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3,669,747

HEAT-SENSITIVE COPY-SHEET

Geoffrey C. Nicholson, St. Paul, and Donald J. Newman,
White Bear Lake, Minn., assignors to Minnesota Min-
ing and Manufacturing Company, St. Paul, Minn.
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8 Claims

ABSTRACT OF THE DISCLOSURE

An integral heat-sensitive copy-sheet contains a protonatable chromogenous dye-forming color progenitor and a cocrystal adduct of an organic amine and volatilizable organic acid.

This invention relates to heat-sensitive copy-sheets useful in making copies of differentially radiation-absorptive graphic originals by a thermographic copying process involving brief exposure of the original to intense radiation while in heat-conductive contact with the copy-sheet. In one specific aspect the invention relates to transparent copy-sheets for making colored projection transparencies, wherein the color is produced by reaction between a volatilizable organic acid and a protonatable chromogenous dye-forming color progenitor.

The preparation of projection transparencies having colored images by heat-induced reaction between organic acids and protonatable chromogenous dye-forming color progenitors has been described in U.S. Pat. No. 3,483,013, the disclosures whereof are to be included herein by reference. In the structure there described, the acidic component is supplied from a separate source sheet and only at the heat image areas, so that color-forming reaction is avoided at background areas.

It is desirable to avoid the inconvenience of the two-sheet system by incorporating both the color progenitor and the source of acid in an integral sheet although preferably in adjacent but distinct strata of the heat-sensitive coating or film. However the degree of separation attainable in such a structure is normally found to be insufficient to prevent some small degree of interaction between the reactants in the separate strata, so that some slight discoloration has previously been found to be unavoidable.

The presence of any significant amount of background discoloration, while causing only slight annoyance in a single sheet, becomes intolerable when several sheets are combined, e.g. in presenting a series of views of increasing complexity by means of overlays on an overhead projector. It has been found that sheets having a background optical density of only about 0.08 represent a borderline situation for such applications, whereas at densities of about 0.03 to 0.05 the coloration is insufficient to be troublesome. These latter values represent substantial freedom from discoloration, the uncoated polyester film itself providing readings in the range of 0.03–0.04. These density values are as determined on the Macbeth Optical Densitometer and represent the maximum values obtained when reading the sample through the full series of color filters accompanying the instrument.

It has now been found possible to produce an integral heat-sensitive copy-sheet structure, and more particularly a transparent structure, wherein the colored image is produced by protonation of a protonatable chromogenous dye-forming color progenitor, while still maintaining extremely low and fully acceptable levels of background optical density, by introducing part or all of the volatilizable organic acid component in the form of the cocrystal adduct of the acid and an organic amine.

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The amount of acid to be employed should be at least sufficient to cause complete conversion of the color progenitor to the colored form upon brief heating of the sheet material in the thermographic copying process, and may be much greater than this amount. Excessive amounts of acid, besides being wasteful, appear as light-diffusing crystalline deposits in the coating and are particularly to be avoided in sheet materials designed for as projection transparencies.

Specific progenitors of primary colors, and specific volatilizable organic acids, are identified in U.S. 3,483,013 and are equally useful in the present invention. Included are Color Precursors No. 1 (cyan), No. X-4405 (yellow), and No. X-4406 (magenta); and various mixtures of these materials may be employed to obtain images of other desired colors. Salicylic and naphthoic acids are useful protonating agents; others include 5-chlorosalicylic acid and bis(trifluoromethylsulfonyl) methane. The acidic component should have a pKa value between 1 and 5 and should be readily volatilizable at 150° C., as evidenced by the rapid disappearance of a small crystal of the acid when dropped upon a smooth clean metal surface maintained at that temperature.

The co-crystal adduct may be pre-formed by simply mixing the acid and amine together in stoichiometrically equivalent proportions in a mutual solvent at room temperature. The adduct may be recovered in solid form by evaporation of solvent, or may be added to the coating composition in solution; or the components may be separately added to the composition for in situ formation of the adduct.

The entire quantity of acid desired for protonation of the color progenitor may be converted to the adduct; and the color progenitor and an adduct of one of the more active amines may if desired be incorporated in the same stratum. Where the two are to be present in separate strata of the heat-sensitive coating, it is surprisingly found that the conversion of only a minor proportion of the acid component to the adduct is effective in reducing the background optical density to the desired low level; whereas in the absence of the adduct, the same quantity of free acid is found to produce a much higher level of backgrounding.

Morpholine is a presently preferred organic amine for forming compatible normally stable readily heat-dissociable co-crystal adducts with the acidic protonating agents. Other useful amines include imidazole, benzyl methyl amine, diethanolamine, naphthylamine, diphenylguanidine, dimethylaniline, benzimidazole, and urea.

A transparent polymeric film-forming binder will desirably be included with the reactant materials in preparing the coating compositions and the coated sheet materials. The binder may itself serve as a support or carrier where films of extreme thinness are desired, but the structure preferably includes a separate carrier or backing sheet. For projection transparencies it is preferred to employ a transparent heat-resistant polymeric film backing, polyester film such as polyethyleneglycol terephthalate film being an outstanding example.

In accordance with the teachings of U.S. 3,483,013 it is preferred to use a vinyl chloride polymer as the binder for the color progenitor, usually as a first stratum of the heat-sensitive coating. Particularly where the second coating composition contains free acid, the binder and solvent of said second coating is selected to avoid any dissolving of, or migration into, the previously dried first stratum. As an example, the first stratum contains vinyl chloride-acetate copolymer as the binder, and the topcoating then contains cellulose nitrate binder in methanol.

Incorporation of small amounts of free amine, e.g. diphenylguanidine, with the color progenitor in the first

stratum results in conversion of a small proportion of the acid of the second stratum to the adduct at the interface and thereby suppresses discoloration of the background; but the amine in many instances is found to react slowly with the color progenitor to reduce the useful life of the sheet, and such structures have for this reason been found undesirable.

Although the invention is particularly useful in providing projection transparencies and has been described primarily in such context, it will be appreciated that the principles involved are of broader scope. As one example, the color progenitor and co-crystal adduct components may be applied to paper in the substantial absence of binders, or with the incorporation of various pigments, fillers or other additives, to provide useful thermographic copy-sheet structures, thermal tell-tales and other useful articles.

The invention will now be further described in terms of specific illustrative examples, wherein all proportions are in parts by weight unless otherwise specified.

EXAMPLE 1

Transparent two mil polyethylene terephthalate polyester film is coated with a first coating of a solution of one part of National Aniline Color Precursor No. 1 and 20 parts of VYHH vinyl chloride-acetate copolymer in 80 parts of methylethyl ketone, applied with a coating knife set at an orifice of two mils. The coating is thoroughly dried and is found to be essentially free of color.

Equimolar proportions of morpholine and bis(trifluoromethylsulfonyl)methane are reacted together in methanol solution and the co-crystal adduct recovered by evaporation of solvent. One part of the adduct is dissolved in ten parts of a 13.5% solution of cellulose nitrate in methanol and the resulting solution is coated over the first coat, again at a thickness of two mils, and dried.

The coated film is imaged thermographically, producing an intense blue image on a clear background. The background optical density is 0.03.

In some instances the first coating solution is found to be lightly colored. The color may be discharged by pretreatment with a minimal amount of methanolic potassium hydroxide solution.

Instead of using preformed co-crystal adduct, the second coating solution may be prepared by adding separately 0.85 part of bis(trifluoromethylsulfonyl)methane and 0.264 part of morpholine to the ten parts of 13.5% solution of cellulose nitrate in methanol.

Polyvinyl pyrrolidone may be substituted for the cellulose nitrate as the binder of the second coat, and Dow PVC polyvinyl chloride for the vinyl chloride-acetate copolymer as the binder of the first coat, with identical results in terms of image formation and background optical density. Another useful first coat binder is styrene-acrylonitrile copolymer.

EXAMPLE 2

One part of Color Precursor No. 1 is dissolved in 50 parts of a 20% solution of VYHH vinyl polymer in methylethyl ketone and the solution is coated on 2 mil polyester film at a thickness of 2 mils, and dried. Portions of the film are coated with each of three different second coating compositions each containing 50 parts of a binder solution. The binder solution contains 13.5% of a 4:1 mixture of cellulose nitrate and polyvinyl butyral, in a solvent composed of methanol and a small proportion of volatile higher alcohols. The first of the three compositions contains 1.25 part of 5-chlorosalicylic acid. The second contains the same acid component together with 0.575 part of 1,3-diphenylguanidine, equivalent to about 3% of the acid. The third contains 0.785 part of the 5-chlorosalicylic acid, which is equivalent to the amount of unreacted acid remaining in the second composition. The several sheets are imaged thermographically to produce equal intensity blue images. The background densities of the three sheets are as follows:

First sheet (full acid)	0.08
Second sheet (3% acid + 3% adduct)	0.03
Third sheet (3% acid)	0.06

Further reductions in the amount of acid are found to cause a lowering of the image intensity which cannot be overcome by increasing the heat input during the thermographic copying step.

In a similar example using salicylic acid and diphenylguanidine, the sheet containing the acid alone produced a background optical density of 0.09, whereas the sheet containing the amine in an amount equal to one-tenth the molar amount of the acid showed a background optical density of 0.04.

EXAMPLE 3

To ten parts of a 10% solution of VYNS vinyl chloride-acetate copolymer in acetone is added 0.1 part of Color Precursor No. 1. The initial faint blue color of the solution is discharged by the addition of 0.02 part of imidazole; an equivalent amount of methanolic potassium hydroxide is equally effective. There is then added 0.5 part of the co-crystal adduct of morpholine and bis(trifluoromethylsulfonyl)methane, and the solution is coated on transparent polyester film and dried. The sheet produces blue images by thermography. The background optical density is 0.07. The background optical density is reduced to 0.05 by substitution of a polyamide binder for the vinyl resin, but with some reduction in stability of the imaged sheet.

EXAMPLE 4

To a solution of 20 parts of styrene-acrylonitrile copolymer in 80 parts of methylethyl ketone is added two parts of Color Precursor No. 1 and ten parts of the co-crystal adduct of morpholine and bis(trifluoromethylsulfonyl)methane. The solution is coated on two mils polyester film at a wet thickness of two mils, and allowed to dry. The background density is 0.08. The sheet produces blue images by thermography.

EXAMPLE 5

To 50 parts of a 20 percent solution of VYHH vinyl polymer in methylethyl ketone is added 0.4 part of Color Precursor X-4405, 0.3 part of Color Precursor X-4406, and 0.3 part of Color Precursor No. 1. The solution is coated on two mil polyester film and dried, the dry coating weight being 0.25 gm./sq. ft. A second coating was then applied, using a coating bar at an orifice of two mils, of a composition prepared of 625 parts 5-chlorosalicylic acid and 153 parts diphenylguanidine in 16,000 parts of a 13.5% solution of cellulose nitrate in methanol, 4000 parts of 13.5% solution of polyvinyl butyral in ethanol, and 2000 parts of heptane. The coated film after drying is transparent and has a background optical density of 0.05. It produces a black image in the thermographic copying process and the copy projects a black image on projection the image remains sharply defined and neither fades nor spreads.

What is claimed is as follows:

1. Heat sensitive sheet material useful in making a copy of a graphic original by the thermographic copying process and including a transparent color-producing film containing a protonatable chromogenous dye-forming color progenitor and a source of organic acid, said organic acid having a pKa value between 1 and 5, volatilizable at 150° C., and in an amount sufficient to protonate said progenitor to form a color body at heated image areas, said source including a solution coatable co-crystal adduct of said organic acid and an organic amine, said adduct being stable with respect to said color progenitor when in solution therewith.

2. Sheet material of claim 1 including a transparent heat-resistant carrier film and wherein said sheet material is clear and transparent and the background optical density is not higher than about 0.08.

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3. Sheet material of claim 2 wherein at least about one-tenth of the total amount of said organic acid is present as the said adduct, the balance being present as free organic acid.

4. Sheet material of claim 3 wherein said progenitor and said source of organic acid are in separate adjacent strata of said color-producing film.

5. Sheet material of claim 2 wherein all of said organic acid is present as said adduct.

6. Sheet material of claim 5 wherein said progenitor and said adduct are intermixed in a common stratum.

7. Method of making a heat-sensitive material containing a protonatable chromogenous dye-forming color progenitor and a source of organic acid, said acid having a pKa value between 1 and 5, volatilizable at 150° C., and in an amount sufficient to protonate said progenitor to form a color body at heated image areas, comprising applying a solution containing said progenitor and a co-crystal adduct of said acid and an organic amine to a substrate and drying to provide a clear transparent film on said substrate.

8. Method of making a heat-sensitive sheet material containing a protonatable chromogenous dye-forming color progenitor and a source of organic acid, said acid

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having a pKa value between 1 and 5, volatilizable at 150° C., and in an amount sufficient to protonate said progenitor to form a color body at heated image area, comprising applying a solution containing said progenitor to a substrate, drying to form a clear transparent film on said substrate, overlaying said film with a solution of said source of said acid, at least one-tenth of which is present as a co-crystal adduct of said acid and an organic amine, and drying to provide a clear transparent film on said substrate.

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