

[54] **SHEET MATERIAL USEFUL IN IMAGE TRANSFER TECHNIQUES**

[75] Inventors: **Victor R. Franer**, Roseville; **Darrell C. Burman**, Bethel, both of Minn.

[73] Assignee: **Minnesota Mining and Manufacturing Company**, St. Paul, Minn.

[22] Filed: **July 12, 1974**

[21] Appl. No.: **488,221**

[52] U.S. Cl. **96/28; 96/67; 96/48 HD; 96/114.1; 117/3.2; 117/68 R; 250/318**

[51] Int. Cl. **G03c 11/12; B41m 3/12; G03c 5/16**

[58] Field of Search **96/67, 28, 48 HD, 114.1; 117/3.2, 68 R, 363; 250/318**

[56] **References Cited**

UNITED STATES PATENTS

3,859,094 1/1975 Franer et al. 96/67

Primary Examiner—Norman G. Torchin

Assistant Examiner—Alfonso T. Suro Picó

Attorney, Agent, or Firm—Alexander, Sell, Steldt & DeLaHunt

[57] **ABSTRACT**

Sheet material is provided which is useful in image transfer techniques whereby an image of an original is formed on a suitable receptor. A method is also provided for forming a colored image of an original on a differently colored receptor.

9 Claims, 5 Drawing Figures

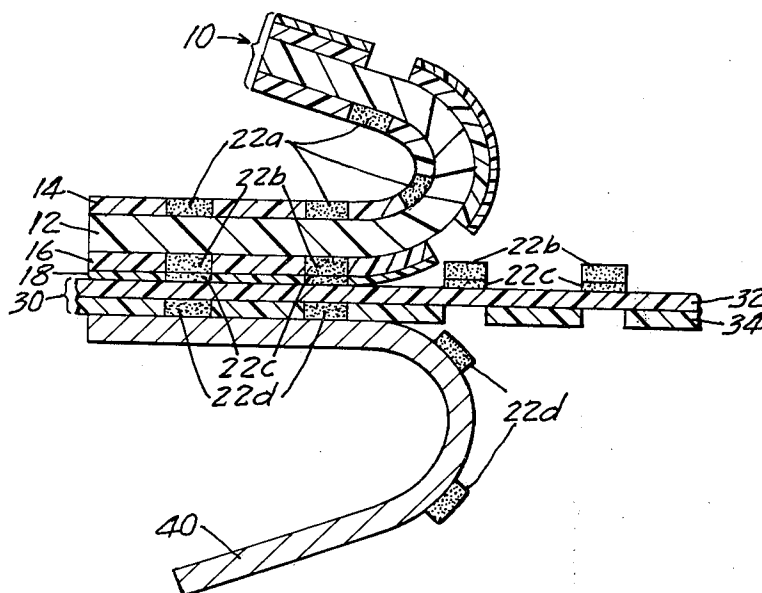


FIG. 1

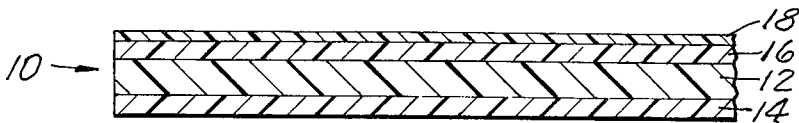


FIG. 2

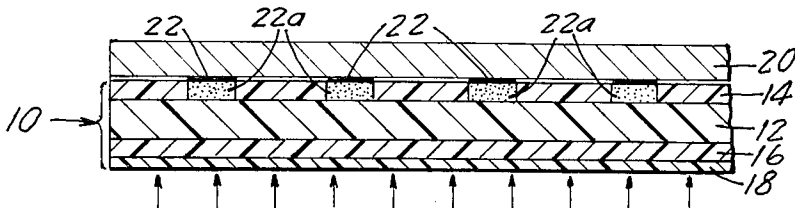


FIG. 3

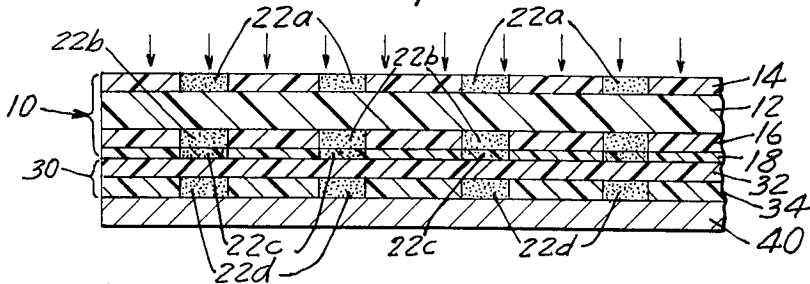


FIG. 4

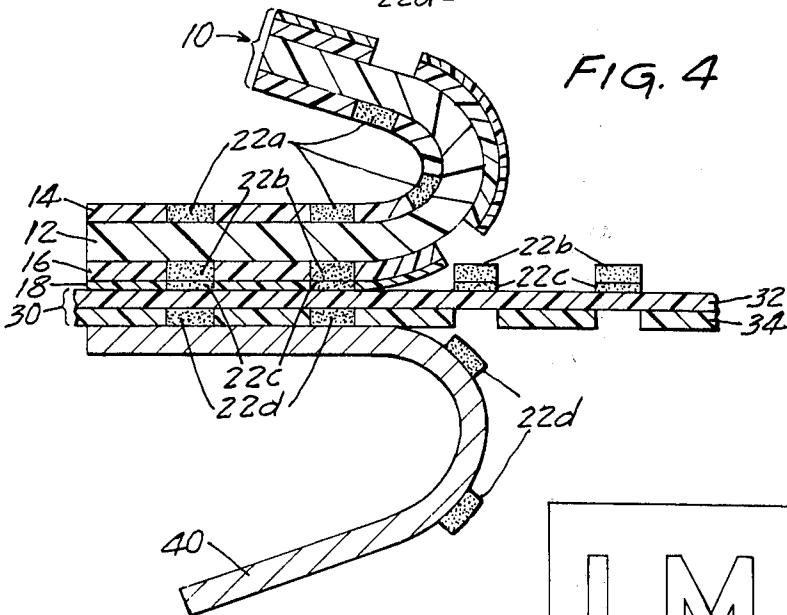
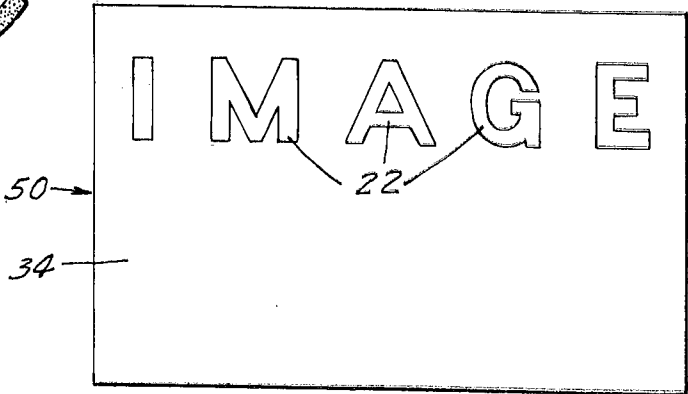


FIG. 5



SHEET MATERIAL USEFUL IN IMAGE TRANSFER TECHNIQUES

This invention relates to imageable sheet material and, more particularly, to imageable sheet material which is useful in image transfer techniques.

Prior to this invention sheet materials have been available which have an imageable layer on one surface and a heat-fusible layer on the opposite surface. Such sheet materials are the subject of our copending application Ser. No. 321,518, filed Jan. 5, 1973 and now U.S. Pat. No. 3,859,094. Such sheet materials have been well accepted and represent an improvement in the field of thermographic image transfer.

The present invention provides sheet materials which are improvements on our prior invention. The present invention also provides a method for forming a colored image of an original on a receptor of a different color.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a sheet material useful in image transfer techniques whereby a copy of an original is first made after which a fusible coating on the sheet material is transferred thermographically in an imagewise manner to a receptor. The sheet material of the invention comprises:

- a. a thin, flexible backing which is transparent to infrared radiation;
- b. an imageable layer coated over one major surface of said backing, said imageable layer being capable of providing infrared-absorptive image areas in one of the following manners:
 - i. upon imagewise exposure thereof to a heat pattern; or
 - ii. upon imagewise exposure thereof to a light pattern followed by development;
- c. a continuous heat-fusible infrared-transparent first layer coated over the other major surface of said backing, said heat-fusible layer comprising a mixture of resin and wax and being tacky at temperatures in the range of about 60° to 310°C.; and
- d. a continuous, non-tacky, infrared-transparent top layer over said first layer, said top layer comprising a mixture of resin and wax and having a softening point at least as high as said first layer, said top layer being at a coating weight in the range of about 0.1 to 0.9 grams per square foot, and said top layer having a matte surface.

The imageable layer of the sheet material can comprise various materials (e.g., those which are imaged by exposure to a heat pattern; those which are imaged by exposure to visible light; or those which are imaged by exposure to ultraviolet radiation).

To form an image of an original on a receptor, the sheet material is used, in one manner, according to the following procedure:

- a. superimposing said sheet material (of the type having a visibly heat-sensitive imageable layer) over a graphic original having infrared-absorptive image areas;
- b. briefly exposing said original to intense infrared radiation whereby infrared-absorptive image areas are formed in said imageable layer corresponding to the image areas of said original;
- c. placing the top layer of said sheet material in contact with a receptor;
- d. exposing said imaged sheet material to intense infrared radiation whereby said top layer and said

first layer, in image areas, become tacky and fuse; and

- e. removing said imaged sheet material from said receptor whereby the portions of said top layer and said first layer corresponding to said image areas remain firmly adherently bonded to said receptor.

In another process a colored image of an original is formed on a differently colored receptor, the process comprising:

- a. providing sheet material of the invention;
- b. superimposing the sheet over an original and exposing to intense infrared radiation (if the sheet is heat-sensitive), or exposing the sheet to a light pattern (if the sheet is light sensitive), so as to form infrared-absorptive image areas in the sheet corresponding to the image areas of the original;
- c. forming a sandwich by placing the top layer of the imaged sheet material in contact with the back side of a visually transparent first receptor sheet which is coated on its front side with a continuous, heat-fusible, colored layer which is tacky at temperatures in the range of about 60° to 310°C.;
- d. superimposing said sandwich over a second receptor;
- e. exposing the imaged sheet material to intense infrared radiation whereby the first layer and the top layer of said sheet, in image areas, become tacky and fuse to the back side of said first receptor sheet, and whereby said heat-fusible layer of said first receptor sheet, in image areas, becomes tacky and fuses to said second receptor; and
- f. removing said second receptor from said first receptor sheet and removing said imaged sheet from the back side of said first receptor sheet, whereby the portions of said first layer and said top layer of said imaged sheet material, in image areas, remain firmly adherently bonded to the back side of said first receptor sheet, and whereby the portions of said heat-fusible layer of said first receptor sheet, in image areas, remain firmly adherently bonded to said second receptor.

With the sheet material of this invention, clear and sharp transferred images are obtained because of complete transfer of the top layer and the first layer at image areas. In preferred embodiments said first layer is colored (with dispersed dye or pigment) although for some applications such layer need not be colored. For example, layers which are oleophilic can be used in the preparation of lithographic plates regardless of color.

DETAILED DESCRIPTION OF THE INVENTION

The invention is described in more detail hereinafter with reference to the accompanying drawings wherein like reference characters refer to the same parts throughout the several views and in which:

FIG. 1 shows the sheet material of the invention;

FIG. 2 shows one method by which the sheet is imaged;

FIGS. 3 and 4 show a method whereby a colored image of a graphic original is formed on a differently colored receptor;

FIG. 5 shows the product produced by a method of the invention.

Referring to FIG. 1 there is shown sheet material 10 comprising a thin, flexible backing 12 which is transparent to infrared radiation. Backing 12 ordinarily is visibly transparent although it could be translucent so

long as it is transparent to infrared radiation. Representative backings include thin (e.g., 0.25 mil to 4 mils) plastic films (e.g., polyester, polystyrene, cellulose acetate), map overlay tracing paper, glassine paper, etc. It is highly preferable that one major surface of backing 12 be quite smooth so that first layer 16 will cleanly transfer therefrom in the processes described hereinafter.

Imageable layer 14 coated over one major surface of backing 12 is of a type which will form infrared-absorptive image areas when exposed and developed. Layer 14 may comprise, e.g., any of the visibly heat-sensitive systems described in Miller, et al., (U.S. Pat. No. 2,663,654) which relates to a system comprising an iron salt of a long chain fatty acid and a phenol co-reactant; Owen (U.S. Pat. No. 2,910,377) which relates to a system comprising a silver soap of a long chain fatty acid and suitable reducing agent; Newman, et al., (U.S. Pat. No. 3,682,684) which relates to a system comprising a mixture of silver and ferric soaps of long chain fatty acids and a phenolic co-reactant; Morgan (U.S. Pat. No. 3,457,075) which relates to a "dry silver" system comprising photosensitive silver halide catalyst-forming means in catalytic proximity with major proportions of organic silver salt oxidizing agents, and reducing agents for silver ion; and Workman (U.S. Pat. No. 3,094,417) which relates to a "dry photo" system. Layer 14 may also comprise a conventional light-sensitive layer, e.g., conventional wet silver photographic emulsion. Layer 14 may also comprise material which is imageable by exposure to ultraviolet light (e.g., diazo resin overcoated with, or physically mixed with, a water-insoluble resinous polymer according to the techniques described in U.S. Pat. No. 3,671,236 (Van Beusekom).

First layer 16 is a continuous coating which is non-tacky at room temperature but is heat-fusible. Layer 16 can be opaque, translucent, or transparent so long as it is transparent to infrared radiation. At elevated temperatures (e.g., 60° to 310°C.) layer 16 becomes quite tacky and fuses. Preferably layer 16 has a rather sharp fusing or melting point. Layer 16 may be colored by the use of conventional dyes or pigments.

Over layer 16 is a continuous top layer 18 which is non-tacky at room temperature, heat-fusible, and infrared-transparent. Top layer 18 has a softening or melting point at least as high as layer 16. The coating weight of layer 18 is in the range of about 0.1 to 0.9 grams per square foot.

Typically layers 16 and 18 each comprise a mixture of resin and wax. Resins which can be used include both natural and synthetic or mixtures thereof. Representative resins include rosins, hydrogenated rosins, rosin esters, copal, coumarone indene resins, polyterpene resins, phenolic rosins, vinsol, polyamide resins, vinyl resins (e.g., vinyl acetate/vinyl chloride copolymers), ketone aldehyde resins, acrylic acid ester derivative polymers (e.g., polyethyl acrylate, butyral methacrylate), polystyrene and low molecular weight styrene copolymers (e.g., M. W. 20,000 to 75,000) and other similar resins.

Waxes which can be used include natural waxes, petroleum waxes, and synthetic waxes. Representative waxes include beeswax, carnauba wax, montan wax, ceresin wax, esparto wax, candelilla wax, Japan wax, paraffin wax, petroleum microcrystalline wax, fatty diamide wax, polyester wax, and other similar waxes.

The resin and wax are typically mixed together by sand milling techniques in solvent media, or by dissolving the materials in a common solvent. The amount of wax used is typically zero to 50% by weight of the resin component with about 30% by weight being a common loading.

The amount and type of the wax component used is selected so as to provide for a rather sharp melting or fusing point at a temperature in the range of 60° to 310°C. It may be said that better transferred image definition is obtained when using layers having relatively sharp melting or fusing points.

Various additives or modifying agents such as plasticizers, fluidizing agents, lubricating agents, etc., may also be used to assist in obtaining the desired melting or fusing point for layers 16 and 18.

Layers 16 and 18 are readily and easily applied to the backing of the sheet material using, e.g., solvent or dispersion coating techniques. Such techniques include knife coating, roll coating, rotogravure coating, air knife coating, curtain coating, etc.

The typical thickness for layer 16 is about 0.125 mil to 1 mil. Preferred thicknesses range from about 0.3 mil to 0.6 mil. The typical coating weight for layer 18 is in the range of about 0.1 to 0.9 grams per square foot.

The top surface of layer 18 is not glossy or smooth but rather is a matte surface (i.e., somewhat rough or pebbled). The desired surface roughness can be obtained in various manners, although one very simple manner is to mix the desired resin and wax in such a manner that particles of about 2.0 to 10 microns (preferably about 5 microns) of wax are dispersed throughout a continuous phase of resin. This surface roughness permits air to remain between the sheet material and a receptor when transferring images to such receptor, the air serving as a slight insulator so as to prevent undue heating and transfer of layers 16 and 18 in areas adjacent to desired image areas.

In FIG. 2 there is shown one method whereby the novel sheet is imaged. Sheet material 10 (having a visibly heat-sensitive imageable layer 14) is positioned under graphic original 20, having infrared-absorptive areas 22, in the manner shown. Next, the graphic original is briefly exposed to intense infrared radiation whereby infrared-absorptive image areas 22a corresponding to the image areas of the original are formed in heat-sensitive layer 14. When the sheet material of the invention is transparent, the imaged sheet material is also useful as a projection transparency.

A preferred technique for imaging the novel sheet in the above-described manner is by passing the superimposed graphic original and novel sheet through a conventional thermographic copying machine (e.g., a Thermofax machine available from Minnesota Mining and Manufacturing Company). In order to prevent portions of layers 16 and 18 from transferring to the belt or roller of the thermographic copying machine during the imaging step, it is preferable to place a silicone-coated carrier sheet (or other suitably coated release sheet) against layer 18. Such carrier sheets are typically plastic films (e.g., cellulose acetate, Teflon, cellulose acetate propionate).

After the novel sheet has been imaged as shown in FIG. 2, it is placed against the back side of a suitable receptor 30 in the manner shown in FIG. 3. A second

receptor 40 is placed against the front side of receptor 30.

Receptor 30 comprises visually transparent backing 32 (preferably a flexible plastic film) and colored layer 34 adhered thereto. Typically layer 34 is a mixture of resin and wax which is colored by dyes or pigments. The resins and waxes which can be used are the same as those described above for layers 16 and 18. Preferably the thickness of layer 34 is in the range of 0.4 to 1.5 mils. Receptor 30 is also infrared-transparent. Layer 34 is tacky at temperatures in the range of about 60°C. to 310°C. Receptor 40 may be any opaque, transparent, or translucent substrate (e.g., metal, plastic, paper, etc.), although it should not be highly absorptive of infrared radiation. Preferably, this receptor is a thin, flexible film or sheet (e.g., paper, plastic, metal). When the receptor is a transparent film, or an embossed plastic film it is useful as a projection transparency. In order to obtain a firmer bond between the fused portions of layer 34 and receptor 40, one surface of receptor 40 may be coated with a conventional primer (e.g., polyamide resin, polyvinyl chloride resin, polyester resin, shellac, cellulose acetate). The image areas on the receptor are water-resistant, smudge-proof, and light-stable.

The sandwich shown in FIG. 3 is exposed to intense infrared radiation (e.g., in a conventional thermographic copying machine) whereby layer 16, in image areas 22b, and layer 18, in image areas 22c, fuse and become tacky. As a result, portions 22c of layer 18 adhere to the back side of receptor 30 and portions 22b of layer 16 remain adhered to portions 22c. Also, layer 34 (on receptor 30), in image areas 22d, fuse and become tacky, thereby becoming adhered to second receptor 40. Image portions 22b, 22c, and 22d are in registry as shown.

In FIG. 4 the imaged sheet material is peeled away from the back side of receptor 30 so as to leave image portions 22b and 22c adhered to receptor 30 in the manner shown. Second receptor 40 is also peeled away from receptor 30 thereby removing image portions 22d. The resulting product 50 is shown in FIG. 5, area 34 being the background and areas 22 being image areas.

The invention is further illustrated by means of the following examples wherein the term "parts" refers to parts by weight unless otherwise indicated.

EXAMPLE 1

A heat-sensitive copying sheet is prepared using a 1 mil plastic film (e.g., polyester). On one surface of the film a visibly heat-sensitive coating is applied using the following coating composition:

	Parts
Silver behenate	26.1
Tetrachlorophthalic anhydride	1.6
Phthalazinone	3.9
Benzotriazole	0.5
Methyl gallate	7.8
Polyvinyl acetate ("Gelva V-100")	60.1

In preparing the composition the polyvinyl acetate is first dissolved in acetone after which the tetrachlorophthalic anhydride, benzotriazole and methyl gallate are added. The silver behenate is mixed with ethanol and methyl ethyl ketone and then homogenized, followed

by the addition thereto of the phthalazinone. This mixture is then added to the solution containing the polyvinyl acetate and the other ingredients.

The other major surface of the film is coated with a colored first layer of the following composition in which the ingredients are mixed until uniform and then sand milled until the wax is of a particle size of 0.5 to 2.5 microns.

	Parts
Polyamide resin ("Versamid 930")	67.1
Fatty diamide wax ("Acrawax C" atomized)	29.7
Pigment	3.2
Heptane/isopropanol (equal weights)	200.0

The composition is knife coated and dried with forced air drying. A layer having a dry thickness of about 0.5 mil is obtained, which is a coating weight of about 1.3 gm/ft.².

Over the top of this layer is coated a top layer of the composition having the following ingredients:

	Parts
Vinyl chloride/vinyl acetate copolymer ("VAGH" commercially available from Union Carbide)	4.00
Triethylene glycol dibenzoate ("Benzoflex S-358" molecular weight 358; commercially available from Vesco Chemicals)	0.33
Fatty diamide synthetic wax (atomized) ("Acrawax-C" commercially available from Glycol)	10.00
Methyl ethyl ketone	28.00
Isopropanol	14.00
Heptane	14.00

The above ingredients are mixed together (the wax having a particle size of 2.0 to 10 microns). This composition is then coated over the first layer using a reverse roll coating technique followed by forced air drying until the solvent is substantially all removed, after which higher temperature forced air drying is used, to leave a dry coating weight of about 0.1 to 0.9 grams per square foot.

The resulting sheet is imaged by superimposing it over a graphic original and exposing to intense infrared radiation (e.g., in a conventional thermographic copying machine). When imaging the sheet in this manner, a plastic film or paper having release properties is placed against the top heat-fusible layer as a carrier sheet so as to avoid partial transfer of portions of the top layer to the belt or rollers in the copying machine.

After the sheet is imaged in the foregoing manner, it is placed against the back side of a first receptor which is coated on its front side with a heat-fusible layer (typically comprising a mixture of resin and wax). This sandwich is then positioned over a second receptor in the manner shown in FIG. 3 and then exposed to infrared radiation. The imaged sheet and the second receptor are then stripped away from the first receptor to produce the product shown in FIG. 5.

EXAMPLE 2

Sheet material is made having an imageable layer prepared by mixing the following compositions:

Composition A	Parts	
Silver behenate	15	
Methyl ethyl ketone	85	5
Tetrachlorophthalic anhydride	0.45	
Stannous stearate	0.009	
Composition B		
Cellulose propionate resin ("PLFS-130", commercially available from Celanese)	7.5	
Polyethylmethacrylate ("Lucite 2042", commercially available from DuPont)	7.5	
Methyl ethyl ketone	85	
Composition C		
Phthalazinone	2.25	
Hindered phenol reducing agent ("CAO-3", commercially available from Catalin)	1.80	
"Ethyl 702" (an antioxidant, commercially available from Shell)	0.105	

After composition A is homogenized it is added to composition B and mixed followed by the addition thereto of composition C with further mixing. The resulting composition is knife coated (wet thickness of 3 mils) onto the back side of a 1-mil plastic film coated with the two heat-fusible layers of Example 1. After drying the resulting sheet material is ready for use.

An intermediate film member comprising map overlay tracing paper coated according to the technique described in Example 3 of U.S. Pat. No. 3,094,417 (Workman) is placed against a graphic original and exposed as described in said example. The exposed intermediate film member is then placed against the imageable layer of the sheet material to form a sandwich construction which is then heated at 250°F. until an image of the graphic original is obtained in the imageable layer. The image is formed by reaction between the 4-methoxy-1-naphthol (from the intermediate film member) and the silver soap (in the imageable layer) in the presence of heat.

The top layer of the imaged sheet is then placed over a first receptor and a second receptor and exposed to brief intense infrared radiation in a thermographic copying machine. Upon separating the imaged sheet, and the second receptor, from the first receptor the product of FIG. 5 is obtained.

EXAMPLE 3

Sheet material is prepared having an imageable layer comprising "dry silver." The "dry silver" composition is prepared with the following ingredients which are added and mixed in the order given:

	Parts	
Silver behenate (15% dispersion in methyl ethyl ketone/toluene (40/60))	100	55
CaBr ₂ (4% solution in methanol)	10	
Hindered phenol reducing agent ("CAO-14", commercially available from Catalin)	7.5	
Merocyanine dye (0.05% in methanol)	5	
Polyvinyl butyral ("Butvar B-76", 10% solution in methyl ethyl ketone/toluene)	60	60

The resulting composition is knife coated (wet thickness 3 mils) onto the back side of a 1-mil plastic film coated with the two heat-fusible layers of Example 1.

The resulting sheet material is exposed to light for 10 seconds at an intensity of 100 foot candles with a step wedge. The latent image so formed in the imageable

layer is developed by heating it at 220°F. for 10 seconds.

The imaged sheet material is then used in the same manner as described in Examples 1 and 2.

EXAMPLE 4

Sheet material is prepared having a light-sensitive imageable layer requiring wet development.

A plastic film coated on one side with the two heat-fusible layers of Example 1 is used as the backing. The back side of the plastic film is then coated with light-sensitive diazo resin as described in Example I of U.S. Pat. No. 3,671,236 (Van Beusekom). Over the diazo resin is coated a water-insoluble resinous polymer containing carbon black.

The resulting sheet material is exposed to light whereby the light-struck areas of the imageable layer polymerize and become insoluble. The imaged sheet is then developed as described in U.S. Pat. No. 3,671,236 whereby non-image areas of the imageable layer are washed away.

The imaged and developed sheet is then used as described in Examples 1 and 2.

What is claimed is:

1. Sheet material useful in image transfer techniques comprising:

- a thin, flexible backing which is transparent to infrared radiation;
- an imageable layer coated over one major surface of said backing, said imageable layer being capable of providing infrared-absorptive image areas in one of the following manners:
 - upon imagewise exposure thereof to a heat pattern; or
 - upon imagewise exposure thereof to a light pattern followed by development;
- a continuous heat-fusible infrared-transparent first layer coated over the other major surface of said backing, said heat-fusible layer comprising a mixture of resin and wax and being tacky at temperatures in the range of about 60° to 310°C.; and
- a continuous, non-tacky, infrared-transparent top layer over said first layer, said top layer comprising a mixture of resin and wax and having a softening point at least as high as said first layer, said top layer being at a coating weight in the range of about 0.1 to 0.9 grams per square foot, and said top layer having a matte surface.

2. Sheet material in accordance with claim 1 wherein said imageable layer is visibly heat-sensitive and forms infrared-absorptive image areas when locally heated.

3. Sheet material in accordance with claim 2 wherein said imageable layer comprises, in intimate association, silver soap of a long chain fatty acid and a phenolic co-reactant for said soap.

4. Sheet material in accordance with claim 2 wherein said imageable layer comprises: a mixture of ferric and silver soaps of long chain fatty acids wherein said silver soap represents between 10 and 80 percent by weight of said mixture; a toner for the silver image; and phenolic co-reactant for said soaps.

5. Sheet material in accordance with claim 1 wherein said imageable layer is light-sensitive.

6. Sheet material in accordance with claim 5 wherein said imageable layer includes a major proportion of organic silver salt oxidizing agent and reducing agent for silver ion.

9

- 7. Sheet material in accordance with claim 1 wherein said backing comprises a transparent plastic film.
- 8. Sheet material in accordance with claim 1 wherein said heat-fusible layer comprises a major amount of polyamide resin and a minor amount of wax.
- 9. Sheet material in accordance with claim 1, wherein said first layer comprises particles of wax dis-

10

persed throughout a continuous phase of resin, said particles being in the range of about 0.5 to 2.5 microns; and wherein said top layer comprises particles of wax dispersed throughout a continuous phase of resin, said particles being in the range of about 2 to 10 microns.

* * * * *

10

15

20

25

30

35

40

45

50

55

60

65