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C. S. MILLER

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HEAT-SENSITIVE COPYING-PAPER

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Fig. 1

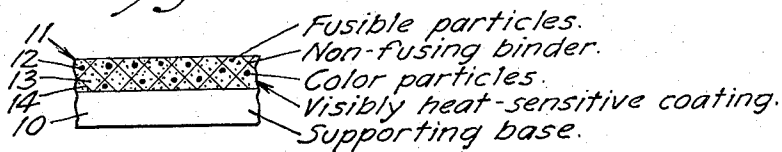
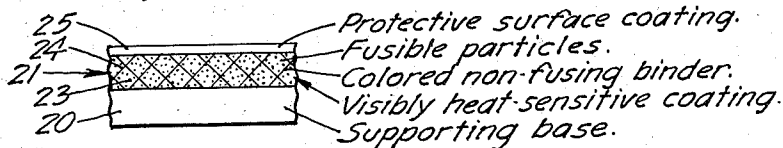


Fig. 2



Inventor
Carl S. Miller
By *Carpenter, Abbott, Coulter & Kinney*
Attorneys

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HEAT-SENSITIVE COPYING-PAPER

Carl S. Miller, St. Paul, Minn., assignor to Minnesota Mining & Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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12 Claims. (Cl. 117—36)

This invention relates to heat-sensitive copying-paper suitable for thermographic reproduction of typewritten messages or other graphic subject-matter. More particularly, the invention relates to heat-sensitive copying-paper having a backing member carrying a firmly bonded, thin, visibly heat-sensitive layer including color material distributed throughout, and visibly obscured by, fusible particulate material.

This application is a continuation-in-part of my co-pending application Serial No. 747,338, filed May 10, 1947, now U.S. Patent No. 2,740,896.

In the thermographic reproduction process here involved and for which my novel sheet material is specifically designed, the heat-sensitive copying-paper is placed in contact with a surface of the original and the latter is then strongly and briefly irradiated with radiant energy which is preferentially absorbed by areas of the original forming the graphic message or subject-matter. The absorbed radiation is converted to heat energy in a pattern corresponding to the graphic subject-matter, and the heat energy flows into the heat-sensitive layer and converts the corresponding areas thereof to a visibly distinct form. In the copying-paper of the present invention, a visible change results when the fusible organic particles melt and coalesce, thus permitting the initially obscured color material to become permanently visible, as will be further illustrated hereinafter.

One typical application of thermographic reproduction as above described is in the copying of typewritten articles. The heat-sensitive copying-paper is held with the heat-sensitive surface in heat-conductive contact with the reverse side of the typewritten page, and suitable precautions are taken to prevent heat loss from the composite. The exposed printed surface of the original is then strongly and briefly irradiated. For small areas, suitable radiation is obtained from a standard 500-watt infra-red bulb with internal reflector, operated under overload conditions of 800 watts input and at a distance of about three inches from the printed surface. The radiation is preferentially absorbed by the typewritten characters, and the heat produced passes through the thin paper to the heat-sensitive copying-paper where a visible reproduction is immediately formed. The operation has been termed "back-printing."

The copying of material printed on heavy paper or cardboard, or of pages printed on both surfaces, is more conveniently accomplished by "front-printing." In this process a thin heat-sensitive copying-paper is used which is capable of readily transmitting the radiation employed without undergoing visible change. The copying-paper is placed against the printed surface but with the heat-sensitive layer exposed, and the original is irradiated through the copying-paper. The heat produced on absorption of the radiation in the printed characters passes through the thin backing to the heat-sensitive surface and results in the formation of a visible reproduction.

Reversing the copying-paper will in either method result in a reverse copy of the original when the copying-

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paper is viewed from the side carrying the heat-sensitive coating.

For copying larger areas, such as typewritten pages, drawings, etc., it has been found convenient to employ a lamp system which focuses a narrow beam of the desired radiation across the page and then to scan the page with the beam. A typical lamp system for use in copying originals printed on the usual office letterheads employs a lamp having a 2000-watt coiled tungsten filament ten inches long, mounted in a reflector so as to produce a beam one-fourth inch wide. Scanning at a rate of three inches per second with this lamp system has been found to produce excellent prints having good contrast and detail when using copying-paper capable of visible conversion at temperatures in the neighborhood of 65° C.

More intense radiation, or somewhat longer exposure time, or operation at higher ambient temperature, makes possible the utilization of copying-papers designed to operate at higher temperatures.

Electrically heated tungsten filaments provide an effective and preferred source of radiation, but the maximum temperature conveniently obtained from such sources in making copies by the methods herein described is not much higher than about 115° C. Most of the more desirable backings or sheet materials which I may employ are cellulosic, or at least organic in character, since highly heat-conductive backings such as metal foil greatly reduce the clarity and definition of the reproduction. The organic backings, as also the paper of the original letter, drawing, or other article of which copies are most frequently desired, are subject to deterioration when heated excessively. Consequently I prefer to select fusible materials which are capable of melting or fusing at temperatures not higher than about 115° C., or in extreme cases not higher than about 150° C. At the same time, it is necessary that the heat-sensitive coating remain unaffected during storage and shipment, and hence I find it necessary to employ fusible materials which will remain in the solid state at temperatures below about 60° C., or at least below about 50° C.

The heat-sensitive layer must be firmly attached to the backing member and must resist transfer in whole or in part to the original when pressed thereagainst during the copying operation. The presence of minor proportions of a binder material capable of forming strong self-supporting films when deposited from solution and which is non-fusing at the fusion temperature of the fusible particles provides effective bonding of the heat-sensitive layer.

For best results in the reproduction of printed matter, and particularly of half-tone prints or the like which contain areas of fine detail as well as massive darkened areas, certain further requirements as to time and temperature of exposure or activation may be noted. The heat-sensitive composition must be capable of changing to a visibly distinct form having a desirably high contrast number with a minimum exposure and over a minimum range of temperature. Compositions which are converted instantaneously on heating to a specific temperature would be highly desirable for many purposes. However, somewhat slower-acting compositions which provide a contrast number of at least about 0.4 within less than one-half second, or preferably less than one-tenth second, and which furthermore provide this entire degree of darkening within a temperature range of not more than about 20° C., and preferably not more than about 5° C., have been found to provide reproductions of good detail and contrast. In determining the contrast number the samples may conveniently be "exposed," at specific temperatures and for specific time intervals as required, by pressing them against heated metal plates,

Typewriter ribbons and printing inks ordinarily contain carbon pigment which is highly absorptive of visible and infra-red radiation, whereas the paper on which such inks are printed is relatively much less absorptive of such radiation; and originals printed with such inks are therefore preferably irradiated with such rays. Other radiations are useful, however, the significant requirements being that the radiation is preferentially absorbed by those areas of the original which define the graphic subject-matter and that it is of sufficient intensity to provide the required heating effect when thus absorbed.

The following examples provide specific temperature-sensitive copying-papers which have been found to produce good results when employed in the reproducing of printed matter in accordance with the procedures described. However, it will be understood that the invention is not to be limited to these specific examples, since various equivalent compositions and backing materials may alternatively be employed.

Example 1

Thin unsized flax paper was coated and impregnated with a mixture of finely divided dispersed particles of methylene blue and of mercuric stearate in a xylol solution of ethyl cellulose. Mercuric stearate is a waxy fusible organic material, insoluble in xylol; the particles fuse together to form a transparent film when heated to about 90–100° C. and permitted to cool. On drying, the sheet was quite transparent, e.g. when the sheet was held in contact with a printed page, the printing could be seen through the sheet; it had a faint blue color, and was unchanged on prolonged exposure to light. When used as a heat-sensitive copying-paper, it produced an intense blue facsimile copy of the graphic original. The sheet was most satisfactorily exposed with the coated surface in contact with the original printed surface, but usefully clear and exact copies could alternatively be prepared with the untreated surface in contact with such printed surface, or with the copying-paper suitably supported against the reverse side of the printed page. In this last-named modification, the thickness of the web supporting the heat-sensitive surface coating could be considerably increased.

Other equivalent particulate fusible materials, soluble strong film-forming binders, color particles, and volatile solvents may replace the specific materials here enumerated. In general, the amount of ethyl cellulose or other binder in such mixtures of binder and fusible particles may range from as low as about 5% up to about 10–20% or somewhat higher, but at much increased amounts the initial opacity of the coating is insufficient. This effect may be avoided by causing the binder component to be deposited as a partially or completely non-transparent, porous, self-sustaining stratum, as will now be disclosed.

Example 2

A liquid coating composition is prepared from the following ingredients.

	Parts by weight
Hydrogenated fatty oil wax, M.P. 65° C. -----	1073.7
Nitrocellulose -----	382
Ethyl cellulose -----	62.4
Diocetyl phthalate -----	224.7
Acetone -----	5800
Toluol -----	2460

The nitrocellulose is first dissolved in a portion of the mixed solvents, and the remainder of the components then added to the solution and reduced to a smooth suspension in a ball mill. Milling is continued until the insoluble wax is completely broken up into uniform microscopic particles and the suspension can be coated in a smooth, uniform, very thin layer.

There is then added a quantity of "Diane blue" pigment to the extent of about 3–12% of the weight of the

non-volatile portion of the suspension, and the pigment is thoroughly dispersed in the liquid. "Diane blue" is an infra-red-transmitting blue lake pigment.

The liquid coating composition is coated on thin clear transparent glassine and dried at room temperature. The product is light blue-gray in color, changing to a transparent blue-black when heated to about 65° C. Copies produced by the "front-printing" process, using this copying-paper and irradiating with radiation high in infra-red, have excellent contrast and detail. The sheet is also useful for "back-printing."

In the foregoing examples the color material is in the form of separate particles which are dispersed throughout the layer of fusible organic particles, the whole being held in place by a film-forming binder component which is infusible at the fusion temperature of the fusible particles. The next example illustrates a structure in which the color material is combined with the binder component. In both structures the particles of fusible material conceal or obscure the color material, the latter then becoming visible when the fusible particles are melted and converted to transparent film-form.

The fusible waxy component of the heat-sensitive coating of Example 2 may readily be extracted, without altering the structure of the non-fusing binder stratum, by means of suitable selective solvents. When this is done, it is found that the binder remains in the form of a light-diffusing and non-transparent porous but still strong and self-supporting web. Such a web may be locally permanently transparentized by impregnating it with a melted drop of the wax, which wets the porous binder layer, has substantially the same refractive index and is transparent in solid film form, and is compatible with the binder.

Example 3

A solution is prepared by dissolving 30 parts of ethyl cellulose, 15 parts of "Rezyl 99" (an inert acetone-soluble non-drying semi-solid glycol phthalate type resinous plasticizer), and 0.3 part of "Victoria Green WB" soluble green dye in 255 parts of acetone. Separately there is prepared a dispersion of lead palmitate in acetone by ball-milling 20 parts of the insoluble waxy soap in 80 parts of the vehicle. Twenty part of the colored solution and 50 parts of the wax dispersion are blended together and coated in a thin uniform layer on a heavy smooth-surfaced backing member such as "Kloth White" paper, using a coating orifice of 6 mils. After drying at room temperature, the coated surface appears white, changing to green when heated to about 103° C. The sheet product is useful for "back-printing."

In this example the soluble dye is retained by the binder which is colored thereby. The particles of lead palmitate obscure the colored binder in the completed copying-paper.

Example 4

Methylene blue chloride, a blue dye, is dispersed in ethyl acetate to a concentration of 2% by ball milling. Mercuric stearate is similarly dispersed in ethyl acetate to a concentration of 20%. Three and one-half parts of the dye suspension and 25 parts of the wax suspension are mixed together, with addition of 4 parts of 125-second nitrocellulose lacquer solution prepared as for conventional viscosity measurements. Coated on one mil flax tissue paper at a coating orifice of 5 mils and dried at room temperature, this composition produces a light blue copying-paper which converts to a brilliant dark blue color at about 90° C. and is useful for both "front-printing" and "back-printing."

Example 5

Solution A:	Parts by weight
Ethyl cellulose -----	30
"Rezyl 99" resin -----	15
"Sudan Yellow RR" -----	0.6
Acetone -----	255

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Dispersion A:	
"Monastral Blue"-----	200
Ethyl cellulose-----	400
"Rezyl 99" resin-----	400
Acetone-----	4000
Dispersion B:	
Lead Myristate-----	20
Acetone-----	80

A mixture of 50 parts dispersion B, 5 parts dispersion A, and 10 parts solution A is coated on plain transparent cellophane at a coating orifice of 4 mils, and the product is dried at room temperature, producing a light blue sheet which changes to dark blue when heated to approximately 85° C. and is useful for both "front-printing" and "back-printing."

Example 6

Lead palmitate is dispersed in acetone to a concentration of 20% by ball milling, and 20 parts of the dispersion is mixed with 10 parts of a colored binder solution containing one part of "Bismarck Brown R Base," 15 parts of "Rezyl 99" resin, and 30 parts of ethyl cellulose, all dissolved in 225 parts of acetone. White paper coated with the mixture at a coating orifice of 3 mils, and dried, provides a copying-paper which changes from light tan to orange-brown at approximately 95° C. and is useful for "back-printing."

The invention is further illustrated by the accompanying drawing, in which Figures 1 and 2 are diagrammatic, enlarged representations in cross-section of typical examples of my novel heat-sensitive copying-paper. In Figure 1, a supporting base 10 is coated on one surface with a heat-sensitive coating 11 containing color particles 12 dispersed therethrough and concealed or obscured by light-diffusing fusible organic particles 13, the coating being held together and to the base 10 by a binder 14 which is non-fusing at the fusion temperature of the fusible particles 13. The fusible material has good wetting properties toward the binder, and the two are preferably of substantially the same refractive index and mutually compatible.

The heat-sensitive copying-paper of Figure 2 likewise has a backing member or supporting base 20 and a visibly heat-sensitive coating 21; in addition, the sheet is provided with a thin protective surface coating 25, and at least one of said base 20 and coating 24 must be transparent. The visibly heat-sensitive coating in the structure of Figure 2 consists of fusible particles 23 which are held together and to the base 20 by a colored binder component 24, the binder component being concealed or obscured by the fusible particles.

The color particles of the structure illustrated in Figure 1 may be completely inert toward the fusible particles and the binder component as in Example 2, in which case the color particles themselves become visible when the fusible material is converted from the opaque particulate to the transparent continuous state. The color particles of Figure 1 may alternatively be partly or completely soluble in the molten fusible material as in Example 1, or may otherwise cause the development of color in the molten fusible material; in such case the particles are reduced in size, or disappear as such, during the copying process, while a visibly distinct appearance is produced at the heated areas. Figure 2 illustrates a structure in which the color material is initially combined with the film-forming non-fusing binder component; the preparation of such a structure is described in Example 3. Still other structures and combinations may be provided in which the fusion of the concealing or obscuring mass of fusible organic particles makes visible a color material contained within said mass of particles.

The thin surface layer of film-forming binder material illustrated in the exemplary structure of Figure 2 further

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protects the heat-sensitive layer from abrasion or other mechanical attack. In order to avoid solution of the fusible particles or binder component and transparentization of the heat-sensitive coating during application of such layer, the volatile vehicle employed in forming such protective surface coatings is selected from those liquids which are non-solvents for the components of the heat-sensitive layer. Suitable film-forming resins or polymers which are soluble in heptane or dispersible in aqueous vehicles, for example, are applicable in forming useful thin protective layers on the heat-sensitive sheet material described in Example 2.

Where the copying-paper employs a transparent backing such as cellophane or glassine, the protective surface coating may be made non-transparent, e. g. by incorporation of a pigment or dye. With such a copying-paper, an infra-red-transmitting colored protective surface coating permits the sheet to be used for either "front-printing" or "back-printing." Opaque backings, on the other hand, require that any protective surface coating be transparent so that the visible change occurring in the heat-sensitive layer may be viewed through such coating.

The waxy fusible metallic soaps of Examples 1 and 3-6 may be prepared by precipitation from an aqueous solution of the sodium salt of the appropriate fatty acid on the addition of an aqueous solution of a corresponding soluble metal salt. The precipitate is recovered, washed, dried, and then suspended in the form of fine particles in the desired volatile vehicle by ball-milling or other suitable means. The hydrogenated fatty oil wax of Example 2, or hydrogenated castor oil wax melting at about 85° C., or other waxes or waxy materials as well as other organic fusible materials melting within the preferred general range of about 60-115° C. are also useful, as well as mixtures of such materials.

The fusible material in particulate form serves to mask or obscure from view most or all of the color material associated therewith. On heating the coating to or above the fusion temperature, the fusible particles melt or fuse and the color material becomes visible, either through the transparent fused and solidified film of fusible material or as a solution in such film or in some other manner. Hence the fusible material must be normally transparent, stable against actinic light or atmospheric humidity experienced during storage and use, and capable of melting to a liquid without appreciable volatilization or decomposition at available and useful temperatures. A number of fusible materials meeting these requirements have been set forth in the accompanying illustrative examples, and others will be apparent in view of the above disclosures. Where slow recrystallization of the consolidated fusible material might subsequently cause opacifying of such layer, improved permanency of copy is attained by using mutually compatible fusible and binder materials or by incorporating small amounts of plasticizers or other modifiers selected to improve the compatibility therebetween.

What I claim is as follows:

1. A heat-sensitive copying-paper adapted, on being placed in heat-conductive contact with an original having preferentially radiation-absorbing areas and on irradiation of said original as hereindescribed, to provide a visible reproduction of said original, said copying-paper comprising a backing member carrying a firmly bonded, thin opaque, visibly heat-sensitive layer comprising color material uniformly interspersed within an obscuring mass of particles of normally transparent stable organic fusible solid melting to a liquid without appreciable volatilization or decomposition at a temperature within the range of about 50-150° C.

2. A heat-sensitive copying-paper adapted, on being placed in heat-conductive contact with an original having preferentially radiation-absorbing areas and on irradiation of said original as herein described, to provide a visible reproduction of said original, said copying-paper

comprising a backing member carrying a thin, opaque, visibly heat-sensitive layer comprising color material uniformly interspersed within an obscuring mass of particles of normally transparent organic fusible solid melting to a liquid without appreciable volatilization or decomposition at a temperature within the range of about 60–115° C., said layer being bonded together and to said backing member by a film-forming binder which is non-fusing at the melting temperature of said fusible particles.

3. The heat-sensitive copying paper of claim 2 in which the color material is present in the form of separate particles.

4. The heat-sensitive copying-paper of claim 3 in which the color material is an inert pigment.

5. The heat-sensitive copying-paper of claim 3 in which the color material is a soluble dye.

6. The heat-sensitive copying-paper of claim 2 in which the binder serves as the color material.

7. The heat-sensitive copying-paper of claim 6 in which the binder is colored with a soluble dye.

8. As a new article of manufacture suitable for use in the copying of printed matter by a rapid direct process involving only the application of intense radiant energy as herein described, a thin sheet material comprising a support member carrying a firmly bonded, thin, opaque coating comprising color material uniformly interspersed within an obscuring mass of particles of a normally transparent waxy material melting at a temperature within the range of about 50–150° C.

9. As a new article of manufacture suitable for use in the copying of printed matter by a rapid direct process involving only the application of intense radiant energy as herein described, a thin sheet material comprising a support member carrying a thin opaque coating compris-

ing color material uniformly interspersed within an obscuring mass of particles of a normally transparent waxy material melting at a temperature within the range of about 50–150° C., said coating being bonded together and to said support member by a film-forming binder which is non-fusing at the melting temperature of said waxy material.

10. The article of claim 9 in which the color material is a soluble dye.

11. The article of claim 10 in which the color material is dissolved in the film-forming binder.

12. A heat-sensitive copying-paper adapted, on being placed in heat-conductive contact with an original having preferentially radiation-absorbing areas and on irradiation of said original as herein described, to provide a visible reproduction of said original, said copying-paper comprising in order a backing member, a firmly bonded, thin, opaque, visibly heat-sensitive layer, and a protective surface coating at least one of said backing member and said surface coating being transparent; said heat sensitive layer comprising color material uniformly interspersed within an obscuring mass of particles of normally transparent stable organic fusible solid melting to a liquid without appreciable volatilization or decomposition at a temperature within the range of about 50–150° C.

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