United States Patent [19]

Franer et al.

[11] **3,859,094**

[45] **Jan. 7, 1975**

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

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

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

[22] Filed: **Jan. 5, 1973**

[21] Appl. No.: **321,518**

[52] **U.S. Cl.**.......................... **96/67,** 96/28, 117/3.2, 117/68 R, 250/318, 117/363

[51] **Int. Cl.**.... **G03c 1/76,** G03c 3/00, G03c 11/12, B41m 3/12

[58] **Field of Search**............ 96/67, 28; 117/3.2, 68, 117/36.3; 250/318

[56] **References Cited**

UNITED STATES PATENTS

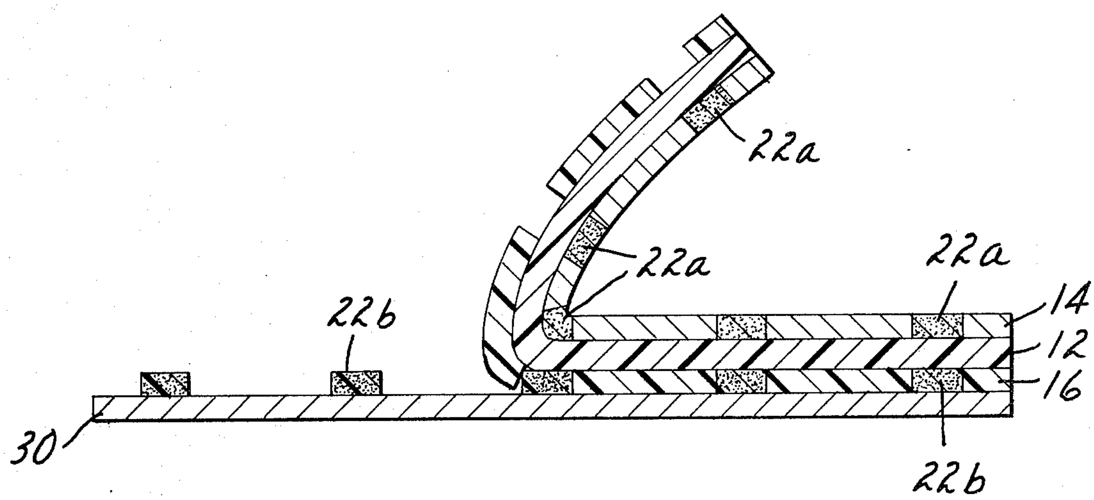
3,131,080	4/1964	Russell	250/318
3,418,468	12/1968	Marx et al.	250/318
3,457,075	7/1969	Morgan et al.	96/67
3,616,015	10/1971	Kingston	117/3.2
3,767,394	10/1973	Wiese et al.	96/67

Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard L. Schilling
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.

8 Claims, 4 Drawing Figures



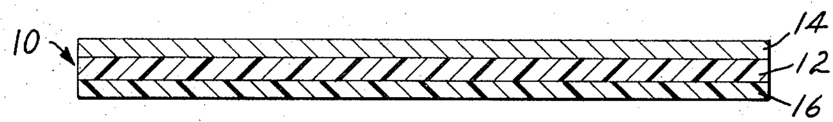


FIG. 1

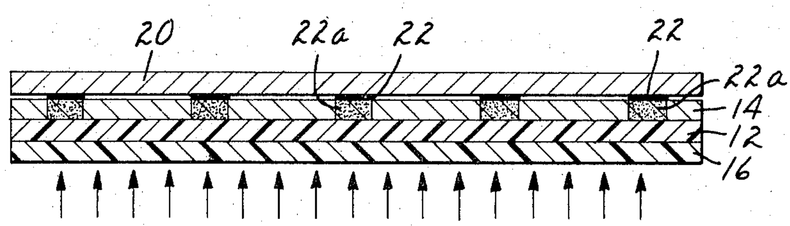


FIG. 2

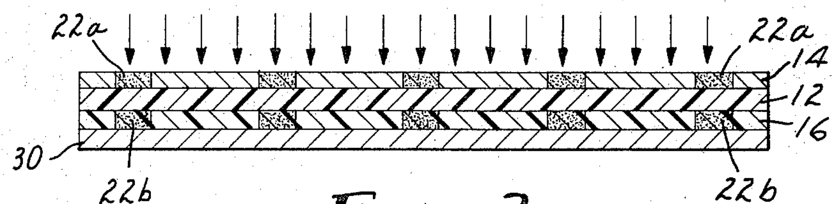


FIG. 3

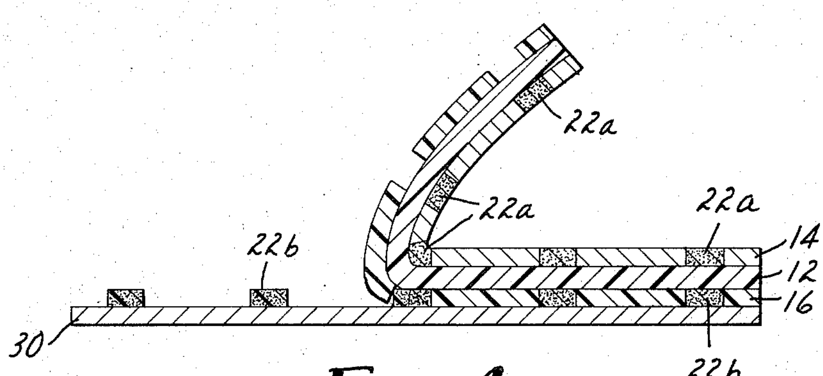


FIG. 4

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.

Others have previously described thermographically induced transfer of a fusible coating from a source sheet to a receptor sheet by infrared irradiation of an adjacent original. However, there are several drawbacks inherent in this technique. For example, spotty, incomplete, or blurred images are often obtained since the heat generated by absorption of the radiation is attenuated by the multiple layers before it reaches the fusible coating on the source sheet. Furthermore, such technique is not suitable for obtaining more than one color image on a single receptor without cutting up the original. Another drawback is the inability to proof the image prior to its transfer from the source sheet. Moreover, such technique is not useful for multiple transfers wherein an image of one color is to be superimposed on the same image of a different color.

These drawbacks are alleviated by the present invention.

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 upon exposure and development; and

c. a continuous, non-tacky, heat-fusible infrared-transparent layer coated over the other major surface of said backing, said heat-fusible layer being tacky at temperatures in the range of about 60° C. to 210° C.

The imageable layer of the novel 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 novel 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 said heat-fusible layer of said sheet material in contact with a receptor;

d. exposing said imaged sheet material to intense infrared radiation whereby said heat-fusible layer, in image areas, becomes tacky and fuses; and

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

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

The novel sheet material also permits one to proof the intended image prior to its transfer from the fusible layer to the receptor. Another advantage derived from the use of the novel sheet material is that transferred images can be obtained wherein one color is superimposed on another color with exact registration. This result is obtained by imaging a first novel sheet after which the heat-fusible layer of the first sheet is placed against the heat-fusible layer of a second novel sheet (having a heat-sensitive imageable layer) to form a sandwich construction. When the sandwich construction is then exposed to brief intense infrared radiation, the second sheet, in image areas, becomes infrared-absorptive. Upon separation of the two sheets, the heat-fusible layer of the first sheet, in image areas, is transferred to the heat-fusible layer of the second sheet. When the second sheet is placed against a receptor and exposed to brief intense infrared radiation, the heat-fusible layer, in image areas, is transferred to the receptor (upon separation of the sheets) whereby the transferred image comprises one color superimposed on another color, i.e., yielding the resultant color mixture. For instance, when the first heat-fusible layer is yellow and the second heat-fusible layer is blue, the resultant color is green.

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 novel sheet is imaged; and

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

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, celluose acetate), map overlay tracing paper, glassine paper, etc. It is highly preferable that one major surface of backing **12** be quite smooth so that heat-fusible 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 coreactant; 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)).

Heat-fusible layer **16** is a continuous coating which is non-tacky at room temperature. Layer **16** can be opaque, translucent, or transparent so long as it is transparent to infrared radiation. At elevated temperatures (e.g., 60° C. to 210° 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.

Typically layer **16** comprises 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, 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, carnuba wax, montan wax, ceresin wax, esparte wax, candlelilla 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 hot melt techniques, 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° C. to 210° C. It may be said that better transferred image definition is obtained when using fusible 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 the heat-fusible layer.

The heat-fusible layer is 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 the heat-fusible layer is about 0.125 mil to 1 mil. Preferred thicknesses range from about 0.3 mil to 0.6 mil.

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 superimposed over 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 **22*a*** 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 the heat-fusible layer **16** 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 the heat-fusible layer **16**. 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 a suitable receptor **30** in the manner shown in FIG. **3**, after which the imaged copy sheet is exposed to intense infrared radiation (e.g., in a conventional thermographic copying machine) whereby the heat-fusible layer, in areas **22*b***, fuses and becomes tacky. As a result, portions **22*b*** of the heat-fusible layer adhere to receptor **30**. When the imaged copy sheet is peeled away from receptor **30** as shown in FIG. **4**, portions **22*b*** of the heat-fusible layer **16** remain firmly adherently bonded to the surface of receptor **30**. Since portions **22i** correspond to the image areas of the graphic original, and when heat-fusible layer **16** is colored, a colored image of the original appears on the receptor. The imaged sheet material is still useful as a projection transparency at this stage so long as it is transparent to visible light.

Receptor **30** 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, the 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 **16** and receptor **30**, one surface of receptor **30** 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.

Multi-colored images can also be formed on a single receptor by imaging a plurality of the copying sheets of the invention and successively transferring colored images to the receptor. Blends of colors can also be effected by (1) imaging a first copying sheet in the manner depicted in FIG. **2**, (2) placing the heat-fusible layer of the first sheet against the heat-fusible layer (of a different color) of a second copying sheet, (3) exposing the first sheet to infrared radiation whereby the heat-fusible layer softens in areas corresponding to image areas, and whereby infrared-absorptive image areas are formed in the visibly heat-sensitive layer corresponding to the image areas of the imaged first sheet, (4) peeling the first sheet away from the second sheet whereby the portions of the heat-fusible layer of the first sheet corresponding to image areas are transferred to the heat-fusible layer of the second sheet, (5) exposing the second sheet to infrared radiation while in contact with a receptor whereby the heat-fusible layer, in image areas, fuses and becomes tacky, and (6) removing the second sheet from the receptor whereby the portions of the heat-fusible layer corresponding to image areas remain firmly adherently bonded to the receptor.

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 one 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 heat-fusible layer of the following composition in which the ingredients are mixed until uniform and then sand milled.

	Parts
Polyamide resin ("Versamid 930")	67.1
Fatty Diamide Wax ("Acrawax C")	29.7
Pigment	3.2

The composition is knife coated at a wet thickness of 3 mils and dried at about 80° C. 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}

The resulting copying 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 copy sheet in this manner, a plastic film having release properties is placed against the heat-fusible layer as a carrier sheet so as to avoid partial transfer of portions of the heat-fusible layer to the belt or rollers in the copying machine.

After the copying sheet is imaged in the foregoing manner, it is placed against a receptor (e.g., a transparent plastic film) and exposed to infrared radiation whereby the portions of the heat-fusible layer correspond to image areas are softened and become tacky. The copy sheet is then peeled away from the receptor leaving colored image areas corresponding to the image areas of the graphic original.

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
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 one mil plastic film coated with the heat-fusible layer 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 heat-fusible layer of the imaged sheet is then placed against a receptor and exposed to brief intense infrared radiation in a thermographic copying machine. Upon separating the imaged sheet from the receptor the heat-fusible layer is transferred to the receptor in an imagewise manner.

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
$CaBr_2$ (4% solution in methanol)	10
Hindered phenol reducing agent ("CAO-14", commercially available from Catalin)	7.5

-Continued

	Parts
Merocyanine dye (0.05% in methanol)	5
Polyvinyl butyral ("Butvar B-76", 10% solution in methyl ethyl ketone/toluene)	60

The resulting composition is knife coated (wet thickness 3 mils) onto the back side of a one mil plastic film coated with the heat-fusible layer 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 heat-fusible layer of the imaged sheet material is then placed against a receptor sheet and exposed to brief intense infrared radiation in a thermographic copying machine. Upon separating the imaged sheet from the receptor, the heatfusible layer is transferred to the receptor in an imagewise manner.

EXAMPLE 4

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

A plastic film coated on one side with the heatfusible layer 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 heat-fusible layer of the imaged and developed sheet is placed against a receptor and exposed to brief intense infrared radiation in a thermographic copying machine. Upon separation of the sheet material from the receptor, the heatfusible layer is transferred to the receptor in an imagewise manner.

EXAMPLE 5

Sheet material of the type described in Example 1 is prepared using instead the following composition for the heatfusible layer:

	Parts
Microcrystalline wax ("Shellwax 400", melting point 177° F., commercially available from Shell)	7.15
Coumarone indene resin ("Nevillac Hard", commercially available from Neville)	7.15
Toluene	85.70

This composition is knife-coated onto the film backing at a wet thickness of 2 mils. The sheet material resulting after drying is used in the same manner as the sheet material of Example 1.

Other variants are possible within the scope of this invention.

What is claimed is:

1. Sheet material useful in image transfer techniques comprising:

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, non-tacky, heat-fusible infrared-transparent layer coated over the other major surface of said backing, said heat-fusible layer being tacky at temperatures in the range of about 60° to 210°C., said heat-fusible layer comprising a mixture of resin and wax.

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.

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.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,859,094

DATED : January 7, 1975

INVENTOR(S) : VICTOR R. FRANER and DARRELL C. BURMAN

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

Col. 4, line 35, "22i" should read -- 22b -- .

Col. 6, line 56, "dry silver" used twice in this line should be in quotes, both occurrences.

Col. 7, line 28, "heatfusible" should read -- heat-fusible -- .

Col. 7, line 45, "heatfusible" should read -- heat-fusible -- .

Col. 7, line 51, "heatfusible" should read -- heat-fusible -- .

Signed and Sealed this

twenty-fifth Day of *November 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks