

United States Patent
Huffman

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[54]	HEAT-SENSITIVE COPY-SHEET		3,167,444	1/1965	Baumann et al.	117/36.8
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[73]	Assignee:	Minnesota Mining and Manufacturing Company, St. Paul, Minn.	2,993,805	7/1961	Kay.....	117/36.7
			3,108,872	10/1963	McMahon	117/36.7
[22]	Filed:	Feb. 18, 1970	<i>Primary Examiner</i> —Murray Katz			
[21]	Appl. No.:	12,427	<i>Attorney</i> —Kinney, Alexander, Sell, Steldt & Delahunt			
[52]	U.S. Cl.	117/36.8, 117/36.2, 117/36.7, 117/155	[57] ABSTRACT			
[51]	Int. Cl.	B41m 5/18	Heat-sensitive copy-sheet coatings comprise highly methanol-soluble amine adducts of organic acidic materials. The sheets may be clear and transparent, becoming light-diffusing on heating. In a preferred form they contain amine-reactive color progenitors and become colored on heating. The presence of a mutual solvent does not cause the color-forming reaction to take place, and the reactants may therefore be coated together in a single application.			
[58]	Field of Search	117/36.8, 36.9, 36.2, 36.7				
[56]	References Cited					
	UNITED STATES PATENTS					
	3,293,061	12/1966	Lawton.....	117/36.8	14 Claims, No Drawings	

HEAT-SENSITIVE COPY-SHEET

This invention relates to heat-sensitive copy-sheets useful in the preparation of copies of graphic originals by thermographic processes involving brief exposure of a differentially radiation-absorptive original to intense heat-producing radiant energy while in heat-conductive contact with the copysheet, and wherein the conversion temperature is between about 90° and about 150° C.

In one aspect the invention relates to clear transparent heat-sensitive copy-sheets useful in the preparation of projection transparencies. In a related aspect the invention relates to copy-sheets with which color projection transparencies may be prepared.

In the preferred practice of the invention the copysheet includes a backing or carrier sheet or film carrying a clear transparent coating comprising a highly methanol-soluble amine adduct of an organic acidic material in conjunction with a polymeric binder.

Heat-dissociable co-crystal complexes or adducts of amines with aromatic hydroxy compounds have previously been suggested as components of heat-sensitive copy-sheets, but only in particulate and light-diffusing form. Thus in U.S. Pat. No. 3,090,697 a dispersion of particles of the heat-dissociable molecular compound or adduct of an amine and a halogenated aromatic hydroxy compound in a suitable binder provides a light-diffusing masking layer which is transparentized on heating. U.S. Pat. Nos. 3,076,707, 3,149,991-2-3, 3,166,433, 3,167,444-5, and 3,185,583-4-5 describe heat-sensitive copysheets containing similar adducts in light-diffusing particulate form, together with amine-reactive color-producing compounds or compositions; heating the sheet causes dissociation of the adduct with liberation of amine and formation of color-bodies.

It has now been found possible to produce clear transparent films and coatings containing heat-dissociable amine adducts in non-particulate form. The coating does not obscure desired colors or markings on the underlying carrier. Where a transparent carrier is employed, the sheet produces excellent projection transparencies.

It has further been found possible to incorporate, in potentially co-reactive association with the amine adduct, various amine-reactive color progenitor compounds and compositions, in many cases without impairing the clarity of the coating, the resulting copy-sheets producing high quality color projection transparencies.

A particular advantage of the compositions and procedures here employed is that the amine adduct and color progenitor are soluble in a common solvent without co-reaction. The materials may therefore be dissolved together and applied as a single stratum, requiring only one coating and drying step. When once applied, the coating is solvent-resistant in that the deliberate or accidental application of solvent does not result in a color-forming reaction. This is in sharp contrast to the behavior of the color-forming components and coatings of the prior art referred to hereinbefore.

The above-described and other advantages are obtained, in accordance with the principles of this invention, by employing heat-dissociable amine adducts of certain organic acidic materials of which benzoic and salicylic acid are presently preferred examples. A preferred class of acidic materials consists of those which exhibit a pKa value not higher than about 6 and preferably are substantially colorless. The preferred adducts are also found to be highly soluble in methanol, which is here defined as soluble to the extent of at least about 20 grams per 100 cc., and preferably at least about 50 grams per 100 cc., as will be further shown in connection with specific Examples.

Among the organic acidic materials which have been found useful are carboxylic acid, sulfonic acid, phenolic, and fluorosulfone compounds. Typical examples include the following, the name of the acid being followed by its pKa value where known: benzoic 4.17, o-chlorobenzoic 2.92, o-bromobenzoic 2.84, p-chlorobenzoic 3.98, o-hydroxybenzoic 2.97, 2,5-dihydroxybenzoic 2.94, 3,4-dihydroxybenzoic 4.48,

o-nitrobenzoic 2.16, trihydroxybenzoic 1.68, o-iodobenzoic 2.85, 2,4-dinitrophenol 3.96, 3,6-dinitrophenol 5.15, gallic 4.41, trichlorophenol 6.00, trinitrophenol 0.80, o-chlorophenylacetic 4.07, o-chlorophenoxyacetic 3.05, o-bromophenoxyacetic 2.60, benzosulfonic 0.70, terephthalic 3.82, alpha naphthol 3.70, o-phthalic 2.89, naphthalenesulfonic 0.57, quinolinic 2.52, thiophenecarboxylic 3.48, mandelic 3.85, maleic 1.83, furancarboxylic 3.15, dihydroxymalic 1.92, ascorbic 4.10, succinic 4.17, malonic 2.80, oxalic 1.46, glyoxylic 4.88, glycolic 3.83, trichloroacetic 4.08, fluoroacetic 2.66, citric, bis(trifluoromethylsulfanyl)methane, xanthanoic, thiophendicarboxylic, cyclohexanecarboxylic, norcamphoric, naphthalenedicarboxylic, naphthalenetetracarboxylic, mellitic, trimesic, biphenyldicarboxylic, resorcinol-o-acetic, anthracenecarboxylic, o-bromotoluic, p-bromomandelic, salicylacetic, dinitrophenylacetic, 2-furanacetate, 4-sulfobenzoic, 3-formylbenzoic, 5-formylsalicylic, lactic, phenanthrenecarboxylic, isophthalic, 2-cyclopentenecarboxylic, naphthylaminetrifluoromethyl, 5-chlorosalicylic, 3,5-dinitrotoluic, benzohydroxamic, indolecarboxylic, xanthenecarboxylic, 2,3-pyridinecarboxylic, pentanetricarboxylic, cyanoacetic.

The amine adducts are very easily made by simple mixing of the two components in solution. The product may be recovered in crystalline form, purified if desired, and redissolved for mixing with the other components and applying to the carrier. More conveniently, the adduct is prepared by adding the components to a solution of the color progenitor material and/or the binder in a mutual volatile solvent, the mixture then being applied directly to the carrier. In a typical preparation, salicylic acid (1.39 gm., 0.1 mol) and piperidine (0.85 gm., 0.1 mol) are mixed together in 20 grams of benzene, the mixture is evaporated to dryness, and the co-crystal adduct is washed with hexane and dried before being re-dissolved in a solution of binder and color progenitor. Alternatively, benzoic acid (0.61 gm., 0.05 mol) is dissolved in 20 gm. of 10 percent solution of cellulose nitrate in methanol, followed by addition of piperidine gm., 0.05 mol) and by 0.05 gm. of hydrindantin as color progenitor, and the solution is applied uniformly to a transparent film backing and dried, forming a colorless, clear and transparent, heat-sensitive sheet material.

Substantially stoichiometric proportions of amine and acid are normally preferred but other ratios are not precluded, provided that the adduct composition contains no free amine, since it is the liberation of the basic organic nitrogen compound by heat-promoted dissociation of the adduct which initiates the color change.

Piperidine and morpholine are presently preferred examples of basic organic amino nitrogen compounds useful in the practice of the invention. Primary, secondary and tertiary amines, and hydrazines, are useful. Typical examples include the following: triethanolamine, ethanolamine, cyclohexylamine, tributylamine, di-n-propylamine, isopropylamine, 2-amino-1-butanol, monoisopropanolamine, propylenediamine, isobutylamine, di-n-hexylamine, di-n-butylamine, hydrazine, di-isopropylamine, diamylamine, methylhydrazine, phenylhydrazine, hexanediamine, methylaniline, aniline, guanidine, propylenediamine, polyglycolamine, ethylenediamine, diethylamine, diethanolamine, hydroxyethyl-diethylenetriamine, isoctylamine, n-decylamine, n-methylethanolamine, tetramethylguanidine, methyl-diethanolamine, 2-amino--propanediol, diethylaminopropylamine, amino-bispropylamine, benzylamine, morpholine, piperidine, dimethylformamide.

The concentration of adduct and of color progenitor in the heat-sensitive sheet materials and coatings of this invention may be widely varied but for economy is preferably not greater than that required to produce an image of adequate contrast by thermographic copying.

The following specific Examples, in which all proportions are in parts by weight unless otherwise specified, will serve further to illustrate but not to limit the invention.

EXAMPLE 1

Co-crystal adduct of equimolar proportions of morpholine and bis(trifluoromethylsulfonyl)methane	2 parts
Indane-1,2,3-trione-2-hydrate (Ninhydrin)	0.75
Cellulose nitrate	5
Methanol	45

The adduct is soluble in methanol at 20° C. to the extent of 80 gm./100 cc.

The reactants and binder are dissolved in the solvent, and the solution is coated on 2 mil transparent heat-resistant Mylar polyester film, using a coating orifice of 2 mils, and dried. The reactants are thereby maintained in potentially coreactive association in the coating. The clear transparent colorless film product is placed against the printed surface of a typed original which is then briefly exposed through the film to intense radiation in an infra-red copying machine. A copy of the printed image appears on the film in transparent blue. On an overhead projector, the transparency projects a blue image on the white screen background.

EXAMPLE 2

Phosphomolybdic acid	9
Co-crystal adduct of phenylhydrazine and 5-chlorosalicylic acid	25
Ascorbic acid	10
Polyvinyl butyral	10
Methanol	90

Coated on clear polyester film, the solution provides a clear colorless product which forms a blue-gray image in the thermographic copying process and projects a black image with white background.

The co-crystal adduct is soluble in methanol to the extent of 58 g./100 cc.

EXAMPLE 3

Dinitroanthraquinone	3
Zinc hydrosulfite	2
Co-crystal adduct of piperidine and thiophene carboxylic acid, sol. 40 g./100 cc.	6
Polyvinyl butyral	13.4
Methanol	76

The coating on polyester film is clear and colorless, converting to dark brown upon thermographic heating at image areas.

EXAMPLE 4

Phloroglucinol	2
Sodium nitroprusside	2
Co-crystal adduct of morpholine and naphthylacetic acid, s. 32 g./100 cc.	4
Cellulose nitrate	10

The solution in methanol is applied to heat-resistant clear polyester film and dried. The heat-sensitive sheet produces a black image.

EXAMPLE 5

Bromocresol purple (colorless form)	1
Co-crystal adduct of piperidine and bromophenoxyacetic acid—s. 70 g./100 cc.	5
Cellulose nitrate	25

Applied from methanol, the composition gives purple images in the thermographic copying process.

EXAMPLE 6

- A. Solution of 10 parts lead chloride in 190 parts of a 10 percent solution of cellulose nitrate in methanol.
- B. Solution, in 190 parts of 10 percent solution of cellulose nitrate in methanol, of 5 parts zinc hydrosulfite and 5 parts cocrystal adduct of ethylene diamine and salicylic acid (s. 45 g./100 cc.).

Solutions A and B are combined and coated on clear polyester film at a wet coating thickness of 2 mils. The dry sheet is clear and colorless, and produces black opaque copy on a clear background in the thermographic copying process.

EXAMPLE 7

A. The co-crystal adduct of morpholine and benzoic acid (s. 70 g./100 cc.) is dissolved in a solution of cellulose nitrate in methanol and the solution coated on polyester film and dried. The product is clear and colorless.

B. Separately, polyester film is coated with a solution of acid-stabilized diazonium salt, azo dye coupler, and ethyl cellulose in ethanol, and dried, producing a clear and slightly yellowish coated film.

The composite of films A and B in face-to-face contact is locally heated at image areas in the thermographic copying process, producing a blue azo dye image on the B sheet. The copy projects as a blue image with a slightly yellowish background.

Alternatively, since the diazonium salt is decomposed by ultraviolet radiation, images may be formed by irradiating the B film through a transparency and then uniformly heating the A sheet against the B film.

Solutions A and B may alternatively be mixed together and applied as a coating on transparent film to produce a transparent heat-sensitive copy-sheet.

The diazonium salt is the zinc sulfate salt of 2,5-dibutoxy morpholinobenzene.

The azo coupler is 2,5-dichloro-1-naphthol.

EXAMPLE 8

Clear 3 mil oriented and heat-shrinkable polystyrene film is coated from a 3 mil orifice with a solution of 0.5 part of ethyl cellulose and 1.0 part of the co-crystal adduct of morpholine and myristic acid (s. > 70 g./100 cc.) in 98.5 parts of a mixture of equal volumes of methanol and ethanol. The dried product is clear and transparent. When thermographically heated at image areas, there is formed a corresponding roughened light-diffusing image which on projection appears as a dark image against a light background.

Both morpholine and myristic acid are softeners or plasticizers for polystyrene.

EXAMPLE 9

One part of the co-crystal adduct of diethylamine and 5-formylsalicylic acid (s. 32 g./100 cc.) is dissolved in 20 parts of a 10 percent solution of VYHH vinyl chloride-acetate copolymer in acetone, and the solution is applied at a thickness of 3 mils on 2 mil Mylar polyester film and dried. A further coating of 2 mils of a 13.5 percent solution of cellulose nitrate in methanol is applied and dried. The resulting clear transparent film produces light-diffusing images at thermographically heated image areas and projects dark images against a light background.

Diethylamine is a colorless liquid which boils at about 55°-56° C. At thermographically achieved temperatures, e.g. about 90°-150° C., the adduct is dissociated, the amine is vaporized, and the vinyl polymer is softened; as a result, a vesicular image is produced. The cellulose nitrate topcoat assists in preventing premature escape of the vaporized amine and in protecting the softer vinyl polymer but is not essential, particularly with somewhat thicker first coatings.

EXAMPLE 10

A solution of one part ninhydrin and three parts of the co-crystal adduct of piperidine and benzoic acid (s. 62 g./100 cc.) in 25 parts of water is applied to white bond paper by floating and draining. The dried sheet is tested as a heat-sensitive copy sheet in the thermographic copying process and produces a purple image on a white background.

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Wetting the sheet with methanol, acetone or other organic solvents does not cause a color reaction and the sheet after drying remains heat-sensitive.

Polyvinyl alcohol or other transparent water-soluble binder may be added to the above aqueous solution, and the mixture coated on transparent regenerated cellulose film, to produce a clear transparent heat-sensitive copy-sheet with which color projection transparencies may be thermographically prepared.

EXAMPLE 11

Colored paper having a pink tint and overprinted with a lightly inked design is coated with a first solution containing one part of hydrindantin dihydrate and two parts cellulose nitrate in 17 parts of methyl Cellosolve, and dried. A second coat of one part of co-crystal adduct of hexylamine and benzoic acid (s. 40 g./100 cc.) in 20 parts of a ten percent solution of cellulose nitrate in methanol is added and dried. The pink tint and overprinted design remain fully visible through the transparent coatings. Localized heating in the thermographic copying process produces clearly visible purple images.

Substitution for the second coat of a composition containing one part of the co-crystal adduct of hexylamine and tetrachlorobisphenol A in 20 parts of a 10 percent solution of polyvinyl butyral in trichlorethane, and wherein the adduct is present as finely divided particles, produces a light-diffusing dry surface layer which obscures the color and design of the paper backing. Replacing the binder and solvent with a system in which the adduct is soluble, for example with a solution of polyvinyl butyral in acetone, results in immediate color-forming reaction when the solution is coated over the first-applied layer containing the hydrindantin dihydrate.

The adduct of tetrachlorobisphenol A with hexylamine has a solubility in methanol of only four g./100 cc. The adduct of this acid with morpholine exhibits maximum solubility as compared with adducts of a large number of other amines, the value being 12 g./100 cc.

EXAMPLE 12

Paper is coated with a mixture of 2.5 parts of lead nitrate: thiourea complex, 2.5 parts of the co-crystal adduct of diethylamine and dinitrotoluic acid, and 10 parts of cellulose nitrate, applied from methyl alcohol and dried, to produce a heat-sensitive copy-sheet which forms black images when heated in the thermographic copying process. The solubility of the adduct is 26 g./100 cc. methanol.

What is claimed is as follows:

1. A heat-sensitive copy-sheet adapted for making reproductions of graphic originals by thermographic copying methods and having a visibly heat-sensitive layer comprising a highly methanol-soluble co-crystal adduct, heat-dissociable at thermographic copying temperature, of a basic organic amino compound and an organic acidic compound having a pKa value not greater than about 6, dissolved in a transparent or-

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ganic binder, said adduct and binder being soluble in a common solvent, said binder being heat-softenable, and at least one of said compounds being vaporizable, at said temperature, to form vesicles at the heated areas within said layer.

2. The heat-sensitive copy-sheet of claim 1 wherein said layer is supported on a clear transparent film backing.

3. The heat-sensitive copy-sheet of claims 1 wherein said adduct is soluble in methanol to the extent of at least about 50 grams per 100 cc.

4. The copy sheet of claim 1 wherein said organic acidic compound is a carboxylic, sulfonic, phenolic or fluorosulfone acidic compound.

5. The copy sheet of claim 4 wherein said organic acidic compound is bis(trifluoromethylsulfonyl) methane.

6. A heat-sensitive copy-sheet adapted for making reproductions of graphic originals by thermographic copying methods and having a visibly heat-sensitive layer comprising a highly methanol-soluble co-crystal adduct, heat-dissociable at thermographic copying temperature, of a basic organic amino compound and an organic acidic compound having pKa value not greater than about 6, dissolved in a transparent organic binder, said adduct and binder being soluble in a common solvent, said layer being supported on a heat-shrinkable clear transparent film and at least one of said compounds being a softener for said film at said temperature.

7. The heat-sensitive copy-sheet of claim 6 wherein said adduct is soluble in methanol to the extent of at least about 50 grams per 100 cc.

8. The copy-sheet of claim 6 wherein said organic acidic compound is a carboxylic, sulfonic, phenolic or fluorosulfone acidic compound.

9. The copy-sheet of claim 8 wherein said organic acidic compound is bis(trifluoromethylsulfonyl) methane.

10. A heat-sensitive copy-sheet adapted for making reproductions of graphic originals by thermographic copying methods and having a visibly heat-sensitive layer comprising a highly methanol-soluble co-crystal adduct, heat-dissociable at thermographic copying temperature, of a basic organic amino compound and an organic acidic compound having a pKa value not greater than about 6, dissolved in a transparent organic binder, said adduct and binder being soluble in a common solvent, said layer including an amine-reactive color progenitor material in potentially coreactive association with said adduct and containing no free amine.

11. The heat-sensitive copy-sheet of claim 10 wherein said layer is supported on a clear transparent film backing.

12. The heat-sensitive copy-sheet of claim 10 wherein said adduct is soluble in methanol to the extent of at least about 50 grams per 100 cc.

13. The copy-sheet of claim 10 wherein said organic acidic compound is a carboxylic, sulfonic, phenolic or fluorosulfone acidic compound.

14. The copy-sheet of claim 13 wherein said organic acidic compound is bis(trifluoromethylsulfonyl) methane.

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