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3,483,013

FADE RESISTANT SHEET FOR MAKING COLOR PROJECTION TRANSPARENCY

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7 Claims

ABSTRACT OF THE DISCLOSURE

A transparent film coated with a protonatable chromogenous dye-forming color progenitor in vinyl chloride polymer, which when heated at image areas in the presence of an acid, forms a fade-resistant colored image which withstands prolonged exposure as a color projection transparency on an overhead projector.

This invention relates to the projection of light-images in color and to materials for use therein.

Overhead projectors, for example as described in U.S. Patent No. 3,126,786, are widely used in classrooms as teaching aids. Projection from transparency reproductions of printed or pictorial originals permits improved communication between instructor and students. Transparencies are easily and quickly prepared by thermographic copying techniques; and transparent film materials suitable for making excellent black-and-white transparencies by such methods have been provided, for example as described in U.S. Patent No. 3,111,584.

Thermographic processes for making color projection transparency copies of printed originals are described in U.S. Patent No. 3,147,377. They involve momentarily subjecting a source sheet to a heat-pattern, in this instance obtained by brief exposure of the differentially radiation-absorptive printed original to intense radiation, to cause transfer of coloring matter from the source sheet to a contacting receptor sheet at the heated areas. Other methods of heating the source sheet at image areas may alternatively be employed, but the thermographic process is both rapid and convenient and is preferred.

Transparencies for the projection of images in color have also been produced thermographically, using color source and receptor sheets employing transferable dyes, as also described in U.S. 3,147,377. The entire quantity of dye forming the transparent colored image must be transferred from the source sheet to the receptor sheet; and it has been found that such transfer is frequently inadequate to provide full-color images of massive printed areas such as are occasionally present in demonstration drawings and figures.

Heat transfer of reactant materials has previously been described, for example in U.S. Patent No. 2,770,534. The transfer of volatile acidic or basic reactants from selectively coated areas of an original to a receptor sheet containing an acid-base indicator results in a color change at corresponding areas of the receptor, the latter then being useful as a temporary mask or filter for photographic purposes. The method requires the use of special inks in printing the original, or tedious re-touching of portions of the original. Masks or filters prepared as described in the patent, while fully operative in the photo-mechanical reproduction of art copy as described therein, fade rapidly under continued high intensity illumination and are unsuitable as color projection transparencies.

Heat-sensitive copy-sheets are known which change color, when thermographically heated, through a dye-forming reaction, for example between a dye-forming

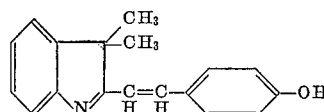
chromogenous electron donor material such as N-bis(p-dimethylaminophenyl)-methyl benzenesulfonamide and an acid reacting compound such as benzoic acid. The copy-sheets, as described in Netherlands patent application No. 6,402,618, published Sept. 16, 1964, are initially lightly colored and form deeply or intensely colored images in the thermographic copying process. The background areas remain heat-sensitive and rapidly discolor when subjected to moderately elevated temperatures of 60–70° C., easily reached in many overhead projectors.

It has now been found possible to produce fade-resistant and heat-resistant color projection transparencies having full-color images in any desired color, by simple thermographic copying processes using couplets of full-coated proton donor reactant source sheets in conjunction with full-coated transparent and substantially colorless receptor sheets containing dye-forming chromogenous electron donor components in a vinyl chloride polymeric binder, all as will be more specifically described and illustrated hereinafter.

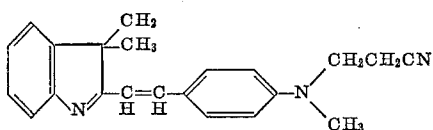
Color projection transparencies prepared in accordance with the principles of the invention are fade-resistant both under normal storage conditions and during extended exposure to intense illumination. As an illustration, transparencies have been made which have undergone no observable change in either the colored image or the clear transparent background areas during more than six months exposure to normal artificial room light, or during continuous projection with an overhead projector (using a 600-watt tungsten filament quartz envelope lamp yielding 2800 lumens at the transparency-supporting stage) for at least about two hours, and in most instances for upwards of four hours. Under such continuous operation the temperature of the stage, and therefore of the transparency, soon reached a temperature of at least about 60–70° C.; yet even under these conditions the background areas remained clear and transparent. The color areas projected images of the same color on a white screen.

The proton donor or acid-supplying reactant source sheet is stable at room and normal storage temperatures but on being briefly heated, i.e. during the thermographic copying process, evolves a volatile acid of a strength and in a quantity sufficient to cause formation of a color-body by reaction with the dye-forming component of the receptor sheet. Salicylic acid in approximately twice its weight of ethyl cellulose and in the form of a thin overall coating on a thin flexible film or paper is a preferred example of a source sheet. Naphthoic acid in a copolymer of vinylidene chloride and acrylonitrile provides another useful source sheet coating. Other acids and acid salts, e.g., as disclosed in Netherlands Patent No. 6,402,618, and which supply a heat-volatile acid are also useful.

N-bis(p-dialkylaminoraryl)methane derivatives as described in the Netherlands patent are examples of dye-forming chromogenous electron donor components which are useful in the practice of the present invention. Another and preferred group of components is represented by various commercially available color precursor materials which likewise become colored when protonated. National Aniline Color Precursor No. 1, identified as N-(bis(4-dimethylaminophenyl)methyl)pyrrolidine and producing a cyan dye when protonated, is illustrative. Color Precursor No. X4405, having the structure.



on protonation produces a yellow dye; and No. X4406, having the structure



is useful as a source of a magenta dye. Mixtures of these and other acid-reactive dye-forming components may be used to produce desired intermediate or modified shades of color.

The dye-forming chromogenous protonatable components are homogeneously incorporated with from about fifteen to about forty-five times their weight of neutral polymeric film-forming binder material consisting essentially of a polymer of monomers including at least about 75% but not more than about 95% of vinyl chloride. A preferred example is "Vinylite VYHH," a copolymer of 87 parts of vinyl chloride and 13 parts of vinyl acetate. The composition is applied as a thin uniform film or coating, from solution in methylethyl ketone or other appropriate volatile vehicle, to a transparent carrier film and dried at moderately elevated temperature. The coating may be removed as a very thin self-sustaining film but preferably is permitted to remain on the carrier sheet.

Polyvinyl chloride polymers are known to be capable of degradation under the influence of light and heat, with evolution of hydrogen chloride. It might therefore be expected that protonatable dye-forming compounds incorporated in polyvinyl chloride polymer films would slowly become colored on exposure to light and heat, whereas films formed with other types of binders would be more resistant to visible change. Surprisingly, it has now been found that the vinyl chloride polymers not only do not cause development of background color, but at the same time greatly extend and improve the retention of color in previously color-developed image areas of the film.

In one illustrative set of experiments, color projection receptor sheets were prepared using one part of Color Precursor No. 1 in 30 parts of each vinyl chloride polymer (VYHH) and ethyl cellulose. Contact with a source sheet containing salicylic acid, with brief heating at image-defining areas, produced a strong cyan color at image areas of each sheet which on the overhead projector gave a distinct cyan projection image. After fifteen minutes the color was almost completely exhausted from the ethyl cellulose binder sheet, whereas the polyvinyl chloride binder sheet remained virtually unchanged during four hours of continuous projection.

Vinyl chloride polymers containing small proportions of carboxyl or other reactive groups are found to undergo reaction with the color progenitor either during application, or during extended aging, or when subjected to moderately elevated temperatures; and these materials are therefore to be rejected in favor of the chemically neutral polymers. Combinations of vinyl chloride with vinyl acetate and within the proportions previously indicated are readily available and fully effective, and are preferred; but neutral copolymers of vinyl chloride with one or more other components, e.g. acrylonitrile, are also useful and are to be included within the scope of the invention. However, polymers of inadequate molecular weight of which are unduly softened, or sticky when heated, or are undesirably colored, are to be avoided.

The amount of color progenitor must be sufficient to provide the desired color intensity, but too large an amount results in an unstable image. Best results have been obtained with proportions within the approximate range of one part of color progenitor in 15 to 45, preferably in approximately 30 parts of binder.

The proportion of color progenitor which becomes converted to the colored form, and therefore the color intensity of the projection image, may be controlled to some extent by regulating the conditions under which the copy is prepared. Increasing the dwell time beneath the

radiation source in the thermographic copying process, for example, results in the transfer of increased amounts of volatilizable acid and, within the limits of the amounts of materials available for reaction, in an increase in the color intensity of the image.

The composition of the receptor sheet film or coating will ordinarily consist exclusively of neutral vinyl chloride polymeric binder and protonatable chromogenous dye-forming component. Other non-reactive components in minor proportions may be added for special purposes, such for example as powdered silica or other inert particulate filler, or aluminum stearate or other inert metal soap, i.e. to prevent blocking or to provide other desired properties; but other reactant materials, and particularly acid-producing or acidic reacting materials, are excluded.

The following specific examples, wherein all proportions are given in parts by weight unless otherwise indicated, are offered as further illustrating but not limiting the invention.

Example 1

An acid source sheet is first prepared by applying to one surface of commercial one-half mil Mylar polyester film a 2½-mil coating of a solution of two parts each of salicylic acid and N-200 ethyl cellulose in 38 parts of methylethyl ketone, followed by drying.

A color projection receptor sheet capable of producing a cyan projection image is prepared by applying to one surface of commercial two-mil Mylar polyester film a solution of one part of National Aniline Color Precursor No. 1 and 30 parts of Vinylite VYHH vinyl chloride-vinyl acetate copolymer in 270 parts of methylethyl ketone, applied at a coating thickness of 3 mils and dried.

The two sheets are placed together in face-to-face contact on a printed original which is then exposed through the two to intense radiation rich in infra-red, for a time just sufficient to produce a strongly colored image in the receptor sheet coating. On a commercial "Thermo-Fax" Model 45 thermographic copying machine using a 130 watt/inch linear coiled tungsten filament lamp in a gold-surfaced reflector which concentrates the radiant energy on a band about ¼ inch in width, the pack is advanced at a speed of about two inches per second.

The printed receptor sheet is placed on the stage of an overhead projector employing a 600-watt projection lamp and the cyan image is continuously projected on the screen for a total of four hours. A slight decrease in image color intensity occurs shortly before the end of the test period. The background remains unchanged.

Equally good results are obtained by substituting Diamond 7103 polymer, having a specific gravity of 1.4 and described as a neutral terpolymer of vinyl chloride, vinyl acetate and a third component believed to be acrylonitrile, for the VYHH polymer.

Example 2

The receptor sheet of Example 1 is first uniformly lightly moistened over the coated surface with a dilute solution of salicylic acid in methylethyl ketone. Sufficient of the solution is added to produce a maximum color change. The color-forming reaction takes place immediately on application of the acid solution.

A source sheet is separately prepared by applying to thin polyester film a coating of a 10% solution of equal parts of 5-amino-1-naphthol and ethyl cellulose in toluene. The dried sheet is placed with the coated surface against the colored coating of the receptor sheet. The couplet is locally heated by the thermographic copying process as described under Example 1. Transfer of the naphthol at heated image areas results in decolorization of the dyed sheet at corresponding areas, and production of a negative color projection transparency. The color remains unchanged during almost four hours of continuous exposure on the overhead projector. In place of the naphthol may be used urea, thiourea, or aminoguanidine bicarbonate.

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What is claimed is as follows:

1. A heat-resistant receptor sheet adapted for making fade-resistant colored images by a process involving heat-induced transfer of salicylic acid vapors to said receptor sheet at image areas, said receptor sheet including a transparent thin heat resistant carrier film and an acid-reactive thin coating consisting essentially of one part by weight of protonatable chromogenous dye-forming color progenitor in solution in from about 15 to about 45 parts of neutral film-forming polymer of monomers including about 75% to about 95% of vinyl chloride characterized by the ability of the imaged sheet to retain a clear transparent background for at least 2 hours at 70° C.

2. The reactor sheet of claim 1 wherein the coating consists essentially of one part of color progenitor in about 30 parts of polymer.

3. The receptor sheet of claim 1 wherein the polymer is a copolymer of about 87 parts of vinyl chloride and correspondingly about 13 parts of vinyl acetate.

4. The receptor sheet of claim 1 wherein the color progenitor is an N-bis(p-dialkylaminoaryl) methane derivative.

5. A couplet of acid source sheet and color-forming receptor sheet adapted for making a heat-resistant copy in fade-resistant color of a differentially radiation-absorptive original by a thermographic copying process, said acid source sheet including an acid source material which liberates a volatile acid on heating, and said receptor sheet including an acid-reactive thin film consisting essentially

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of one part by weight of protonatable chromogenous dye-forming color progenitor in solution in from about 15 to about 45 parts of neutral film-forming polymer of monomers including about 75% to about 95% of vinyl chloride.

6. A couplet as defined in claim 5 wherein said acid source sheet comprises a heat-resistant carrier web coated with a binder containing said acid source material, and wherein said receptor sheet comprises a heat-resistant thin transparent carrier film coated with said color progenitor in said polymer.

7. A couplet as defined in claim 6 wherein said acid source material is salicylic acid, said polymer is a copolymer of approximately 87 parts vinyl chloride and 13 parts vinyl acetate, and said film is a polyester film.

References Cited

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3,146,348	8/1964	Workman	117—36.2
3,280,735	10/1966	Clark et al.	250—65.1
3,346,571	10/1967	Spatz et al.	117—36.2
3,147,377	9/1964	Newman	117—36.1

MURRAY KATZ, Primary Examiner

U.S. Cl. X.R.

117—138.8; 260—41

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,483,013 Dated December 9, 1969

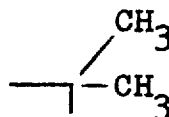
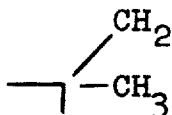
Inventor(s) JOHN R. BERG and JOSEPH A. WIESE, Jr.

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

In the specification:

Column 2, line 54, that portion reading "p-dialkyl-aminoraryl" should read -- p-dialkylaminoaryl -- .

Top of column 3, that portion of the structural formula reading should read



Column 3, line 14, "neurtal" should read -- neutral --.

In the claims:

Claim 1, line 1, after "A", insert -- transparent -- .

Claim 2, line 1, for "reactor" substitute -- receptor -- .

Claim 5, line 1, after "and", insert -- transparent --.

SIGNED AND
SEALED
JUN 2 1970

(SEAL)

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