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HEAT REACTIVE TRANSPARENT COPY SHEET

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U.S. Cl. 117—36.8 7 Claims

ABSTRACT OF THE DISCLOSURE

A transparent copy sheet capable of acquiring a stable color in selected regions contrasting with the background color of the sheet upon exposing these regions to an elevated temperature, comprising a transparent substrate and a coating comprising (1) ninhydrin; (2) an organic amino compound containing at least one amino group selected from the class consisting of primary and secondary amines, and which is normally reactive with ninhydrin at temperatures below this elevated temperature to form a dye; and (3) a selected substituted urea or thiourea stabilizer.

This invention relates to heat sensitive, transparent copy sheet suitable, e.g., for projection of images onto a screen by overhead transmitted light projections.

The object of this invention is to provide a transparent, substantially colorless heat-sensitive copy sheet, capable of having formed thereon stable heat-induced images of contrasting color.

Another object is to provide copy sheets for making transparent visual aids suitable for use with overhead light projectors, which can be rapidly, clearly, and accurately imaged by conventional thermocopy procedures.

Another object is to provide improved transparent visual aids having images displayed in transparent regions of contrasting color.

A further object is to provide improved stabilized heat-sensitive dye systems.

The invention features a transparent copy sheet capable of acquiring a stable color in selected regions contrasting with the background color of the sheet upon exposing these regions to an elevated temperature, comprising a transparent substrate and a coating comprising (1) ninhydrin; (2) an organic amino compound containing at least one amino group selected from the class consisting of primary and secondary amines, and which is normally reactive with ninhydrin at temperatures below this elevated temperature to form a dye; and (3) a substituted urea or thiourea stabilizer as hereinafter defined.

In particular, one preferred class of stabilizers has the formula:

$$R{-}NH{-}\overset{\overset{X}{\|}}{C}{-}NH_2,$$

where X is selected from the group consisting of oxygen and sulfur, and R is selected from the group consisting of aliphatic, alicyclic, aromatic and heterocyclic radicals forming a C—N bond with the remainder of the stabilizer. Particularly preferred where totally colorless backgrounds are desired are stabilizers in which R is a straight chain aliphatic hydrocarbon radical having from 1 to 3 carbon atoms, such as methyl, ethyl, n-propyl and allyl radicals. Other preferred radicals include phenyl, chloro-o-tolyl, 2-benzimidazoyl and cyclohexyl. N,N'-dimethylurea, N,N'-dimethylthiourea, and barbituric acid are also useful stabilizers. Where R is a straight chain aliphatic hydrocarbon radical having from 1 to 3 carbon atoms, at least about 0.05 mole of stabilizer per mole of ninhydrin is preferred.

That ninhydrin and an amine react to form a dye is known, the reaction occurs on contact and takes place readily at room temperature and more rapidly at temperatures on the order of 55° C. Hence, a coating of ninhydrin

and amine alone on a substrate does not provide a copy sheet useful at room temperature. However, the aforesaid stabilizer prevents the formation of a colored dye at room temperature, while allowing the dye-forming reaction to proceed at an elevated temperature, in accordance with a selective exposure of the sheet to a hot image (about 75° to 110° C.), to form a corresponding colored image on the sheet. Upon cooling, the contrasting color image remains at the exposed region of the sheet, while the remainder of the sheet retains a transparent, contrasting, preferably colorless hue. The stabilizer also prevents background discoloration due to an undesired dye-forming reaction during exposure of the sheet to heat from overhead light projectors. In particular, such a stabilized color sheet will not undergo substantial background coloration during 24 hour exposure in an enclosed oven at 55° C.

The imaging process may be carried out rapidly in a conventional thermocopy machine of the type generally used to make opaque prints, such as that available under the trade name "Thermofax," or by a heated stylus, or by other conventional thermocopy procedures. The hot image may be in the form of a graphic (e.g., typewritten) original, which, when heated and brought into contact with such a copy sheet in a thermocopy machine, will develop, at temperatures well above ambient, a heat pattern in the areas containing graphic matter which pattern will be transferred, as a positive, directly to the copy sheet, portions of the sheet contacting the graphic image acquiring an image of color indicative of the amine-ninhydrin reaction. Moreover, the colored, imaged regions of the copy sheet are suitable for projection of light therethrough, onto a screen, as by an overhead transmitted light projector.

Although the ninhydrin-amine reaction is well-known, certain amines are preferred. Among the preferred amines are the heterocyclic amines such as morpholine, piperidine, and pyrrolidine, and derivatives thereof in which the N-position and at least one adjacent position of the morpholino, piperidino, or pyrrolidino group are unsubstituted. Suitable piperidine derivatives include 4,4'-trimethylene dipiperidine, 4-(3-(4-piperidyl)propyl) - N - piperidino ethanol, bis-piperidinomethane, 4-(N-propionyl aniline) piperidine, 4-(2-keto-1-benzimidazolinyl) piperidine and 4 - benzyl piperidine. In general, for heterocyclic amines, the amount of amine to ninhydrin may be varied in accordance with the deepness of color desired for the colored image, with a presently preferred range being .25 to 25 moles of ninhydrin per available amino hydrogen at an above-described N-position on the amine.

To form a copy sheet, the ninhydrin, amine, and stabilizer are laid down in a thin coating on a transparent substrate in an inert medium containing an evaporizable solvent. To assure against unwanted transfer of the applied coating or ingredients thereof to contacting media, such as the heated graphic original, the coating solution contains a transparent film-forming binder. In addition, an accelerator for the color-forming reaction is preferably included, as well as a visible radiation stabilizing agent (about .05 to .3 part by weight based on total coating weight). The accelerator speeds the image-forming reaction to assure completeness of reaction in a conventionally-timed thermocopy machine, whereas the stabilizing agent protects against image fading or background discoloration by visible radiation.

According to a preferred mixing procedure, the ninhydrin and the amine are first each mixed separately with the film-forming binder in a suitable solvent system, with the accelerator and light stabilizer in the ninhydrin solution. The stabilizer is then added to the ninhydrin solution, after which the ninhydrin and amine solutions are

mixed to form the coating solution. The coating is applied in a thin (1 to 9 lbs. per 3000 sq. ft., preferably 2.5 to 3.5 lbs. per 3000 sq. ft.) layer onto the transparent substrate, and dried to form a copy sheet.

The film-forming binder may be one of a number of well-known transparent film-forming resins. In general, the binder chosen must not significantly alter the reaction temperature of the color-forming reaction, must be substantially nonreactive with the other ingredients, must be permanently adherent to the substrate, must not tack at imaging temperatures or at ambient temperature and humidity, and must be applicable in a film of the desired density. Among the suitable binders are: cellulose esters and ethers, such as ethyl cellulose, cellulose acetate, cellulose butyrate, and cellulose acetate butyrate copolymers, acrylic esters including polymethacrylates such as polymethylacrylates and polybutylmethacrylates, polyvinyl acetate and vinyl chloride copolymers thereof, polyvinyl methacrylates, and polyvinyl butyrals. The choice of binder of course depends, inter alia, on the identity of the substrate, it being desirable to match the plastic properties of binder and substrate.

A preferred substrate is a polyester sheet available from E. I. du Pont de Nemours & Co. under the trade name "Mylar." Other suitable substrates, which must be transparent as well as capable of remaining non-tacky during thermal imaging, include polycarbonates, polyamides (nylon), polystyrene, and cellulose acetate butyrate copolymers.

The solvent chosen should be incapable of dissolving or weakening the substrate, while being suitable for dissolving the binder and reactive components of the coatings. Among the useful solvents with a Mylar substrate are alcohols including methanol and ethanol, ketones such as methylethylketone, di-n-butyl ketone, and ethanol-di-n-butyl ketone, aromatic hydrocarbons such as benzene and toluene, esters such as ethyl acetate and butyl acetate, ethers, and hydrocarbons.

Useful accelerators are described in U.S. Pat. No. 3,293,061, and include aromatic hydroxy compounds (mono, di- and tri-hydroxy), fatty acids, solid aromatic acids (such as toluic acids, benzoic acid, phenoxyacetic and phenyl acetic acids), solid ketones, and anhydrides of the fatty and solid acids. A particularly preferred accelerator is toluic acid.

Among the suitable visible radiation stabilizers are the aromatic reducing compounds such as hydroquinone and gallic acid.

The copy sheets of the present invention are stable to room temperature, and at temperatures up to about 55° C., such as might be encountered if the sheets were stored in hot areas. The sheets are also stable in the presence of visible light and moisture. They can be imaged on a conventional thermocopy machine, with a high degree of latitude—i.e., the exposure conditions may be chosen to provide, in a single, rapid operation (e.g., at a single setting of a commercial thermocopy machine) a finished image in which both the thin, fine lined regions and the larger regions are of comparable deep color and sharp definition. When the image is projected on a screen, the projected image is vivid, easily read, and of high contrast.

Other objects, features and advantages will appear to one skilled in the art from the following examples, which illustrate preferred embodiments of the invention but are not intended in any way to limit the scope thereof:

EXAMPLE 1

A resin solution was prepared by mixing the following, in parts by weight:

Polymethylmethacrylate ("Elvacite 2044," from E. I. du Pont de Nemours & Co.)	45
"Nitrocel RS, 5 to 6 seconds" (from Hercules Powder Co.)	20
Methylethylketone	386
Methanol	134

An amine mix (Mix A) was prepared by dissolving 4,4'-trimethylene dipiperidine in resin solution in the amount of 2.6 grams of 4,4'-trimethylene dipiperidine per 124 grams of resin solution.

A ninhydrin mix (Mix B) was prepared by dissolving ninhydrin and o-toluic acid in resin solution in the amount of 9.5 grams of ninhydrin and 1.2 grams of o-toluic acid per 124 grams of resin solution.

The following components were then added, successively, to Mix B in the amounts indicated: 0.3 gram of ethyl urea stabilizer per 9.5 grams of ninhydrin; and, 60 grams of Mix A per 100 grams of Mix B.

This coating solution was then coated onto a 3 mil Mylar master sheet using a No. 24 wire wound Meyer drawdown rod. The coating was dried at room temperature, leaving a dry coating weight of about 3 lbs. of coating per 3000 sq. ft. of sheet.

An 8½ in. x 11 in. copy sheet cut from the master sheet was imaged in a "Thermofax Secretary" thermocopy machine, with a typewritten white bond sheet as the original. The resultant imaged sheet contained a purple printed image on an otherwise colorless transparent background, and gave a high contrast, sharp, easily read projected printed image on a screen when lighted by an overhead light projector.

Other 8½ in. x 11 in. copy sheets cut from the master sheet, but not imaged, were tested to determine their stability to elevated temperatures which are below the temperature at which the sheet is imaged in a thermocopy machine, but nevertheless above ordinary room temperature. The sheets were tested by being hung for 24 hours in a 55° C. (131° F.) oven. The resultant sheets showed no coloration.

For comparison purposes, a sheet was made, otherwise identical to that described above, except that no stabilizer was used. The entire sheet turned dark purple when heated at 24 hours in a 55° C. oven.

EXAMPLE 2

The same procedures as described in Example 1 were carried out, except that a number of different amino compounds were used in lieu of the 4,4'-trimethylene dipiperidine of Example 1, namely: morpholine; piperidine; pyrrolidine; 4-(3-(4-piperidyl)propyl)-N-piperidino ethanol; bis-piperidinomethane; 4-(N-propionyl aniline) piperidine; 4-(2 - keto-1 - benzimidazolinyl)piperidine; and 4-benzyl piperidine.

The imaging properties and temperature stability (effect of heating at 55° C. for 24 hours) of the resultant copy sheets were substantially identical to those of the copy sheet of Example 1, the background remaining at all times colorless and transparent.

EXAMPLE 3

A number of copy sheets were made in accordance with the procedure of Example 1, except that the following amino compounds and stabilizers were used, with the other ingredients remaining the same:

Amino compound (in Mix A)	Stabilizer
4,4'-trimethylene dipiperidine	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.
Morpholine	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl urea.
Do	Allyl thiourea.
Piperidine	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.
Pyrrolidine	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.
4-(3-(4-piperidyl)propyl-N-piperidine ethanol	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.
Bis-piperidinomethane	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.

Amino compound (in Mix A)	Stabilizer
4-(N-propionyl aniline) piperidine	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.
4-(2-keto-1-benzimidazolinyl)-piperidine	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.
4-benzyl piperidine	n-Propyl urea.
Do	Allyl urea.
Do	N-Methyl thiourea.
Do	Allyl thiourea.

All of these copy sheets formed sharp, clear and transparent colored images while the background remained transparent and colorless during imaging. The sheets showed no discoloration upon being heated for 24 hours at 55° C.

EXAMPLE 4

A number of copy sheets were made in accordance with the procedure of Example 1 except that the following stabilizers were used instead of ethyl urea: viz, phenyl urea; 5-chloro-o-tolyl urea; 2-benzimidozoyl urea; and, 1-phenyl-2-thiourea. Although the resultant imaged sheet in each case contained a colored image on an otherwise substantially colorless transparent background, the sheets did color slightly upon being heated at 55° C. for 24 hours. However, the contrast between imaged and aged background portions of the sheets is sufficient to provide a clear, sharp projected image on a screen when the sheet is lighted with an overhead light projector.

EXAMPLE 5

The procedures of Example 1 were repeated, except that barbituric acid was substituted for ethyl urea as the stabilizer. The resultant copy sheet was of comparable characteristics to those of the copy sheets in Example 4, a slight background discoloration being observed on heating at 55° C. for 24 hours, which is nonetheless insufficient to affect the clarity of the projected image.

EXAMPLE 6

The procedures of Example 1 were repeated, except that N,N'-dimethyl urea was substituted for ethyl urea as the stabilizer. The resultant copy sheet was of comparable characteristics to those of the copy sheets in Example 4, a slight background discoloration being observed on heating at 55° C. for 24 hours, which is nonetheless insufficient to affect the clarity of the projected image.

EXAMPLE 7

A number of copy sheets were prepared, in accordance with the procedures of Example 1, in which each of the stabilizers of Examples 4–6 was used with each of the following amino compounds: morpholine; piperidine; pyrrolidine; 4-(3-(4-piperidyl)propyl)-N-piperidino ethanol; bis-piperidinomethane; 4-(N-propionyl aniline) piperidine; 4-(2-keto-1-benzimidazolinyl) piperidine; and 4-benzyl piperidine. The resultant copy sheets were of comparable characteristics to those obtained in Examples 4 to 6 using 4,4'-trimethylene dipiperidine.

EXAMPLES 8–13

An amine mix (Mix C) was prepared by dissolving 4,4'-trimethylene dipiperidine in the resin solution of Example 1, in the amount of 2.6 gms. of 4,4'-trimethylene dipiperidine per 24 gms. of resin solution.

A ninhydrin mix (Mix D) was prepared by dissolving ninhydrin in the resin solution of Example 1, in the amount of 9.5 gms. of ninhydrin per 124 gms. of resin solution.

A number of coating solutions, tabulated below, were then prepared, containing varying amounts of amine, o-toluic acid, and ethyl urea stabilizer. In each example, the coating solution was prepared by adding to Mix B successively, in the amounts shown in the table below: o-toluic acid (gms. per 9.5 gms. of ninhydrin); ethyl urea stabilizer (gms. per 9.5 gms. of ninhydrin); and, Mix A (sufficient to provide the gms. indicated of 4,4'-trimethylene piperidine, per 9.5 gms. of ninhydrin). The total amount of resin solution, in gms. per 9.5 gms. of ninhydrin, is also tabulated below.

Each coating solution was then coated into a 3 mil Mylar master sheet using a No. 24 wire wound Meyer drawdown rod. The coating was dried at room temperature, leaving a dry coating weight of about 2.5 to 3.5 lbs. of coating per 3000 sq. ft. of sheet.

An 8½ in. x 11 in. copy sheet, cut from each master sheet, was imaged in a "Thermofax Secretary" thermocopy machine, with a typewritten white bond sheet as the original. The resultant imaged sheet contained a purple printed image on an otherwise colorless transparent background, and gave a high contrast, sharp, easily read projected printed image on a screen when lighted by an overhead light projector.

Other 8½ in. x 11 in. sheets, cut from each master sheet, but not imaged, were heated for 24 hours in a 55° C. oven as described in Example 1. Sheets so treated showed no coloration.

Example	Mix C	Ninhydrin	o-Toluic acid	Amine	Stabilizer
8	248	9.5	1.2	2.6	3.6
9	236	9.5	1.1	2.34	3.24
10	212	9.5	0.9	1.82	2.52
11	188	9.5	0.7	1.30	1.80
12	152	9.5	0.4	0.52	0.72
13	140	9.5	0.3	0.26	0.36

EXAMPLES 14–19

A resin solution was prepared by mixing the following, in parts by weight:

Polymethylmethacrylate ("Elvacite 2044" from E. I. du Pont de Nemours & Co.)	45
"Nitrocel RS, 5 to 6 seconds" (from Hercules Powder Co.)	20
Methylethylketone	386
Methanol	134

The following mixes were then prepared, in parts by weight:

Mix E (Amine)

Resin solution	124
4,4'-trimethylene dipiperidine	2.6

Mix F (Ninhydrin)

Resin solution	124
Ninhydrin	9.5

To a specified parts by weight, as indicated below, of Mix F was added a specified parts by weight of o-toluic acid and a specified parts by weight of ethyl urea stabilizer, as tabulated below. Mix E was then added to the aforesaid Mix F—o-toluic acid—stabilizer system to form a single coating solution.

This coating solution was then coated onto a 3 mil Mylar master sheet using a No. 24 wire wound Meyer drawdown rod. The coating was dried at room temperature, leaving a dry coating weight of about 2.5 to 3.5 lbs. of coating per 3000 sq. ft. of sheet.

The sheets had imaging properties comparable to the sheets of Examples 8–13, and showed no coloration after being heated at 55° C. for 24 hours.

Example	Mix F	Ninhydrin	o-Toluic acid	Amine	Stabilizer
14	124	9.5	1.2	2.6	3.6
15	112	8.55	1.2	2.6	3.6
16	88	6.65	1.2	2.6	3.6
17	64	4.75	1.2	2.6	3.6
18	28	1.9	1.2	2.6	3.6
19	16	0.95	1.2	2.6	3.6

EXAMPLES 20–25

The following coating solutions were prepared by dissolving the ninhydrin and amine components separately

in the resin solution of Example 1, adding o-toluic acid and ethyl urea stabilizer to the ninhydrin solution, and then admixing the solutions, all parts being parts by weight. The resultant copy sheets had imaging properties comparable to the sheets of Example 1, and showed no coloration after being heated for 24 hours at 55° C.

Example Number	20	21	22	23	24	25
Resin solution	120	120	120	120	120	120
Ninhydrin	2	2	2	2	2	2
4,4'-trimethylene dipiperidine	1.1	1.1	1.1			
4(3-(4-piperidyl)-propyl)-N-piperidino-ethanol				1.1	1.1	1.1
0-Toluic acid	1.0	1.0	1.0	1.0	1.0	1.0
Ethyl urea	2	1	0.5	2	1	0.5

EXAMPLES 26–33

The following coating solutions were prepared by dissolving the ninhydrin and 4,4'-trimethylene dipiperidine components separately in the resin solution of Example 1, adding o-toluic acid and stabilizer to the ninhydrin solution, and then admixing the solutions, all parts being parts by weight. The resultant copy sheets had imaging properties comparable to the sheets of Example 3, using the same stabilizer, respectively, as well as comparable stability to being heated at 55° C. for 24 hours.

Example Number	26	27	28	29	30	31	32	33
Resin solution	159	159	159	159	159	159	159	159
Ninhydrin	7.6	7.6	7.6	7.6	7.6	7.6	7.6	7.6
4,4'-trimethylene dipiperidine	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08
o-Toluic acid	0.96	0.96	0.96	0.96	9.06	0.96	0.96	0.96
n-Propyl urea	1.92	1.28						
Allyl urea			1.92	1.28				
N-methyl thiourea					1.92	1.28		
Allyl thiourea							1.92	1.28

Other embodiments will appear to those skilled in the art and are within the following claims.

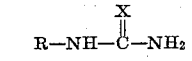
What is claimed is:

1. A transparent copy sheet capable of acquiring a stable color in selected regions contrasting with the background color of said sheet upon exposing said regions to an elevated temperature, said sheet comprising a transparent substrate and a coating comprising:

(A) ninhydrin;

(B) an organic amino compound containing at least one amino group selected from the class consisting of primary and secondary amines, and which is normally reactive with ninhydrin at temperatures below said elevated temperature to form a dye; and

(C) at least about 0.05 mole of stabilizer per mole of ninhydrin, said stabilizer having the formula:



where X is selected from the group consisting of oxygen and sulfur, and

R is selected from the group consisting of aliphatic, alicyclic, aromatic and heterocyclic radicals forming a C—N bond with the remainder of said stabilizer.

2. The copy sheet of claim 1 wherein R is a straight chain aliphatic hydrocarbon radical having from 1 to 3 carbon atoms.

3. The copy sheet of claim 1 wherein said amino compound contains a heterocyclic amino radical having a secondary amino group in the heterocyclic ring, and at least one unsubstituted ring carbon adjacent said amino group.

4. The copy sheet of claim 3 wherein said heterocyclic amino radical is selected from the class consisting of piperidino, morpholino, and pyrrolidino radicals.

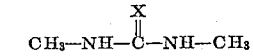
5. The copy sheet of claim 1 wherein R is selected from the group consisting of phenyl, chloro-o-tolyl, and 2-benzimidazoyl radicals.

6. A transparent copy sheet capable of acquiring a stable color in selected regions contrasting with the background color of said sheet upon exposing said regions to an elevated temperature, said sheet comprising a transparent substrate and a coating comprising:

(A) ninhydrin;

(B) an organic amino compound containing at least one amino group selected from the class consisting of primary and secondary amines, and which is normally reactive with ninhydrin at temperatures below said elevated temperature to form a dye; and

(C) at least about 0.05 mole of stabilizer per mole of ninhydrin, said stabilizer having the formula:



where X is selected from the group consisting of oxygen and sulfur.

7. A transparent copy sheet capable of acquiring a stable color in selected regions contrasting with the background color of said sheet upon exposing said regions to an elevated temperature, said sheet comprising a transparent substrate and a coating comprising:

(A) ninhydrin;

(B) an organic amino compound containing at least one amino group selected from the class consisting of primary and secondary amines, and which is normally reactive with ninhydrin at temperatures below said elevated temperature to form a dye; and

(C) barbituric acid.

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MURRAY KATZ, Primary Examiner

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