 grams chlorinated paraffin (Chlorowax 70) and

2 grams bis-(4,4'-dimethylamino-phenyl) phenyl methane (same formula as that just above) in

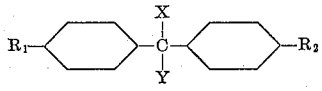
20 grams methyl ethyl ketone

10 grams of solution (a) and 5 grams of solution (b) are then mixed together to form a coating solution.

A special slide is prepared for coating. This slide, having a thin conductive tin oxide layer on one surface, is provided with an additional layer of metal such as nickel or gold by means of vacuum evaporation. Nickel, for example, is evaporated onto the tin oxide layer to a thickness which provides a coating having a resistance of from about 35 to about 110 ohms per square. Contact to the nickel coating is provided for by applying thin strips of conducting silver paint along opposite edges of the nickel layer. The nickel and tin oxide layers are sufficiently thin so as not to detrimentally affect the use of such slides for optical projection. This specially prepared slide is then flow-coated with the aforementioned coating solution to provide thereon, when dried, a photoconductive layer with a thickness of about 25 to 50 microns.

A cross-linked film is produced on the photoconductive coating by actinic radiation as in Example I. The slide is then charged and exposed to a projected image. Exposure is conveniently accomplished with a tungsten lamp using, for example 15,000 foot candle seconds illumination. A light-scattering image is then obtained by passing current through the nickel film to heat develop the slide. Heat development can be accomplished in as little as $\frac{1}{30}$ of one second with from about 6 to 17 watt seconds of heating.

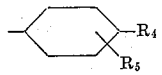
There are many dye-intermediates, other than those specifically set forth in Examples II and III which can be used in the photoconductive layers described herein. In general, suitable dye intermediates which are soluble in suitable thermoplastic resinous materials are selected. Preferred dye intermediates have the general 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,



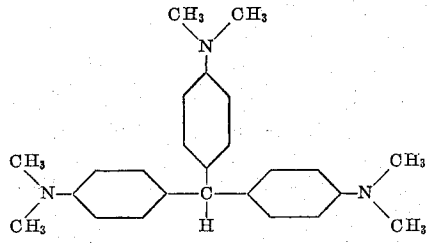
wherein R_3 is selected from the class consisting of H, OH, CH_3, OCH_3, R_1 and



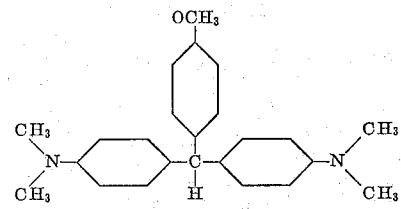
wherein R_4 and R_5 are selected from the class consisting of H, OH, CH_3 and OCH_3; and Y is H except when X+Y is double bonded oxygen.

Example of suitable dye intermediates, other than those of Examples II and III, include the following:

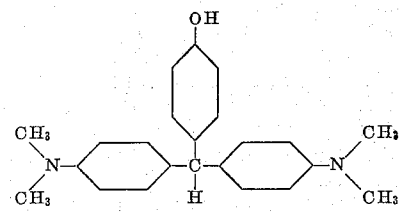
(1) The leuco base of crystal violet, tris-(4,4',4''-dimethylaminophenyl) methane.



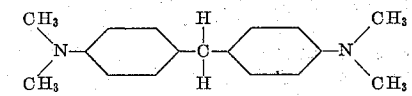
(2) Bis - (4,4'-dimethylaminophenyl)-4''-methoxyphenyl methane.



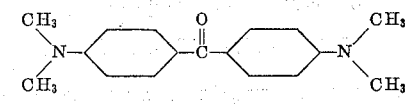
(3) Bis - (4,4'- dimethylaminophenyl)-4''-hydroxyphenyl methane.



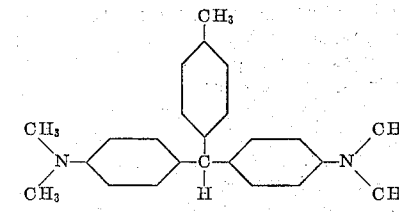
(4) Bis-(4,4'-dimethylamino phenyl)methane.



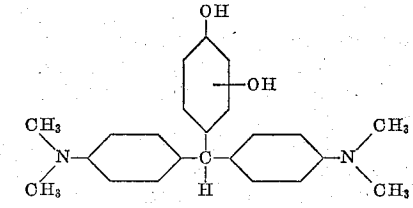
(5) 4,4'-bis-(dimethylamino) benzophenone (Michler's ketone).



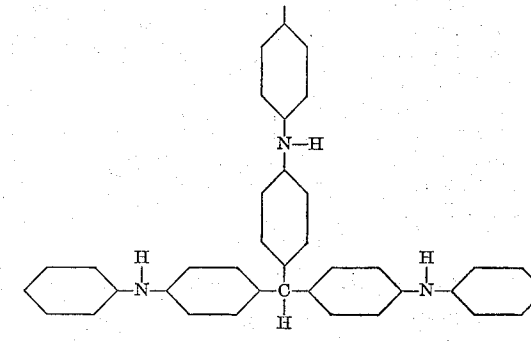
(6) Bis-(4,4'-dimethylaminophenyl) 4''-tolyl methane.



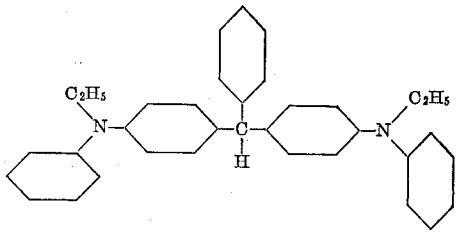
(7) Bis-(4,4'-dimethylaminophenyl) 2'',4'' - dihydroxyphenyl.



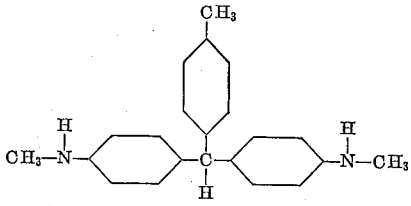
(8) Tris-(4,4',4''-phenylaminophenyl) methane.



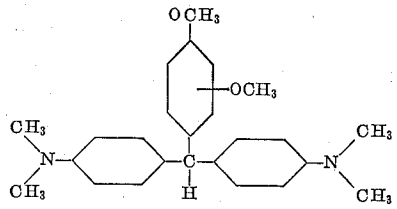
(9) Bis-(4,4'-ethylphenylamino phenyl) phenyl methane.



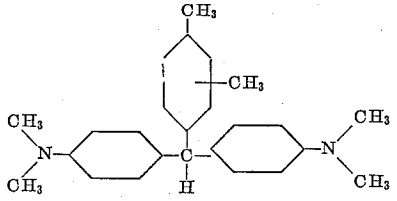
(10) Bis-(4,4'-methylaminophenyl) 4'' tolyl methane.



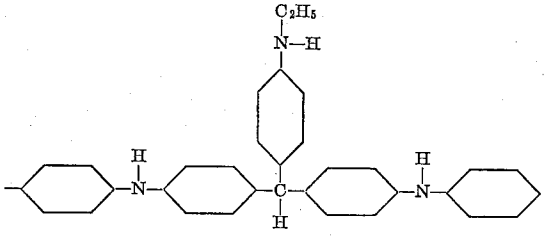
(11) Bis-(4,4'-dimethylaminophenyl)-2'',4'' - dimethoxyphenyl methane.



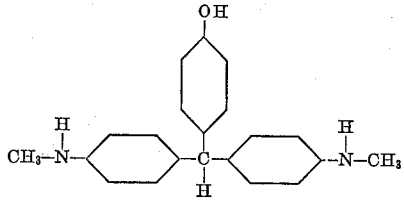
(12) Bis - (4,4' - dimethylaminophenyl) - 2'', 4'' - xylyl methane.



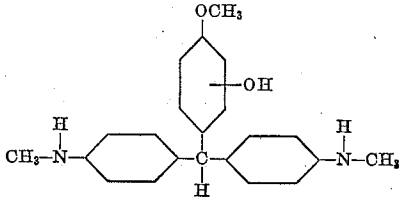
(13) Bis - (4,4' - phenylaminophenyl) - 4''-ethylaminophenyl methane.



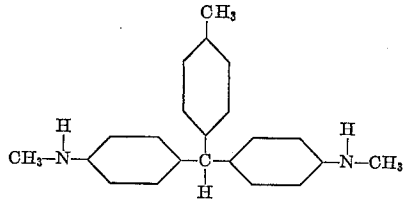
(14) Bis - (4,4' - methylaminophenyl) - 4'' - hydroxyphenyl methane.



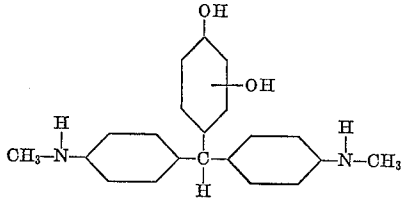
(15) Bis - (4,4' - methylaminophenyl) - 4'' - methoxyphenyl methane.



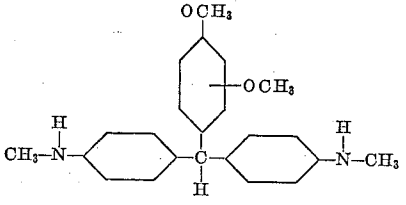
(16) Bis-(4,4'-methylaminophenyl)-4''-tolyl methane.



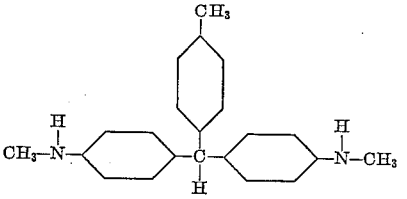
(17) Bis - (4,4' - methylaminophenyl)-2'',4''-dihydroxyphenyl methane.



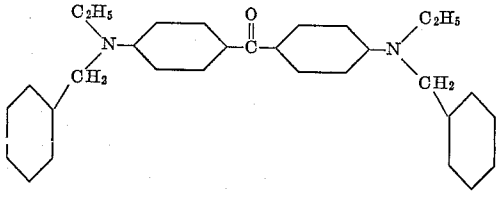
(18) Bis - (4,4' - methylaminophenyl)-2'',4''-dimethoxyphenyl methane.



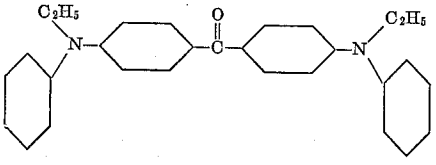
(19) Bis-(4,4'-methylaminophenyl)-2'',4''-xylyl methane.



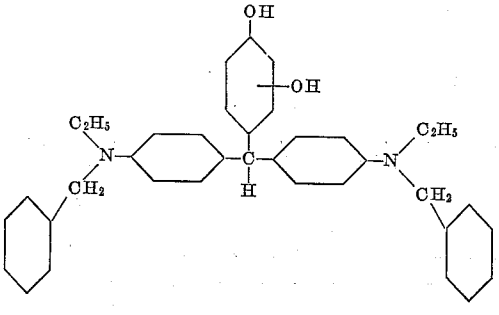
(20) 4,4'-bis(ethyl-benzylamino)benzophenone.



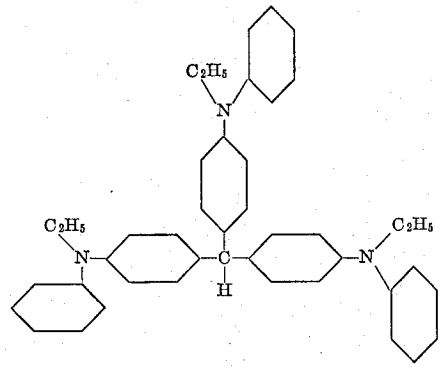
(21) 4,4'-bis(ethyl-phenylamino)benzophenone.



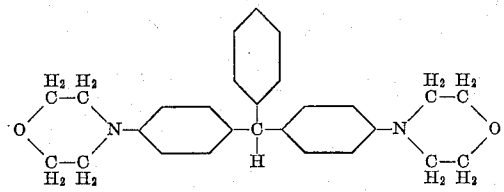
(22) Bis - (4,4' - ethyl - benzylaminophenyl)-2'',4''-dihydroxyphenyl methane.



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



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



ACTINIC RADIATION RECORDING

The present invention includes novel methods of electrostatic printing other than as previously described. These methods include the steps of exposing a heat-deformable polymeric coating, such as polystyrene, to an image pattern of actinic radiation to create, in the exposed areas, a latent image comprising cross-linked polymeric material. After exposure, a uniform over all electrostatic charge is produced on the coating and it is then heated to at least the softening temperature of the non-cross-linked polymeric coating material. This procedure produces a light scattering image in the same manner as described heretofore.

In one of these methods, cross-linking is accomplished in the same manner as described with respect to Example I, for example, by exposure to ultra violet, electron bombardment, X-ray or other suitable actinic radiation. However, instead of subjecting the entire surface of the polystyrene coating to actinic radiation, as in Example I, exposure is accomplished in image configuration. For example, a mask, stencil or photographic transparency can be superimposed on the coating and exposure made therethrough so that a cross-linked film is produced on the coating only in those areas under the open or transparent areas of the mask. Exposure may be accomplished in a similar manner with X-ray or electron bombardment. As an alternative, imagewise exposure may be accomplished by scanning an electron beam over the surface of the coating. However, exposure is accomplished, a light-scattering image is produced by uniformly charging and heat developing the coating in the same manner as described heretofore.

In another of these methods, one starts with a recording member which includes a layer of thermoplastic polymeric material coated with a thin film of insoluble material. The film may comprise cross-linked polymeric material as in Example I or it may comprise a different material. An example of the latter type is prepared as follows:

Example IV

A solution is prepared comprising 20% by weight of polystyrene dissolved in toluene. This solution is poured onto a lantern slide coated with conductive tin oxide. The slide is allowed to drain for about one minute and is dried on a hot plate in about ½ minute at 140° C. Suitable thermoplastic materials may be substituted here-

in for the polystyrene in the same way as in Example I. The sensitivity of the polystyrene to actinic radiation can be enhanced by including therein a dye intermediate in the same manner as in Example II.

After coating, as above, the slide is immersed in a water solution containing about 0.02% by weight of polyvinyl alcohol. The lantern slide is then flushed with deionized water and briefly heated on the hot plate until dry. A lantern slide prepared in this manner has a surface film of polyvinyl alcohol less than 100 Angstrom units in thickness overlying a polystyrene layer of about 19 microns or slightly less in thickness adhering to the tin oxide coating on the lantern slide.

One method by which a visible, light-scattering image can be produced on the slide of Examples I or IV is by superimposing thereon a mask, stencil or photographic transparency and then subjecting the coated surface of the slide to actinic radiation from an ultra-violet source. Such a source may comprise, for example, a commercially available low pressure mercury vapor resonance germicidal lamp. When the slide is exposed through a mask to such a lamp (8 watt) at a distance of about ⅛ inch the ultra-violet light will penetrate the thin film on the slide and cross-link the underlying polystyrene layer at least to the minimum depth of about 500 A. in about 1½ minutes. Cross-linking time can be considerably reduced by exposure to the more intense light of an arc lamp.

After exposure, a corona generating unit is passed over the polyvinyl alcohol film on the slide to provide an overall electrostatic charge on the film. A suitable corona generating unit may comprise 1 or more fine wires, 2 to 3 mils in diameter, maintained at a potential of from about 5,000 to 9,000 volts.

Having produced a substantially uniform electrostatic charge on the coated slide, it is then heated to a temperature sufficient to soften those portions of the polystyrene layer which have not been exposed to and cross-linked by actinic radiation. When so heated, the polyvinyl alcohol film overlying the softened portions of the polystyrene breaks up and distorts the surface of the coated slide to produce a light-scattering image thereon much like that of frosted glass. Heat development of a light-scattering image can be readily accomplished by contacting the uncoated side of the slide to a hot plate maintained at about 140° C. until the light-scattering or frosted image is seen to form. This will occur in about 9 seconds or less. With the hot plate at 215° C., heat development can be accomplished in about one second. Wherever actinic radiation has penetrated the polyvinyl alcohol film to cross-link or harden the underlying polystyrene, no light-scattering effect is produced.

As mentioned heretofore, actinic radiation other than ultra violet may be used during the exposure step to produce crosslinking in the polystyrene layer. These include electron bombardment, X-ray or alpha particle bombardment and others. For example, the polystyrene layer can be cross-linked to more than the minimum required depth by exposure to a 5,000 volt (or more) electron beam using about 10^{-5} coulombs per square centimeter. Adequate cross-linking can also be obtained by exposure for about one-half hour at 10 inches to a 20 milliampere 45,000 volt tungsten-target X-ray source.

Light scattering images can be produced on the slides of the following examples in the same manner as described with respect to the slide of Example IV. With the addition of a suitable dye intermediate, sensitivity to actinic radiation can be enhanced.

Example V

A conductive glass slide is coated with a layer of polystyrene as in Example I. The coated slide is then immersed in a solution of 1 part by weight of gelatin in 10^5 parts water and is then flushed with distilled water and dried.

Example VI

A solution is prepared comprising 2.5% by weight of a thermoplastic hydrocarbon resin (Piccotex 120) in toluene. As in Example IV a conductive glass slide is coated with this solution and a thin film of polyvinyl alcohol.

Example VII

A lantern slide is provided with a polystyrene layer and overcoated with a thin film (50 A.) of cross-linked polystyrene. Overcoating is accomplished by discharge depositing styrene in vacuo, for example, by the method described in U.S. Patent 2,932,591 to J. Goddinan, issued April 12, 1960.

Example VIII

A lantern slide is prepared with a polystyrene coating (Example I) which, when dry, is overcoated with a gold deposit having a mean thickness of about 0.4 A. Such overcoating is conveniently accomplished by means of well known vacuum evaporation or sputtering techniques.

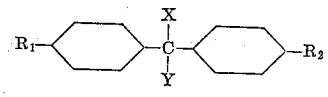
Example IX

A lantern slide is prepared with a thermoplastic resin coating as in Example IV which is overcoated with an aluminum oxide deposit having a mean thickness of about 0.4 A. Overcoating is accomplished by vacuum evaporation of aluminum onto the resin coating. Upon exposure to air the aluminum becomes converted to aluminum oxide.

What is claimed is:

1. A method of producing a recording element comprising the steps of:

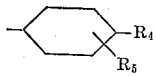
preparing a solution of an insulating, normally thermoplastic polymeric material capable of being rendered substantially non-thermoplastic by being subected to actinic radiation, and a dye-intermediate having the general formula:



wherein R_1 and R_2 are selected from the class consisting of monoalkylamino, di-alkylamino, monoarylamino 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 and 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;

forming a layer having a thickness of greater than about 11 microns from said polymeric material and said dye intermediate; and

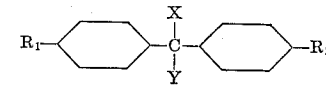
controllable exposing one surface of said layer to said actinic radiation to produce an adherent film at said surface having a maximum thickness of about 500 angstrom units and substantially non-thermoplastic properties.

2. The method of claim **1** wherein said actinic radiation comprises ultra-violet light.

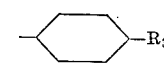
3. A method of forming an electrophotographic recording element comprising the steps of:

forming a solution of an insulating, normally-thermoplastic polymeric material capable of being rendered substantially non-thermoplastic by being subjected to actinic radiation, dissolving in said solution at least

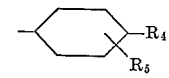
one dye-intermediate soluble in said polymeric material and having the formula:



wherein R_1 and R_2 are selected from the class consisting of monoalkylamino, di-alkylamino, monoarylamino, 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 and 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;

coating a substrate with said solution including said dye intermediate and drying said coating to form a layer having a thickness of greater than about 11 microns comprising a solid solution of said dye-intermediate in said polymeric material; and,

controllably exposing a surface of said layer to said actinic radiation to produce an adherent film at said surface having a maximum thickness of about 500 Angstrom units and substantially nonthermoplastic properties.

4. The method of claim **3** wherein said actinic radiation comprises ultra-violet light.

5. A recording element for electrophotographic printing comprising:

a normally thermoplastic photoconductive insulating layer having a thickness of greater than about 11 microns of polymeric material having molecular chains therein capable of being cross-linked to form a substantially non-thermoplastic polymeric material when subjected to actinic radiation;

a dye-intermediate in said polymeric material, said layer having a resistivity in darkness of at least 10^9 ohm-centimeters and a resistivity when irradiated of at least two orders of magnitude less than said resistivity in darkness; and,

a substantially non-thermoplastic film on said layer including said cross-linked polymeric material, said film having a maximum thickness of up to about 500 angstrom units.

6. A recording element for electrophotographic printing comprising:

a substantially transparent substrate having a coating thereon comprising a substantially transparent, normally thermoplastic, photoconductive insulating layer having a thickness of greater than about 11 microns of polymeric material having molecular chains therein capable of being cross-linked to form a substantially non-thermoplastic polymeric material when subjected to actinic radiation;

a dye-intermediate in said polymeric material, said layer having a resistivity in darkness of at least 10^9 ohm-centimeters and a resistivity when irradiated of at least two orders of magnitude less than said resistivity in darkness; and,

a substantially non-thermoplastic film on said layer including said cross-linked polymeric material, said film having a maximum thickness of up to about 500 angstrom units.

7. A recording element for electrophotographic printing comprising:

a normally thermoplastic photoconductive insulating layer having a thickness of greater than about 11 microns of polymeric material having

dissolved therein at least one dye-intermediate reactive with said polymeric material, and

at least a trace amount of a dye formed in situ from at least one said dye intermediate,

said layer having a resistivity in darkness of at least 10^9 ohm-centimeters and a resistivity when irradiated of at least two orders of magnitude less than said resistivity in darkness,

said polymeric material having molecular chains therein capable of being cross-linked to form a substantially non-thermoplastic polymeric material when subjected to actinic radiation; and a substantially non-thermoplastic film on said layer including said cross-linked polymeric material, said film having a maximum thickness of about 500 angstrom units.

8. A recording element for electrophotographic printing comprising:

a substantially transparent substrate having

a coating thereon comprising a substantially transparent, normally thermoplastic, photoconductive insulating layer having a thickness of greater than about 11 microns of polymeric material having dissolved therein at least one dye-intermediate reactive with said polymeric material, and

at least a trace amount of a dye formed in situ from at least one said dye intermediate,

said layer having a resistivity in darkness of at least 10^9 ohm-centimeters and a resistivity when irradiated of at least two orders of magnitude less than said resistivity in darkness,

said polymeric material having molecular chains therein capable of being cross-linked to form a substantially non-thermoplastic polymeric material when subjected to actinic radiation; and

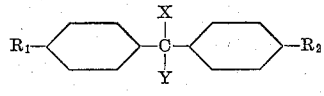
a substantially non-thermoplastic film on said layer including said cross-linked polymeric material, said film having a maximum thickness of about 500 Angstrom units.

9. A recording element for electrophotographic printing comprising:

a normally thermoplastic, photoconductive insulating layer having a thickness of greater than about 11 microns of polymeric material having molecular chains therein capable of being cross-linked to form a substantially non-thermoplastic polymeric material when subjected to actinic radiation, said polymeric material having

dissolved therein at least one dye intermediate reactive with said polymeric material and including

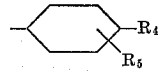
at least a trace amount of a dye reactively-formed in situ from at least one said dye intermediate having the general formula:



wherein R_1 and R_2 are selected from the class consisting of monoalkylamino, dialkylamino, 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,

said layer having a resistivity in darkness of at least 10^9 ohm-centimeters and a resistivity when irradiated of at least two orders of magnitude less than said resistivity in darkness; and

a substantially non-thermoplastic film on said layer including said cross-linked polymeric material, said film having a maximum thickness of up to about 500 Angstrom units.

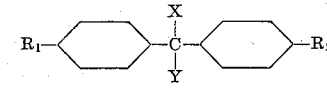
10. A recording element for electrophotographic printing comprising:

a substantially transparent substrate having

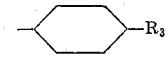
a coating thereon comprising a substantially transparent, normally thermoplastic, photoconductive insulating layer having a thickness of greater than about 11 microns of polymeric material having molecular chains therein capable of being cross-linked to form a substantially non-thermoplastic polymeric material when subjected to actinic radiation, said polymeric material having

dissolved therein at least one dye intermediate reactive with said polymeric material and including

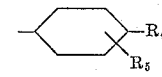
at least a trace amount of a dye reactively-formed in situ from at least one said dye intermediate having the general formula:



wherein R_1 and R_2 are selected from the class consisting of monoalkylamino, dialkylamino, 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,

said layer having a resistivity in darkness of at least 10^9 ohm-centimeters and a resistivity when irradiated of at least two orders of magnitude less than said resistivity in darkness; and a substantially non-thermoplastic film on said layer including said cross-linked polymeric material, said film having a maximum thickness of up to about 500 Angstrom units.

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