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De Laurentis et al.

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[54] **THERMOGRAPHIC COPY SHEETS AND PROCESS**

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Related U.S. Application Data

[63] Continuation of Ser. No. 81,737, Oct. 19, 1970, abandoned.

[52] **U.S. Cl.** **117/36.9**

[51] **Int. Cl.** **B41m 5/18**

[58] **Field of Search** 117/36.9, 36.8, 36.2

[56] **References Cited**

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[57] **ABSTRACT**

Heat-sensitive copy film for projection transparency use, comprising a clear plastic film foundation carrying two superposed clear resinous layers which do not melt under conditions of use and which contain co-reactive color-formers. One layer contains a colorless acid-sensitive dye precursor dissolved in a first resin binder and is applied from a first volatile solvent. The other layer contains a heat-vaporizable aromatic acid dissoved in a second resin binder and is applied from a second volatile solvent. The volatile solvent used to apply the top layer is a non-solvent for both the resin binder and the color-former of the base layer.

8 Claims, 2 Drawing Figures

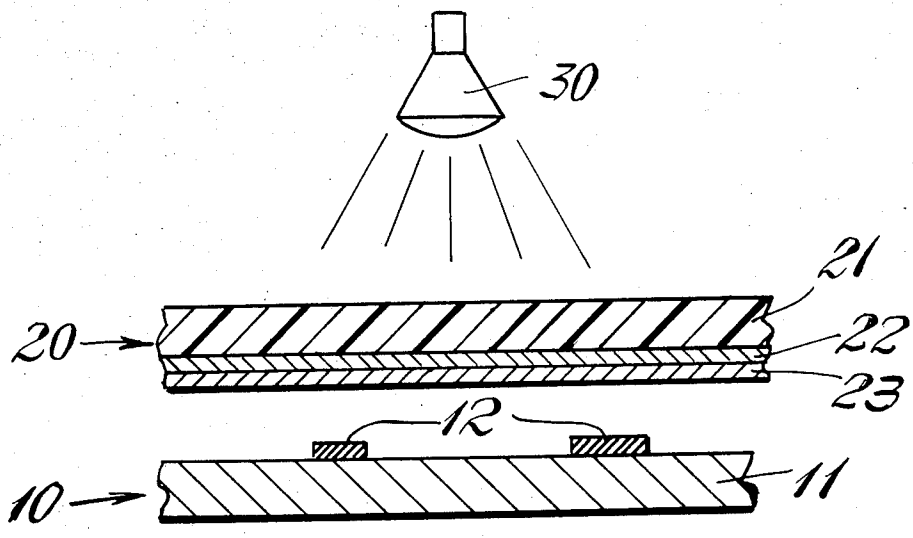


Fig. 1

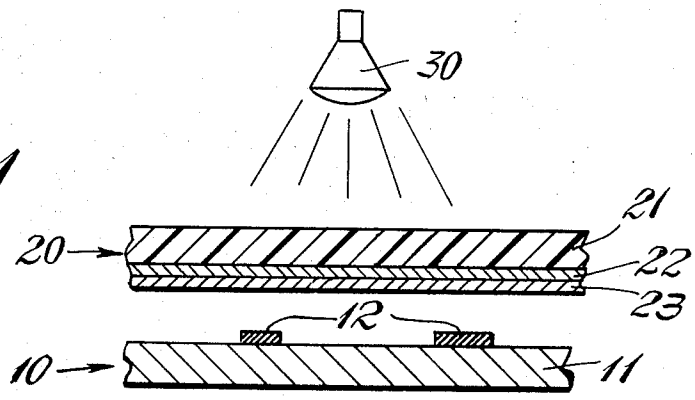
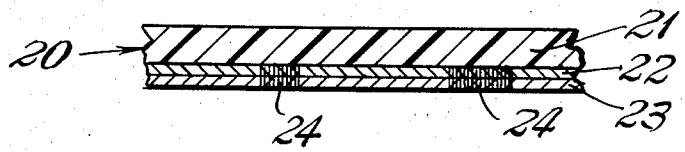


Fig. 2



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THERMOGRAPHIC COPY SHEETS AND PROCESS

This is a continuation of application Ser. No. 81,737 filed Oct. 19, 1970, and now abandoned.

The present invention relates to the field of thermography in which a duplicate copy of an imaged original sheet can be produced on a heat-sensitive copy sheet under the effects of infrared radiation. A variety of heat-sensitive copy sheets are known which have a semi-opaque heat-reactive layer on a translucent paper or transparent film foundation. The heat-reactive layer contains solid particulate color-formers which contribute to the semi-opaqueness of the layer and which react to form a contrasting color in the heated areas. Such color-formers are inert with respect to each other in the solid state and thus may be copresent in a single heat-sensitive layer. However the semi-opaque nature of such a layer precludes the use of such a system for the production of copy sheets suitable for projection transparency work.

It is known to provide donor sheet-receptor sheet thermographic units for the production of projection transparencies. Such units comprise a receptor sheet, which is a clear plastic film carrying a clear resinous coating containing a dissolved color-former, and a donor sheet carrying a semi-opaque layer of undissolved color-former, which is heat-transferable to the receptor sheet to form colored images thereon. The imaged receptor sheet is suitable for use as a projection transparency. However such units are more expensive to manufacture and more difficult to use than a single heat-sensitive copy sheet.

It is the principal object of the present invention to provide a clear heat-sensitive copy film for projection transparency use.

It is another object of this invention to provide a clear heat-sensitive copy film which is stable and resistant to discoloration in the unheated background areas during storage and use under normal conditions.

It is still another object of this invention to provide a clear heat-sensitive copy film which produces sharp, intensely colored images in heated areas, which images are stable against spreading and fading under conditions of normal storage and use.

These and other objects and advantages of this invention will be evident to those skilled in the art in the light of the present disclosure including the drawing in which:

FIG. 1 is a diagrammatic cross-section, to an enlarged scale, of an imaged original sheet and a heat-sensitive copy film superposed for exposure to an infrared radiation source, and separated for purposes of illustration.

FIG. 2 illustrates the heat-sensitive copy film of FIG. 1 after exposure to form heat-reacted images thereon.

The objects and advantages of the present invention are accomplished by the discovery that certain colorless color-forming chemicals may be dissolved in certain resinous binder systems and superposed as clear layers on a clear plastic film foundation to provide heat-sensitive films having the advantageous properties discussed hereinbefore.

The color-forming chemicals suitable for use according to the present invention are the substantially colorless acid-sensitive dye precursors and the heat-vaporizable aromatic acids. Such compounds are well known color-formers for a variety of uses but their use for heat-copying has been limited to systems in which the acid and the dye precursor have been present on separate sheets. The dye precursor is very sensitive to the acid and develops an intense color on contact therewith.

The resinous binder systems useful according to the invention are those which permit the dye precursor and the aromatic acid to be dissolved therein to form clear solutions and which are incompatible with respect to one another on the plastic film foundation.

The resinous binder system for the base layer, adjacent the film foundation, preferably contains the dissolved dye precursor and is applied to the film foundation using a volatile solvent which does not attack the film foundation.

The resinous binder system for the top layer, applied directly over the base layer, preferably contains the dissolved aromatic acid and is applied to the base layer using a volatile solvent which does not dissolve the resin or dye precursor of the base layer.

In this manner the clear layers containing the dissolved color-formers can be placed in intimate contact with each other, and unexpectedly the layers are stable against background color development even when the imaged film is subjected to the heat of an overhead projector for several hours. This is unexpected in view of the fugitive nature of the aromatic acids which normally sublime or vaporize to varying degrees even under gentle heating.

Referring to the drawing, the present heat-sensitive copy films are imaged in the reflex thermographic process as shown in FIG. **1.** The imaged original sheet **10** comprising a foundation **11** carrying infrared radiation-absorbing images **12** is positioned with its images **12** against the coated side of the heat-sensitive copy film **20.** The copy film **20** comprises a clear film **21** carrying a clear resinous dye precursor layer **22** and a clear resinous acid-donor layer **23.** The superposed sheets are briefly exposed to an infrared radiation lamp **30** In conventional manner to heat the images **12** and the corresponding areas of the copy film **20.** Layers **22** and **23** react in the heated areas **24,** shown in FIG. **2,** which correspond to images **12** on the original.

The unimaged copy film is clear and has the appearance of an uncoated sheet of colorless or tinted film. The imaged copy film is a direct-reading copy of the imaged original, when viewed from the uncoated side of the film foundation. The image areas **24** are so intense in color and the copy film **20** is so clear that it is difficult to tell whether the image areas are on one surface or the other or permeate the entire film.

The imaged copy film **20** may be stored for prolonged periods of time and may be projected by an overhead projector for several hours without any change in the image areas **24** or the background areas. Such projectors generally heat the film to a temperature of about 150° F, so that the stability of the present copy film under such conditions is quite unexpected in view of the volatility of the aromatic acid contained therein.

The stability of the present copy film appears to be due to the isolation of the dissolved color-formers in separate non-melting resinous systems, each color-former being dissolved in a resin which is incompatible with the resin in which the other color-former is dissolved, whereby migration of one color-former into the layer containing the other color-former is prevented

except under the effects of heating to a temperature of at least about 190° F.

The resinous binder system for the dye precursor comprises a volatile solvent which is a good solvent for the resin binder and for the dye precursor. The resin binder must comprise either a vinyl chloride polymer, or a mixture of a vinylidene chloride homopolymer or copolymer and another modifying resin. The preferred vinyl chloride polymer is a copolymer such as Vinylite VYHH which contains about 13 percent vinyl acetate. Mixtures of vinyl chloride copolymers or of vinylidene chloride homopolymers and copolymers with other compatible modifying resins such as butadiene-styrene, styrene-acrylonitrile, chlorinated rubber, acrylic resins, and the like synthetic thermoplastic resins, provide excellent results.

It is not completely clear why the use of resin binders other than the vinyl chloride and vinylidene chloride polymers result in products having insufficient stability. Even the vinylidene chloride homopolymers and copolymers must be used in association with another modifying resin which comprises at least about 25 percent by weight and up to about 95 percent by weight of the total mixture. Otherwise the coated film has unsatisfactory stability and develops background discoloration upon slight aging at ordinary room temperature.

Suitable dye precursors include the bis (p-dialkylaminoaryl) methane derivatives of the type disclosed in U.S. Pat. Nos. 2,981,733; 2,981,738 and 3,230,875. Such compounds have good solubility in toluene and mixtures thereof with methyl ethyl ketone and ethyl acetate.

The resinous binder system for the vaporizable aromatic acid comprises a volatile solvent which is a good solvent for the resinous binder and for the aromatic acid. The binder material comprises a mixture of polyvinyl butyral, such as available under the trademark Vinylite XYSG, and an alcohol-soluble cellulose acetate butyrate. Volatile alcohols are the preferred solvents since they are good solvents for the vaporizable aromatic acids.

The preferred vaporizable acids are 5-bromo salicyclic acid and 5-chloro salicylic acid. However other acids such as acetyl salicylic acid and salicylic acid also provide good results.

The amount of color-former in each of the coreactive layers constitutes only a small part of the layer content. In general, the color-former, either dye precursor or aromatic acid, preferably comprises from about 2 percent to about 15 percent by weight based upon the dry weight of the total layer. The remainder of each layer generally consists of the resin content. The layers are preferably applied in a weight of from about 1 to 5 pounds per **3000** square feet of film.

The film foundations suitable for use according to this invention are preferably films which are heat-stable and colorless, although films tinted with dyes which do not absorb infrared radiation are also suitable. Polyethylene terephthalate polyester (Mylar) having a thickness of 2 mils is preferred because of its heat-stability, inertness to the solvents used to apply the coreactant layers and its high transmission of infrared radiation. However heat-contractile films can also be used, such as polystyrene, since the amount of heat required for the present reaction can be kept below the contraction temperature of the film. Soluble films such as polystyrene require the use of a solvent barrier layer, such as a clear water-applied layer of polyvinyl alcohol, between the polystyrene and the base coreactive layer to prevent the stronger solvents of the base layer from reaching the film surface.

The following example is given by way of illustration and should not be considered limitative.

A web of transparent polyethylene terephthalate polyester having a thickness of 2 mils is coated with the following colorless composition in a weight of about 2 pounds per 3,000 square feet:

Ingredients	Parts by Weight
Acrylonitrile-vinylidene chloride copolymer (Saran F-310)	2.
Acrylonitrile-styrene copolymer (Tyril 780)	14.
Color Precursor No. 1 Blue	0.3
Color Precursor No. 21 Yellow	0.4
Color Precursor No. 22 Red	0.3
Methyl ethyl ketone	63.
Ethyl acetate	10.
Toluene	10.

The dye precursors, all commercially available from Allied Chemical Company, were first completely dissolved together in a portion of the total solvent content which was then mixed with the solution of the resins.

The applied coating was dried completely by evaporation of the solvents to form a thin imperceptible colorless base layer on the colorless film foundation. Then a coating of the following colorless composition was applied over the first coating in a weight of about 2 pounds per 3,000 square feet:

Ingredients	Parts by Weight
Cellulose acetate-butyrate	2.5
Polyvinyl butyral (Vinylite XYSG)	7.5
5-bromo salicylic acid	4.0
Ethyl alcohol	86.0

The acid was first dissolved completely in a portion of the alcohol and the solution was added to the resin solution. The applied coating was dried completely by evaporation of the alcohol to form a thin imperceptible colorless top layer over the base layer.

The coated web was cut into sheet lengths for thermographic use. The copy film sheets were as illustrated by FIG. **1** and had a Mylar film base **21,** a base layer **22** containing the dye precursor and a top layer **23** containing the vaporizable acid.

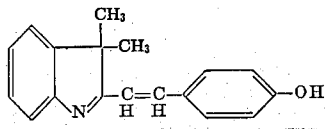
The sheets were used to produce imaged transparencies corresponding to an imaged original sheet by positioning the copy film against the original, as shown in FIG. **1,** and passing the sheets through a conventional infrared radiation exposure machine such as a Thermo-Fax machine. After exposure to the infrared lamp in the machine for a few seconds, the copy film develops sharp clear image areas **24** corresponding to the location of the images **12** on the original.

The imaged copy film may be exposed to sunlight for prolonged periods of time and may be projected on an overhead projector for several hours without any noticeable change in the intensity and sharpness of the image areas and without any noticeable change in the clarity of the background areas of the film.

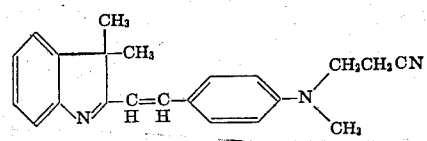
The resinous binder materials of the two layers present on the copy films of this invention must be substantially incompatible with each other in order for the present copy films to be stable. Thus neither resinous binder must be soluble in nor a solvent for the other to any substantial degree. It appears that each of the color-formers is isolated within its own binder system and is masked from contact with the other color-former by means of the incompatibility barrier between the resin systems.

However in the case of the use of mixtures of resins as the binder material for one or both of the present layers, such resins must be substantially compatible with each other in the same layer in order for the layer to be clear. Thus such resins, in the amounts used, must be capable of remaining codissolved as a solid solution after being dissolved in a common volatile solvent, applied as a thin layer and dried by evaporation of the solvent. Any separation of the resins during drying results in a cloudy or milky non-clear layer.

Allied Chemical Color Precursor No. 1 is identified as 4-(bis(p-dimethylamino phenyl) methyl) morpholine and is disclosed in U.S. Pat. No. 2,981,733 mentioned hereinbefore. Allied Chemical Color Precursor No. 21 is a yellow-color-forming dye precursor described in Example 3 of U.S. Pat. No. 3,346,571 and having the structure:



Allied Chemical Color Precursor No. 22 is a red-color-forming dye precursor described in Example 1 of U.S. Pat. No. 3,346,571 and having the structure:



Mixtures of complementary dye precursors can be used to produce a variety of colors including black.

Variations and modifications may be made within the scope of the claims and portions of the improvements may be used without others.

We claim:

1. Heat-sensitive copy film for projection transparency use comprising a thin clear plastic film foundation having thereon two superposed clear resinous layers which do not melt under conditions of use, one layer comprising a substantially-colorless acid-sensitive dye precursor dissolved in a resinous binder from the group consisting of vinyl chloride polymers and mixtures of vinyl chloride polymers and of vinylidene chloride polymers with from about 25 percent up to 95 percent by weight of another compatible modifying resin, and the other layer consisting essentially of a substantially-colorless heat-vaporizable aromatic acid dissolved in an alcohol-soluble resinous binder comprising a mixture of cellulose acetate butyrate and polyvinyl butyral, which mixture is substantially incompatible with the resinous binder material of the said one layer.

2. Heat-sensitive copy film according to claim **1** in which the resinous binder for the dye precursor comprises a mixture of a minor amount by weight of a copolymer of vinylidene chloride and acrylonitrile and a major amount by weight of a styrene copolymer.

3. Heat-sensitive copy film according to claim **1** in which the dye precursor and the aromatic acid are present in amounts equal to from about 2 percent up to 15 percent by weight of the total weight of their respective layers.

4. Heat-sensitive copy film according to claim **1** in which the superposed layers are each present in a weight of from about 1 to 5 pounds per 3,000 square feet of said film.

5. Process of producing a heat-sensitive copy film for projection transparency use comprising the steps of:

a. coating a thin clear plastic film foundation with a first composition comprising a substantially-colorless acid-sensitive dye precursor, a resinous binder material in which said dye precursor is soluble and which is selected from the group consisting of vinyl chloride polymers and mixtures of vinyl chloride polymers and of vinylidene chloride polymers with from about 25 percent to 95 percent by weight of another compatible modifying resin, and a volatile organic solvent for said dye precursor and for said resinous binder material and which is a non-solvent for said film foundation,

b. evaporating said solvent to form a clear resinous base layer which does not melt under conditions of use,

c. coating said base layer with a second composition consisting essentially of a substantially colorless heat-vaporizable aromatic acid, an alcohol-soluble resinous binder material comprising a mixture of cellulose acetate butyrate and polyvinyl butyral in which mixture said acid is soluble and which mixture is substantially incompatible with the resinous binder material of the base layer, and an alcohol solvent for said acid and resinous binder material which is a non-solvent for the dye precursor and for the resinous binder material of said base layer, and

d. evaporating said solvent to form a clear resinous supercoating which does not melt under conditions of use.

6. Process according to claim **5** in which the base layer and the supercoating have a weight of from about 1 to 5 pounds per 3,000 square feet of the film.

7. Process according to claim **5** in which the resinous binder material of the base layer comprises a mixture of a minor amount by weight of a copolymer of vinylidene chloride and acrylonitrile and a major amount by weight of a styrene copolymer.

8. Process according to claim **5** in which the dye precursor and the aromatic acid are present in amounts equal to from about 2 percent up to 15 percent by weight of the total dry weight of their respective layers.

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