

[72] Inventor **Joseph A. Wiese, Jr.**
 3 M, Center, St. Paul, Minn. 55101
 [21] Appl. No. **858,172**
 [22] Filed **Sept. 15, 1969**
 [45] Patented **Sept. 28, 1971**

[56] **References Cited**
UNITED STATES PATENTS
 3,108,896 10/1963 Owen 117/36.2
 3,483,013 12/1969 Berg et al..... 117/36.2

Primary Examiner—James W. Lawrence
Assistant Examiner—D. C. Nelms
Attorney—Kinney, Alexander, Sell, Steldt & Delahunt

[54] **NEGATIVE PROJECTION TRANSPARENCIES AND METHOD**
 7 Claims, No Drawings
 [52] U.S. Cl..... **250/65 T, 117/36.2**
 [51] Int. Cl..... **G01n 21/34**
 [50] Field of Search..... **250/65 T; 117/36.2, 36.8, 36.9**

ABSTRACT: Clear-colored film products, which are decolorized at image areas by thermographic heating to form negative projection transparencies of positive originals, contain a colored reaction product of a color precursor and a volatilizable acid. The colored compound is decomposed and the liberated acid is volatilized and removed at the heated image areas, leaving a clear colorless transparent image.

NEGATIVE PROJECTION TRANSPARENCIES AND METHOD

This invention relates to imaging and to sheet materials useful therein. More particularly, the invention relates to sheet materials from which negative copies of graphic images may be prepared in various colors by thermographic copying procedures. In a still more specific aspect the invention relates to clear-colored film products which are decolorized by brief heating to thermographic copying temperatures. Products of the invention are therefore useful, for example, in the preparation of negative color projection transparencies of differentially infrared-absorptive printed originals.

In a preferred form the product of the invention consists of a heat-resistant, thin, transparent, flexible, film backing coated over one surface with a thin layer of a polymeric binder containing dissolved therein the colored reaction product of a protonatable color precursor and a volatilizable acid. Sufficient of the colored material is present to provide only the desired density of color; the sheet is clear and does not cause diffusion of the transmitted rays. Concentrations of only about 1 to 3 percent of color precursor in the polymeric binder are usually ample where the total coating is of the order of 2 to 3 microns in thickness.

The amount of volatilizable acid present in the coating is at least sufficient to provide the desired color density within the capabilities of the sheet, and preferably is at least sufficient to react with all of the progenitor material. A slight excess of acid may be included and may be desirable for improved stability at room temperature, but large excesses are likely to appear in crystalline light-diffusing form, are uneconomical and unnecessary, and are therefore to be avoided.

The heat transfer of acid vapors from a source sheet to a receptor sheet containing an acid-reactive color progenitor, with formation of stable colored images, has previously been described, see for example Berg et al. application Ser. No. 590,211 filed Oct. 28, 1966, now U.S. Pat. No. 3,483,613. The present invention is based on the surprising discovery that such color-forming reactions are reversible simply by heating, the acid component being readily removed and the color body being returned to the colorless or leuco state.

The following specific examples, in which all proportions are in parts by weight unless otherwise indicated, will serve further to illustrate the practice of the invention.

EXAMPLE 1

A solution of two parts of N-(bis-(4-dimethylaminophenyl)methyl)pyrrolidine, seven parts of salicylic acid, and 100 parts of "VYHH" vinyl chloride-vinyl acetate copolymer binder in 900 parts of 2-butanone is coated on 1 mil transparent, heat-resistant Mylar polyester film and the solvent removed by evaporation, leaving a clear, dark blue coating about one-tenth mil (2.5 microns) in thickness. The film is placed with the coated surface against the surface of an original printed in black ink on white paper, and which is then briefly exposed through the colored film to intense infrared radiation in a thermographic copying machine. The heat pattern created at the printed image areas is sufficient to volatilize and remove the acid component, leaving a clear transparent image. The film is placed on the stage of an overhead projector and is found to project a white image with a blue background. The projected image is visibly unchanged during more than 4 hours of projection.

Equally effective results are obtained by employing equal amounts of salicylic acid and color former, in a somewhat thicker coating to compensate for the resulting decrease in color intensity. With more than about four parts of acid per part of color former, crystallization is observed and the coating is not completely clear but instead causes diffusion of transmitted light.

The mobility of the acid component has been demonstrated in the following manner. The colored film is placed in face-to-face contact with a film provided with a colorless, acid-free coating of the same color progenitor and binder, and the com-

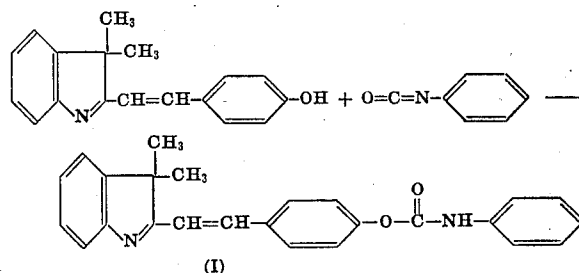
posite is heated thermographically at image areas, the infrared radiation passing through the composite to the printed original. A colorless image appears on the colored film, and a corresponding colored image appears on the colorless film. However, the colorless film remains unimaged when a thin polyester film is first placed between the two coated films, only the colored film then displaying the image pattern.

EXAMPLE 2

A solution of 2.5 parts of oxalic acid, 2.0 parts of N-(n-butyl)-N'-bis(4-dimethylaminophenyl) methylene urea, and 100 parts of "Gelva V-100" polyvinyl acetate binder in 900 parts of 2-butanone is coated on 2-mil Mylar transparent polyester film from a 3-mil orifice and dried to provide a clear magenta-colored film which becomes colorless at heated image areas in the thermographic copying process and projects a white image on a magenta background when placed on the overhead projector.

EXAMPLE 3

One part of "Color Precursor X-4405" is dissolved in five parts of phenyl isocyanate with gentle heating. The initial orange-yellow color rapidly disappears and pale yellow crystals are deposited. The crystals are recovered, washed with hexane, and dried. They melt at 150°-175° C. with decomposition and discoloration. The reaction is as follows:



Twenty parts of compound I and 25 parts of benzoic acid are added to a solution of 500 parts of ethyl cellulose in 9,500 parts of 2-butanone. The solution is coated at 3 mils on 2-mil Mylar transparent polyester film and dried, producing a clear, moderately intense, yellow coating. Under thermographic copying procedures the yellow color disappears at the heated image areas. The resulting projection transparency projects a white image and a yellow background.

The same compositions may be coated on paper to provide negative copies of graphic originals in the thermographic copying process. Removal of color may equally well be accomplished by other heating means, for example with a heated stylus or by contact with heated metal type. In all cases the loss of color is occasioned by volatilization and removal of the volatilizable acid component.

The operability of any specified combination of color progenitor and volatilizable acid may be determined experimentally by the following simple test procedure. A strip of porous paper, such as Whatman No. 1 filter paper, is first dipped into a solution of 10 mg. of the color progenitor in 10 ml. of 2-butanone, and dried. The strip is then dipped into a dilute aqueous solution of the acid, and again dried. The acid converts the progenitor to the colored protonated form. The strip is then placed briefly against a heated metal plate, such as "Heizbank" melting point apparatus providing a range of temperatures along the surface of a polished metal bar heated from one end, and observed for color change. Combinations which under such test conditions show full loss of color at temperatures between about 50° and about 250° C., or preferably between about 125° and about 175° C., produce negative projection transparency coatings useful in making transparencies by the thermographic copying process as hereinbefore described.

What is claimed is as follows:

1. A colored sheet material useful in making negative copies of graphic originals by the thermographic copying process, said product including a thin uniform color layer comprising a heat-decomposable colored reaction product of a protonatable chromogenous dye-forming color progenitor and an organic acid volatilizable from said product at a temperature within the range of 50° and 250° C.

2. The product of claim 1 wherein said reaction product is in solution in a polymeric binder.

3. The product of claim 2 wherein said layer is transparent and is carried on a heat-resistant transparent backing.

4. The product of claim 3 wherein said layer is about 2-3 microns in thickness and the colored reaction product is present therein in a concentration of about 1 to 3 percent.

5. The product of claim 4 wherein said acid is salicylic acid.

6. The method comprising placing a colored sheet material, having a thin uniform color layer comprising a heat-decomposable, colored reaction product of a protonatable chromogenous dye-forming color progenitor and an organic acid volatilizable from said product at a temperature within the range of 50° to 250° C., in heat-conductive contact with a differentially infrared-absorptive graphic original, and briefly exposing said original form, intense infrared radiation to produce a negative copy of said original in said color layer.

7. The method of claim 6 wherein said sheet material is in face-to-face contact with a second sheet material having a thin, uniform, substantially colorless, and acid-free coating comprising a said color progenitor.

15

20

25

30

35

40

45

50

55

60

65

70

75

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,609,360 Dated September 28, 1971

Inventor(s) 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:

Column 1, line 31, after "diffusing" delete "from" and insert
--form--

Column 4, line 9, after "original" and before "intense"
delete "form," and insert --to--

Signed and sealed this 29th day of February 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents