

[54] **THERMOGRAPHIC TRANSFER SHEET AND
PROCESS OF COPYING THEREWITH**

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[22] Filed: **July 12, 1971**

[21] Appl. No.: **161,763**

[52] U.S. Cl. **117/36.2, 117/138.8 F, 250/65 T**

[51] Int. Cl. **B41m 5/22**

[58] Field of Search **117/36.2; 250/65.1**

[56] **References Cited**

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Primary Examiner—Murray Katz
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[57] **ABSTRACT**

Thermographic transfer sheet and method for making and using same. Transfer sheet comprises a plastic film foundation carrying a thin, non-transferable imaging layer comprising a crystalline, vaporizable aromatic acid, a film-forming binder material and an inert solid particulate filler material. The filler material impedes crystal growth and disrupts the continuity of the layer whereby the aromatic acid vapors are liberated under the effect of heating.

10 Claims, 2 Drawing Figures

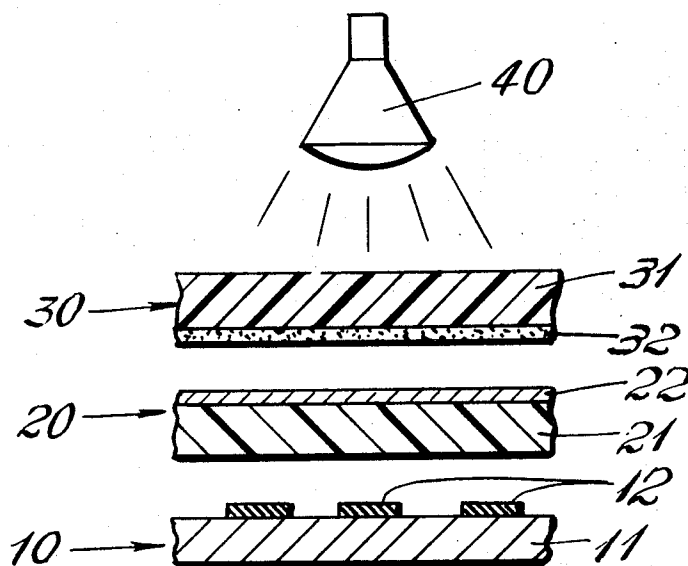


Fig. 1

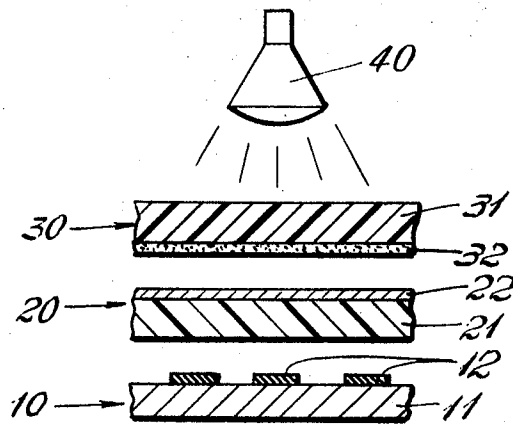
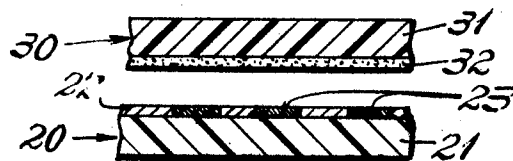


Fig. 2



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THERMOGRAPHIC TRANSFER SHEET AND PROCESS OF COPYING THEREWITH

The present invention is concerned with overcoming these disadvantages and particularly with providing a thermographic transfer sheet suitable for the formation of sharp colored images on a projection transparency film by means of chemical reaction in the reflex thermographic process.

It is an object of this invention to provide coated thermal transfer sheets which are capable of transferring vapors of aromatic acid to a film copy sheet in roller-type thermal copying machines without adhesion occurring between the donor coating and the film copy sheet and without any solid transfer of the donor coating to the film copy sheet.

It is another object of this invention to provide a vapor transfer film having a coating containing a crystalline vaporizable donor material which is present in the form of exceptionally small, fine crystals having a reduced tendency towards solid transfer.

It is yet another object of the present invention to provide a vapor transfer film having a coating which is non-tacky or non-adhesive even when heated to the thermographic temperature range and thus has no affinity for the receptor film.

These and other objects and advantages of this invention will be clear 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 a vapor supply sheet, a film copy sheet and an imaged original sheet superposed in reflex position under exposure to an infrared radiation source, the sheets being in spaced relationship for purposes of illustration, and

FIG. 2 illustrates the vapor supply sheet and film copy sheet of FIG. 1 after exposure to infrared radiation, images being formed on the film copy sheet in areas corresponding to the location of the images present on the original sheet of FIG. 1.

The objects and advantages of the present invention are accomplished by the discovery that the inclusion of a small amount of a finely divided inert filler material in a solvent-applied vapor supply layer comprising film-forming binder material and vaporizable crystalline aromatic acid functions to restrict the size of the crystals of aromatic acid recrystallized out of the solvent and to reduce the adhesive properties of the vapor supply layer whereby adhesion and solid transfer of the vapor supply layer to the film copy sheet during reflex thermographic exposure is prevented.

The inclusion of inert filler particles in a vapor supply sheet for use in the reflex thermographic process is unobvious because such particles are opaque and/or reflective of infrared radiation. Thus the art recognizes that the presence of such materials in a reflex thermal transfer sheet restricts the ability of the infrared radiation to penetrate through to the underlying original images. This is particularly true in the case of thermal transfer layers containing a crystalline aromatic acid donor compound since such compounds tend to refract and/or reflect infrared radiation to some extent because of their generally large crystalline structure. However I have discovered that these two materials, each of which normally has an adverse effect on infrared radiation, cooperate when used in predetermined

relative amounts to provide a vapor supply sheet having greater infrared permeability than when the crystalline aromatic acid is used alone, provided that the filler particles have an average particle size less than about 1 micron.

This invention is based upon the discovery that the presence of from about 0.05 to about 0.5 parts by weight of the finely divided inert filler per part by weight of crystalline aromatic acid in a solution of a film-forming binder material causes the crystalline aromatic acid to recrystallize out of solution in the form of exceptionally small fine crystals having reduced refracting and reflecting properties for infrared radiation and having reduced tendency to transfer in solid crystalline form in the thermographic process. It appears that the fine inert filler particles provide a multiplicity of spaced recrystallization sites for the aromatic acid whereby recrystallization is diluted by distribution throughout the vapor supply layer rather than being concentrated in the form of a lesser number of large crystals. Another advantage of having the aromatic acid present in the form of small fine crystals is that such crystals vaporize more quickly and completely in heated areas whereby the tendency towards heat-transfer of solid crystals is avoided.

Aside from this critical property of the inert filler, such material also has the effect of reducing the tendency of the film-forming binder material from becoming adhesive or tacky when heated to the thermographic temperature range, and the effect of disrupting the continuity of the vapor supply layer whereby the vaporized aromatic acid is able to escape even from interior parts of the supply layer.

The film-forming binder materials useful according to this invention are those which are soluble in a volatile organic solvent which is also a solvent for the crystalline aromatic acid. The preferred solvents are ethyl alcohol and mixtures of methyl ethyl ketone with a minor amount of toluene or xylene. Thus the preferred binders are alcohol-soluble resins such as polyvinyl butyrate (Vinylite XYSG) and cellulose acetate-butyrate, and methyl ethyl ketone-soluble resins such as styrene-butadiene, copolymers (Pliolite S-730), styrene-acrylonitrile copolymers (Tyril), and the like. In some cases it is preferred to include small amounts of a plasticizer for the binder in order to render the binder more cohesive and less brittle or frangible. In all cases the solvent is a non-solvent for the film foundation to which the donor composition is applied.

The ratio of binder material to crystalline aromatic acid may be varied somewhat depending upon the identity of the materials used. However the amount of the binder material generally ranges between about 1 and 5 parts by weight per part by weight of the aromatic acid. Smaller amounts are insufficient to completely bind the acid crystals whereby the layer is chalky or dusty, while larger amounts provide a layer which tends to become excessively tacky or sticky during thermographic exposure and which tends to be pulled over to the copy film during separation of the sheets. The addition of larger amounts of the inert filler overcomes this disadvantage but reduces the infrared permeability of the vapor supply layer whereby it is unsuitable for use in the reflex process.

The inert filler materials useful according to the present invention are those which do not absorb infrared radiation to any substantial degree and which have a

fine average particle size less than about 1 micron and preferably less than about 0.1 micron in diameter. Such materials are powdery in appearance and provide a large number of crystallization sites for the aromatic acid per unit weight of filler. Also such fine particles provide less of an infrared radiation barrier than larger particles and have a greater ability to reduce the tackiness of the binder material, per unit weight, than do larger particles. The preferred filler is silica, available under the trademark Cab-O-Sil M5. This material has an average particle size of 0.012 micron. Also suitable are clay, titania, alumina, calcium carbonate, talc, and the like.

Referring to the drawing, FIG. 1 illustrates an imaged original sheet 10, a copy sheet 20, a vapor supply sheet 30 and an infrared radiation lamp 40. The original sheet 10 comprises a foundation 11 such as paper or plastic film carrying infrared radiation-absorbing original images 12 such as typed or printed carbon black-containing images. The copy sheet 20 comprises a transparent plastic film foundation 21 carrying a transparent imaging layer 22 containing colorless acid-sensitive color-forming material. The vapor supply sheet 30 comprises a transparent plastic film foundation 31 carrying a translucent solvent-applied vapor supply layer 32 comprising film-forming binder material, crystalline vaporizable aromatic acid and filler material.

The sheets are positioned in intimate contact and exposed to the infrared lamp 40 for a few seconds. The radiation is transmitted to the images 12 which become heated. An imagewise heat pattern is conducted back to the vapor supply layer to heat corresponding areas thereof and cause vaporization of the aromatic acid in said areas. The vapors contact and penetrate corresponding areas of the imaging layer 22 to react with the acid-sensitive color-former therein and thereby develop its color. Thereafter the sheets are separated.

FIG. 2 illustrates the separated supply and copy sheets. The copy sheet 20 has colored image areas 23 in its imaging layer 22 corresponding to the image areas of the original sheet 10. The vapor supply sheet 30 has its vapor supply layer 32 retained thereon, the only difference from its original appearance being an increased translucency in the areas from which some of the aromatic acid crystals have been vaporized over to the imaging layer 22.

The film copy sheets 20 used according to the present invention are those having a transparent film foundation 21 such as polystyrene, polyethylene terephthalate, cellulose acetate, and the like. The imaging layer 22 comprises a resinous binder material such as polyvinyl chloride, polyvinylidene chloride, or the like, alone or mixed with other resins, and a small amount of an acid-sensitive colorless color-forming material, and is applied by means of a volatile solvent which is a non-solvent for the film foundation.

Preferred acid-sensitive color-formers include the bis (p-dialkylaminoaryl) methane derivatives disclosed in U.S. Pat. Nos. 2,981,733; 2,981,738; 3,230,875 and 3,346,571. The most preferred color-formers are those commercially available from Allied Chemical Company under the names Color Precursor No. 1 (morpholine derivative disclosed in claim 12 of U.S. Pat. No. 2,981,733), Color Precursor No. 21 (indole derivative disclosed in claim 5 of U.S. Pat. No. 3,346,571) and

Color Precursor No. 22 (disclosed in Example 1 of U.S. Pat. No. 3,346,571), and mixtures of such materials.

The preferred vaporizable aromatic acids for use in the present donor coatings are those which volatilize at the thermographic temperature which generally ranges from about 190° F to about 225° F. Preferred are salicylic acid, acetyl salicylic acid, 5-chlorobenzoic acid, and the like.

The following examples are given by way of illustration and should not be considered limitative.

EXAMPLE 1

An acid vapor donor sheet 30, as shown in FIG. 1 of the drawing, is produced in the following manner. A 0.5 mil film 31 of polyethylene terephthalate is coated on one surface with a thin layer of the following composition:

Ingredients	Parts by Weight
Polyvinyl butyral (Vinylite XYSG)	10
Salicylic acid	4
Diocetyl phthalate	2
Silica (Cab-O-Sil M-5)	1
Ethyl Alcohol	83

The composition comprises a solution of the ingredients in the ethyl alcohol with the silica uniformly dispersed throughout. After coating and evaporation of the ethyl alcohol, the layer 32 has a dry weight of about 1 pound per 3,300 square feet of film. The dried coating 32 on the film foundation 31 is nearly clear and highly transparent due to the extremely fine crystalline structure of the salicylic acid.

A companion reactive receptor sheet 20 is produced in the following manner. A 1.0 mil film 21 of polyethylene terephthalate is coated on one surface with a thin layer of the following composition:

Ingredients	Parts by Weight
Acrylonitrile-vinylidene chloride copolymer	2
Acrylonitrile-styrene copolymer	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 were first dissolved together in a portion of the solvent mixture and the solution was added to a solution of the resins in the remainder of the solvent mixture. The composition was applied in a weight of 2 pounds per 3,300 square feet of film and was solidified by evaporation of the solvents. The dried coating 22 is nearly imperceptible on the film foundation 21.

The receptor sheet 20 and the vapor donor sheet 30 are preferably united along one edge by means of a weak adhesive line to form an assembly or unit. During storage an interleaf sheet is preferably interposed between the sheets to space the donor layers 32 and the receptor layer 22 to prevent reaction between the layers.

The assembly is used in the reflex copying process to copy an original sheet in the manner illustrated by FIG. 1 of the drawing. The original sheet 10 comprises a paper foundation 11 having thereon carbon black-containing typed images 12. The original sheet and the assembly are positioned as shown and exposed to an infrared lamp 40 by passing the sheets through a conventional thermal copying machine of the belt or roller type.

The sheets emerge from the machine after an exposure of a few seconds during which period an image-wise heat pattern having a temperature in the area of from about 200° F to 250° F is conducted to vapor donor layer 32 to cause portions of the salicylic acid in the donor layer, in areas corresponding to the location of the original images 12, to vaporize against and into contacting portions of the reactive receptor layer 22. The imagewise reaction of the acid vapors with the color-formers in layer 22 develops black-colored images 23 in layer 22 corresponding to the original images 12, as shown in FIG. 2. Imaged receptor sheet 20 is a sharp, stable copy of the original sheet 10 and is suitable for use as a projection transparency. The transparency is stable because it is free of unreacted or crystalline salicylic acid, the presence of which would cause gradual spreading or broadening of image areas 23 due to migration and reaction with the undeveloped color precursors in areas adjacent the image areas 23.

The following example illustrates other suitable acid vapor donor sheet compositions which can be produced, coated onto film foundations and used in the same manner disclosed in Example 1.

EXAMPLE 2

Vapor donor compositions for use on a styrene film foundation are formulated as follows:

Ingredients	Parts by Weight		
Cellulose acetate-butyrate	2.5	0	0
Polyvinyl butyral (Vinylite XYSG)	7.5	10	5
Diocetyl phthalate	0	2	1
5-bromo salicylic acid	4	0	0
Salicylic acid	0	6	4
Glyoxal (40percent)	0	1	0.5
Silica (Cab-O-Sil M-5)	1	1	0.5
Ethyl Alcohol	85	80	89

The receptor composition of Example 1 may be modified to contain 1 part by weight of any one of the three color-formers, where blue, yellow or red copies are desired.

The vapor donor sheets of the present invention are also useful for thermally producing light-refractive images on a plain, untreated plastic film such as heat-contractile polystyrene, cellulose acetate, polyethylene terephthalate, or the like. This is accomplished by the reflex exposure method discussed herein, the plain film being substituted for the reactive receptor film of the Examples. The images formed on the plain film are frosted in appearance and comprise the acid crystals which have recrystallized from the vapor state in the form of larger crystals than those present in the vapor donor layer. Such images project as black images due to the light-refractive properties of the crystals.

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

I claim:

1. Thermographic transfer sheet which is transmissive of infrared radiation comprising a thin plastic film foundation having thereon a thin heat-non-transferable layer comprising 1 part by weight of a heat-vaporizable crystalline aromatic acid having a vaporization temper-

ature between about 190° F and 225° F, from 0.05 to 0.5 part by weight of a finely divided, powdery, inert filler having an average particle size less than about 1 micron which inhibits the crystal growth of said aromatic acid and from 1 to 5 parts by weight of a synthetic thermoplastic film-forming binder material which is soluble in a volatile solvent capable of dissolving said acid but incapable of dissolving said plastic film foundation, said layer being capable of liberating vapors of said aromatic acid when heated to thermographic temperatures.

2. Transfer sheet according to claim 1 in which the film foundation comprises polystyrene.

3. Transfer sheet according to claim 1 in which the aromatic acid comprises salicylic acid.

4. Transfer sheet according to claim 1 in which the filler comprises silica.

5. Transfer sheet according to claim 1 in association with a reactive receptor sheet comprising a plastic film foundation having thereon a coating comprising a substantially colorless chemical compound which is reactive with the vapors of said aromatic acid to form an intensely colored reaction product.

6. Reflex thermographic process for producing a copy of an imaged original sheet comprising superposing a transfer sheet, a copy sheet and an imaged original sheet and applying infrared radiation through said transfer and copy sheets to said original images to cause imagewise heating of said transfer sheet and imagewise transfer of imaging material to said copy sheet to form a copy of said original sheet, characterized in that said transfer sheet comprises a thin plastic film foundation having thereon a thin heat-non-transferable layer comprising 1 part by weight of a heat-vaporizable crystalline aromatic acid imaging material having a vaporization temperature between about 190° F and 225° F, from 0.05 to 0.5 part by weight of a finely divided, powdery, inert filler having an average particle size less than about 1 micron which inhibits the crystal growth of said aromatic acid and from 1 to 5 parts by weight of a synthetic thermoplastic film-forming binder material which is soluble in a volatile solvent capable of dissolving said acid but incapable of dissolving said plastic film foundation, said layer transferring vapors of said aromatic acid imaging material to said copy sheet to form a copy of said imaged original sheet.

7. Process according to claim 6 in which said copy sheet comprises a plastic film foundation having thereon a coating comprising a substantially colorless chemical compound which is reactive with the vapors of said aromatic acid to form an intensely colored reaction product.

8. Process according to claim 6 in which the aromatic acid comprises salicylic acid.

9. Process according to claim 6 in which the inert filler comprises silica.

10. Process according to claim 7 in which said copy sheet is releasably attached along one edge to said transfer sheet to comprise a unit.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,751,286 Dated August 7, 1973

Inventor(s) Douglas A. Newman

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet in the ABSTRACT lines 6 and 7, cancel "impedes crystal growth" and insert -- provides a multiplicity of crystallization sites for the aromatic acid, thus inducing the formation of fine acid crystals, --; line 9, after "heating." insert -- It is known in the thermographic copying process to transfer vaporizable imaging materials from one sheet to a copy sheet in areas corresponding to the imaged areas of an original sheet by means of infrared radiation to produce an imaged projection transparency. According to such known methods, the imaging material is present in a supply sheet as an impregnation or as a coating containing a film-forming binder material. Impregnated paper sheets are unsatisfactory for use in the reflex process for imaging plastic film copy sheets because of their reflective properties and because of their tendency to produce a paper fiber imprint on the film copy sheet.

Conventional coated vapor-transfer sheets are also unsatisfactory, particularly for use in roller-type thermal copying machines and in connection with certain film copy sheets because of the tendency of the coating to soften and adhere to the film copy sheet and transfer thereto as a solid mass when the sheets are separated. This is particularly disadvantageous when the copy is a colored copy produced by the reaction of the vaporizable aromatic acid with an acid-sensitive color-former

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,751,286 Dated August 7, 1973

Inventor(s) Douglas A. Newman Page - 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

present in a coating on the film copy sheet. In areas where the images are formed by vapor transfer and reaction, the images project as colored images whereas in areas where a mass-transfer of the donor coating occurs, the formed images contain crystalline aromatic acid which is refractive and the images project as black images. --. Column 2, line 48, after "solvent" insert -- used --.

Signed and sealed this 20th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,751,286 Dated August 7, 1973

Inventor(s) Douglas A. Newman

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet in the ABSTRACT lines 6 and 7, cancel "impedes crystal growth" and insert -- provides a multiplicity of crystallization sites for the aromatic acid, thus inducing the formation of fine acid crystals, --; Column 1, between the title and line 4 insert -- It is known in the thermographic copying process to transfer vaporizable imaging materials from one sheet to a copy sheet in areas corresponding to the imaged areas of an original sheet by means of infrared radiation to produce and imaged projection transparency. According to such known methods, the imaging material is present in a supply sheet as an impregnation or as a coating containing a film-forming binder material. Impregnated paper sheets are unsatisfactory for use in the reflex process for imaging plastic film copy sheets because of their reflective properties and because of their tendency to produce a paper fiber imprint on the film copy sheet.

Conventional coated vapor-transfer sheets are also unsatisfactory, particularly for use in roller-type thermal copying machines and in connection with certain film copy sheets because of the tendency of the coating to soften and adhere to the film copy sheet and transfer thereto as a solid mass when the sheets are separated. This is particularly disadvantageous when the copy is a colored copy produced by the reaction of the vaporizable aromatic acid with an acid-sensitive color-former present in a coating on the film copy sheet. In areas where the images are formed by vapor transfer and reaction, the images project as colored images whereas in areas where a mass-transfer of the donor coating occurs, the formed images contain crystalline aromatic acid which is refractive and the images project as black images. Column 2, line 48, after "solvent" insert -- used --.

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CERTIFICATE OF CORRECTION

Patent No. 3,751,286

Dated August 7, 1973

Inventor(s) Douglas A. Newman

Page - 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Delete claims 1 and 6 as printed and substitute the following claims 1 and 6.

1. Thermographic transfer sheet which is transmissive of infrared radiation comprising a thin plastic film foundation having thereon a thin heat-non-transferable layer comprising 1 part by weight of a heat-vaporizable crystalline aromatic acid having a vaporization temperature between about 190° F and 225° F and being capable of color-forming reaction on contact with a colorless acid-sensitive color-forming compound, from 0.05 to 0.5 part by weight of a finely-divided, powdery, inert filler having an average particle size less than about 1 micron and from 1 to 5 parts by weight of a synthetic thermoplastic film-forming binder material which is soluble in a volatile solvent capable of dissolving said acid but incapable of dissolving said plastic film foundation, said filler providing a multiplicity of spaced crystallization sites for said aromatic acid, thus inducing the formation of a multiplicity of fine crystals of said acid, said filler also reducing the tendency of the film-forming binder material from becoming adhesive and tacky when heated to thermographic temperatures and disrupting the continuity of the layer to facilitate the vaporization of the aromatic acid, said layer being capable of liberating vapors of said aromatic acid when heated to thermographic temperatures.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,751,286 Dated August 7, 1973

Inventor(s) Douglas A. Newman Page - 3

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

6. Reflex thermographic process for producing a copy of an imaged original sheet comprising superposing a transfer sheet, a copy sheet and an imaged original sheet and applying infrared radiation through said transfer and copy sheets to said original images to cause imagewise heating of said transfer sheet and imagewise transfer of imaging material to said copy sheet to form a copy of said original sheet, characterized in that said transfer sheet comprises a thin plastic film foundation having thereon a thin heat-non-transferable layer comprising 1 part by weight of a heat-vaporizable crystalline aromatic acid imaging material having a vaporization temperature between about 190° F and 225° F and being capable of color-forming reaction on contact with a colorless acid-sensitive color-forming compound, from 0.05 to 0.5 part by weight of a finely-divided, powdery, inert filler having an average particle size less than about 1 micron and from 1 to 5 parts by weight of a synthetic thermoplastic film-forming binder material which is soluble in a volatile solvent capable of dissolving said acid but incapable of dissolving said plastic film foundation, said filler providing a multiplicity of spaced crystallization sites for said aromatic acid, thus inducing the formation of a multiplicity of fine crystals of said acid, said filler also reducing the tendency of the film-forming binder material from becoming adhesive and tacky when heated to thermographic temperatures and disrupting the continuity of the layer to facilitate the

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CERTIFICATE OF CORRECTION

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Dated August 7, 1973

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Page - 4

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

the vaporization of the aromatic acid, said layer transferring vapors of said aromatic acid imaging material to said copy sheet to form a copy of said imaged original sheet.

This certificate supersedes Certificate of Correction issued August 20, 1974.

Signed and sealed this 18th day of February 1975.

(SEAL)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks