Dec. 22, 1953 C. S. MILLER ET AL 2,663,656

HEAT-SENSITIVE COPYING PAPER

Filed May 15, 1952 2 Sheets-Sheet 1

Fig. 1

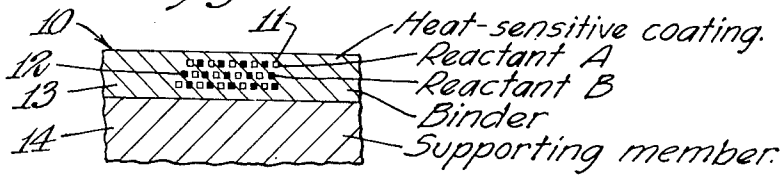


Fig. 2

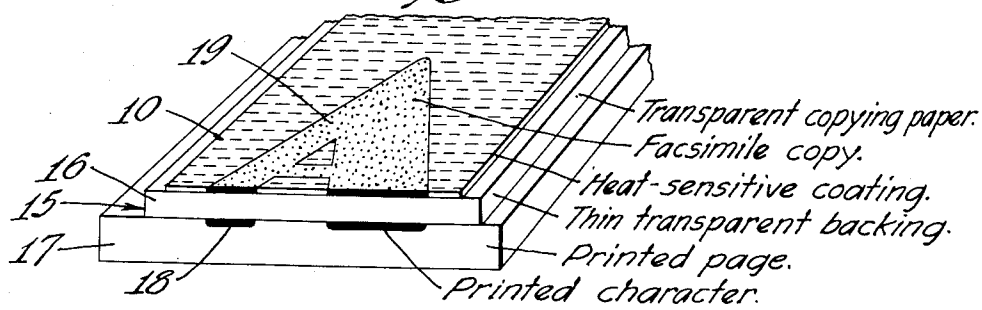


Fig. 3

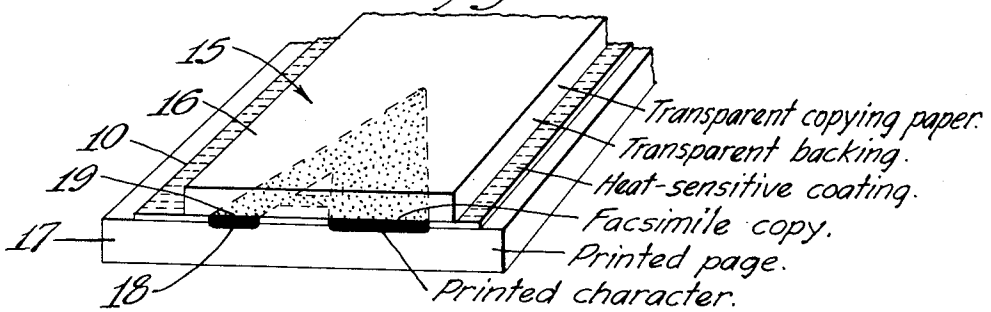
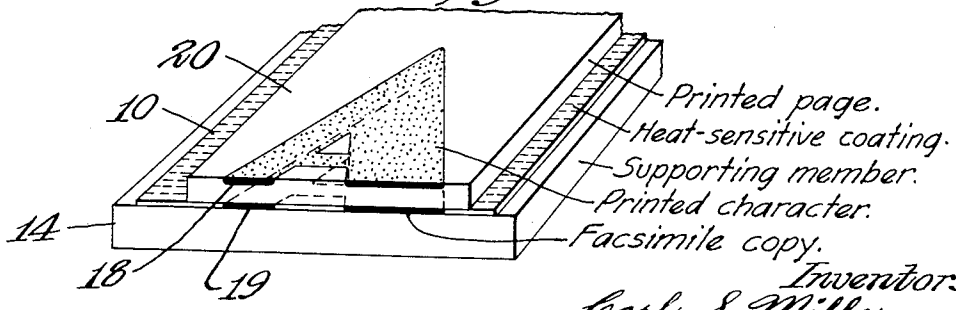


Fig. 4



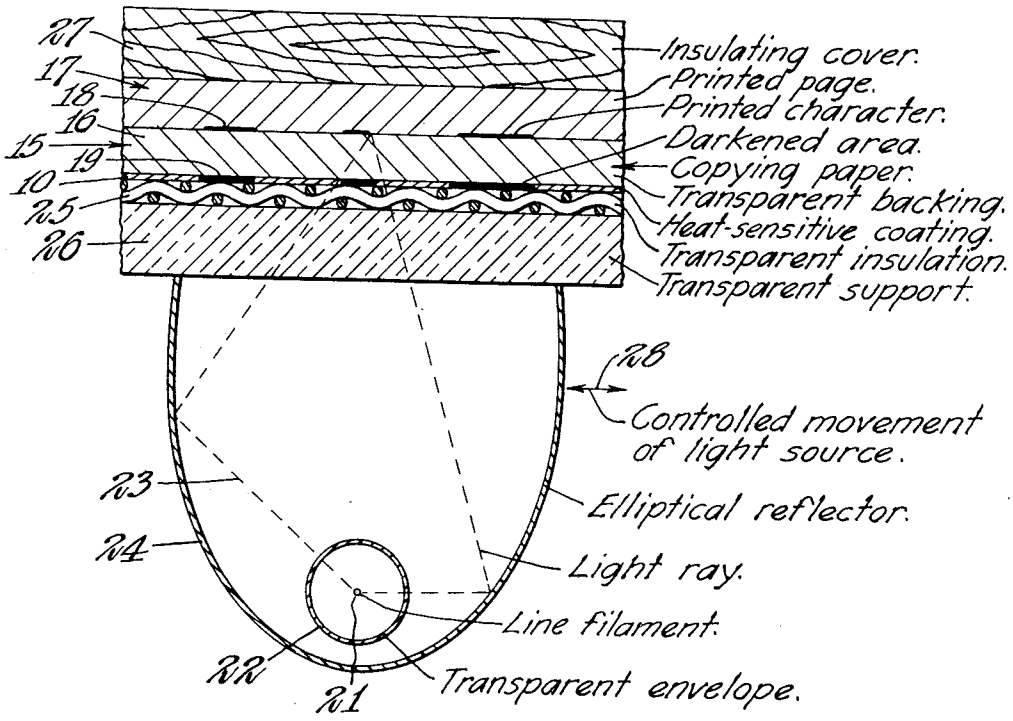
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HEAT-SENSITIVE COPYING PAPER

Filed May 15, 1952 2 Sheets-Sheet 2

Fig. 5



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HEAT-SENSITIVE COPYING PAPER

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Application May 15, 1952, Serial No. 288,005

7 Claims. (Cl. 117—36)

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This invention is concerned with duplicator sheet material or copying-paper useful in preparing copies of printed matter or the like, and with compositions and methods related thereto. The invention particularly contemplates heat-sensitive coatings and coated sheet materials of a novel type, and methods of utilizing such materials in preparing duplicate copies of printed or other graphic subject-matter by simple exposure to high intensity irradiation and without subsequent developing or fixing operations.

This application is a continuation-in-part of our co-pending application Serial No. 737,339, filed May 10, 1947.

Prior art copying-papers of which we are aware, which are subjected to exposure to visible light or similar forms of radiant energy in the preparation of copies of graphic subject-matter, must be protected from light before use, and require various processing steps, in addition to the initial controlled exposure, for the production of visible light-stable copies.

Our new heat-sensitive copying-paper, on the contrary, is not itself affected by radiant energy such as visible or ultra-violet light, and may therefore be left exposed to such radiations both before and after printing. Nevertheless, radiant energy may be employed as the sole agency for the production of visible light-stable and permanent copies of graphic subject-matter on our novel copying-paper, or on other surfaces carrying our novel heat-sensitive compositions, by processes as hereinafter set forth.

The processes by which we are enabled to achieve this result, e. g. in the preparation of copies of the printed pages of books or the like, involve the irradiation of the printed surface, the resultant formation of an elevated-temperature pattern corresponding to the graphic subject-matter of such printed surfaces, and the utilization of this elevated-temperature pattern in the development of a facsimile copy of the graphic subject-matter on the heat-sensitive copying-paper.

Formulas may be found in the prior art for various heat-sensitive paints, coated sheet materials, and the like. All such products of which we are aware exhibit one or more significant deficiencies when compared with our novel heat-sensitive compositions and coated products. They may be sensitive to light as well as heat. They may require an extremely high temperature, or a relatively long time at a specific temperature, or heating over a wide range of temperature, to produce a visible change of sufficient intensity. The change obtained at elevated temperatures may be reversible on cooling, i. e. the product exhibits thermotropy. These and other deficiencies of prior art materials are avoided by the use of our novel compositions and products, particularly in connection with the copying of printed matter such as books, drawings or diagrams, pictures, etc. by means of our novel copying-paper herein described and illustrated.

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The heat-sensitive compositions of our invention are comprised of solid ionizable reactants of which at least one is an electron donor component and another an electron acceptor component, which are potentially chemically capable of irreversibly and rapidly reacting in an electron donor-acceptor type reaction at normal room temperature to produce a visibly different reaction product, but which are normally maintained in physically distinct relationship and physically prevented from so reacting. In many cases the electron donor component contains two or more donor groups so that one or more ring structures are formed in the reaction, and such donor components are therefore classifiable as chelating agents. The structure of the sheet material is so designed that an increase in temperature to a predetermined level allows the reaction to take place. The reaction is believed to be initiated by the melting, or softening, or other physical change, of one or more of the reactive substances. Whatever the specific physical change employed, the application of heat results in an immediate reaction of the reactants and formation of a colored, opaque, or otherwise visibly different reaction product.

The rapid rate of reaction obtainable by this means is particularly advantageous where the reactive material in sheet form is to be used as a heat-sensitive copying-paper. For the most effective reproduction of drawings or the like containing fine lines as well as massive dark areas, a high contrast number, as hereinafter defined, must be obtained when the sheet is heated through a narrow range of temperature not greater than about 20° C. and preferably about 5° C., within a period of time not greater than one second, and preferably within about one-tenth of a second, in order to obtain desirable contrast and detail.

Where these limitations are exceeded, the reproductions obtained may be blurred, "fuzzy," or otherwise of poor quality. For example, a heat-sensitive sheet material which darkens over a wide range of temperature, e. g. which provides a contrast number of 0.2 when heated to 70° C. but does not reach a contrast number of 0.8 until heated to 110° C., will ordinarily not produce a print having good contrast between light and dark areas.

A convenient method of determining the rate of reaction as well as the required temperature of activation for a particular copying-paper involves placing portions of the sheet against a series of metal surfaces each at a different but controlled temperature, and for various intervals of time. Our preferred copying-papers, when so tested, show a reaction from the original state to a color intensity or opacity equivalent to a contrast number of at least about 0.4,

and preferably about 0.9, when heated at the required temperature level and within a temperature range of not more than about 20° C., and within a contact time of not more than about one-tenth second.

In determining the contrast number of a copying-paper, suitably exposed samples having printed (darkened) and unprinted (undarkened) areas are held against a flat magnesium carbonate block (a "standard magnesium carbonate surface" as defined in the paint industry). A beam of white light (north exposure daylight) is directed against the outer surface of the sample at an angle of 45°, and the intensity of the light reflected normal to the surface is measured by means of a suitable photometer. The contrast number is defined as the following ratio

$$\frac{I_u - I_d}{I_u}$$

where I represents intensity, and subscripts u and d refer to measurements made over the undarkened area and the darkened area, respectively.

The following examples of specific compositions and structures will serve more clearly to point out and explain the novel concept here involved, but are not to be construed as limitative.

Example 1

Lead myristate was prepared by adding an aqueous solution of lead acetate to an aqueous solution of the sodium soap of commercial myristic acid. The washed and dried product was dispersed in three times its weight of heptane by ball milling with flint balls. A dispersion of S-diphenyl carbazide in four times its weight of heptane was separately similarly prepared. Twenty parts by weight of each dispersion was mixed together, and 5 parts of a 30% solution of cyclicized rubber ("Pliolite") added. The mixture was coated on condenser-tissue and dried at room temperature. The dried sheet was white in appearance, quickly changing to scarlet when heated to approximately 85–90° C. It was useful as a heat-sensitive copying-paper.

Example 2

A dispersion was prepared, by ball milling, of 100 parts by weight of cadmium stearate in 500 parts of heptane. The cadmium stearate was prepared by precipitation from a solution of the sodium soap of triple-pressed stearic acid. Separately, a dispersion of 20 parts of diphenyl carbazone in 200 parts of heptane, and a solution of 10 parts of crepe rubber in 90 parts of heptane, were provided. The two dispersions and the solution were mixed in the weight ratio of 1:2:3 to provide a liquid mixture which was coated onto flax tissue and dried at room temperature. The sheet was yellowish tan, rapidly changing to red at approximately 100° C., and served as a useful heat-sensitive copying-paper.

Example 3

Mercuric stearate was substituted for the cadmium stearate and S-diphenyl carbazide for the diphenyl carbazone of Example 2, the remaining ingredients and the relative proportions remaining the same. The coated sheet was light gray, changing rapidly to purple when heated to approximately 90° C., and could be used to provide copies of printed matter by thermocopying methods herein described.

Example 4

Cupric stearate replaced the cadmium stearate of Example 2 in this example. Additionally, there was added to the mixture a small amount of sodium iodide, to prevent premature reaction and reduction of contrast. The sheet was light tan in color, changing rapidly to purple when heated to 75–85° C., and produced thermocopies having adequate contrast and detail.

Example 5

Thirty parts by weight of a dispersion of diphenyl carbazone in ten times its weight of heptane were mixed with 5 parts of a 5% solution of rubber in heptane and coated in a thin layer on flax tissue. Over the dried coating there was then applied a further coating of a mixture of 30 parts of a dispersion of zinc stearate in 5 times its weight of heptane, and 5 parts of the 5% rubber solution. The coated and dried sheet appeared snow white; it printed to a scarlet image at approximately 100° C.

Each of the color producing reactants of the above examples is present in solid particulate form, closely associated with the solid particles of the other reactant but physically separated therefrom by the intervening rubber or other binder. The binder separates the particles and at the same time holds them in position on the sheet. It also prevents contact of the particles with adjacent surfaces of other papers or the like during the thermocopying process. For these purposes, many other film-forming binder materials are applicable, only providing that the reactants are each insoluble in the binder solution so that they do not dissolve and react during mixing and coating. Methyl cellulose and polyvinyl butyral are examples of other useful film-forming binders.

In these compositions and coated sheet materials, at least one of the reactants must be capable of melting or fusing at a temperature within the range of about 60–120° C. The polyvalent metal soaps of Examples 1–5 each melt within these temperature limitations, particularly when made from commercial long-chain fatty acids as described in Examples 1 and 2; such compounds are rather readily prepared, give a desirably sharp color reaction with appropriate organic reagents, and are generally preferred by us. However, these organic reagents react equally well with the polyvalent metal ions in other forms, and hence other fusible or infusible metallic compounds may also be employed, provided only that at least one of the reactants be fusible within the range of 60–120° C.

A great many reactions are known, and others are constantly being discovered, by means of which most if not all of the polyvalent metals may be identified. Many of these reactions are susceptible of utilization as color-reactions for the purposes of our invention. There must be at least two solid reactants. They must be in closely associated, preferably particulate form, but in non-reactive relationship, e. g. separated from each other by a film-forming binder material. At least one of the reactants must be fusible at a temperature within the range of about 60–120° C. The reactants must be visibly inter-reactive at normal room temperatures; i. e., they must be capable of reacting together to produce a strongly colored or otherwise visibly distinct reaction product when dissolved together in a solvent at normal room temperatures.

Ordinarily, neither of the reactants should initially be strongly colored, since color in the copying-sheet would reduce the available degree of contrast. However, the procedure employed in Example 5, of applying two separate layers which intermix only at the interface, affords one way of minimizing the effects of strongly colored reactants. Highly odorous, or volatile, or light-sensitive solid reactants may be used in copying-sheets designed for special purposes or for temperary use, but in general are undesirable.

It is possible to select, from known sources, many type reactions which may be made to occur at normal room temperatures and for which reactants may be selected having the required physical properties as hereinabove enumerated. For example, lists of "spot test" reagents, based on information published by Dr. F. Feigl in his book "Qualitative Analysis by Spot Tests," are available. These organic reagents are used in detecting many multivalent metal ions, and appropriate reagents which produce highly colored compounds or complexes with such metal ions may readily be selected from such a list. The metal ion may be provided in the form of a fusible salt or soap, as already indicated. The two or more components are then dispersed in a non-solvent volatile vehicle, together with a soluble film-forming binder, and coated on a thin paper or other carrier web as herein described, to provide a heat-sensitive copying-paper.

Typical examples of spot test reagents, with a list of metallic ions with which each may be coupled, follows.

Organic spot test reagent	Metal
3-nitrosalicylic acid	Al, Cd, Ct, Co, Cu, Ba, Fe, Pb, Mg, Mn, Ni, Zn.
2-nitroresorcinol	Al, Cd, Ca, Co, Cu, Ba, Fe, Pb, Mg, Mn, Ni, Zn.
8-hydroxyquinoline	Cd, Cu, Fe, Pb, Mn, Ni, Zn.
S-diphenylcarbazide	Cd, Co, Cu, Fe, Pb, Ni, Zn.
Dinitrodiphenylcarbazide	Cd.
Resorcinol	Cd.
Dihydroxytartaric acid osazone	Ca.
1-amino-2-naphthol-4 sulfonic acid	Ca.
Chloranilic acid	Ca.
Picrolonic acid	Ca.
Diphenylcarbazone	Co, Cu, Pb, Mg, Mn, Hg, Ni, Zn.
Dithio oxamide	Co, Cu, Pb, Ni.
Diphenylthiocarbazone	Co, Cu, Ba, Fe, Pb, Hg, Zn.
Thiosalicylic acid	Co, Cu.
2,4-dinitro-1-naphthol	Co.
2-mercapto-4-phenyl thiazole	Co, Pb.
Picric acid	Co.
Nitrosonaphthol	Co.
Rubeanic acid	Co, Cu, Ni.
3,5-dimethylpyrazole	Co.
a-Naphthylamine dithiocarbamic acid.	Cu, Fe.
Rhodanine	Cu, Hg.
p-Dimethylamino benzylidene rhodanine.	Cu, Fe, Mg, Hg.
Diphenylthiocarbazide	Cu, Fe, Hg, Zn.
Dimethylglyoxime	Cu, Fe, Ni.
Benzoine oxime	Cu.
Salicylaldoxime	Cu, Pb.
Benzidene	Cu, Pb, Mn.
Benzotriazole	Cu.
Alpha furil dioxime	Cu.
Thionalide	Cu.
5-phenylthiohydantoic acid	Cu.
Sodium rhodizonate	Ba.
a,a'-Dipyridyl	Fe.
Triphenyl thiophosphate	Pb, Ni.
Gallocyanine	Pb.
Carminic acid	Pb.
p,p'-Tetramethyldiaminodiphenylmethane.	Pb, Mn.
Quinalizarine	Mg.
5-p-acetylaminophenylazo-8-hydroxyquinoline hydrochloride.	Mg.
p-Nitrobenzeneazoresorcinol	Mg.
Dicyandiamidine sulfate	Ni.
Potassium dithio oxalate	Ni.
Anthranilic acid	Zn.
Diphenylbenzidene	Zn.
p-Ethoxychrysoidin hydrochloride	Zn.

Where the spot test reagent is itself fusible within the range of about 60–120° C., it is not essential that the metal ion be present in a fusible compound. For example, 2-nitroresorcinol melts at 83–85° C., and 8-hydroxyquinoline melts at 75–76° C. In most cases, however, it is desirable to employ a fusible salt of the polyvalent metal; and we much prefer soaps of these metals and long-chain fatty acids, e. g. stearic, palmitic, or myristic acid, as previously described.

The reactive solid components are conveniently applied to paper or other supporting structure as a dispersion in a solution of a bonding agent in a suitable volatile vehicle, as disclosed in the above examples. The bonding agent assists in retaining the reactants on the surface of the support. However, other methods of applying the reactants to the supporting surface and of maintaining them in proper relationship thereon may alternatively be employed. For example, a polymerizable monomer may be substituted for the solution of bonding agent; after application, the monomer may be polymerized in situ to form a binder film. The powdered reactants may be dispersed within, or on the surface of, a fibrous web or other supporting structure in the substantial absence of any added bonding agent. Additionally, the use of a film-forming bonding agent, such for example as the "Pliolite" of Example 1 as a self-supporting film as well as a binder and carrier for the reactive ingredients is also contemplated. In this type of product, the film-forming composition containing the color-producing reactants may be coated and dried on a temporary support, and the dry film subsequently removed by stripping to provide an exceedingly thin copying-paper.

Certain advantageous results may be obtained by proper selection and proportioning of the bonding agent as well as the reactants, and in our preferred compositions we therefore contemplate the use of a suitable inert bonding agent or combination of bonding agents in significant proportions. The degree of contrast obtainable with our copying-paper is readily controlled, for example, by suitably proportioning the relative amounts of binder and of reactants. Thus, increased contrast has been obtained by increasing the percentage of binder, and thereby presumably increasing the distance and the amount of non-reactive material between or around the individual particles of reactants. Conversely, a reduction in the percentage of bonding agent reduces the contrast and increases the detail obtainable in the resultant copy.

Changes in the particle size and shape of any one or all of the reactant materials, and in the relative amounts of the individual reactants, will also have some effect on the results obtained. Stoichiometric relationships between reactants may be determined in many cases, but are not necessarily most advantageous. The proportions shown in the specific examples of the particular reactants therein disclosed have been found to produce good results, and may be used as a guide for the proper proportioning of other reactants; but many variations will be found to produce acceptable products and are here contemplated. Where desired, various inert materials, such for example as pigments or the like, may be added to the sensitizing compositions of our invention. Additional surface coatings, e. g. of film-forming materials, may be applied as protective or mask-

ing layers, or to impart desirable color, or for other purposes. Other modifications will be apparent.

In order to assure a clear understanding of the structure of our novel product and the manner in which it may be utilized, e. g. in the copying of printed matter, reference is made to the accompanying drawing, in which:

Figure 1 is a conventionalized and enlarged cross-section of one example of a suitable heat-sensitive coating on a supporting member;

Figures 2, 3, and 4 are perspective views (partially cut away) of three different arrangements of a printed surface in relation to the coated surface of the copying paper in obtaining facsimile reproductions of printed or other graphic matter on the heat-sensitive coated copying-papers of this invention; and

Figure 5 is a diagrammatic, sectional view of one example of structure, including a suitable source of radiant energy, that may be employed for copying printed sheet material.

In Figure 1, a heat-sensitive layer 10, consisting of two finely-divided reactant materials 11 and 12, the individual solid particles of which are contained within a binder material 13, is supported on a supporting member 14.

In Figure 2, a transparent heat-sensitive copying-paper 15, consisting of a heat-sensitive layer 10 on a thin transparent backing 16 (both shown in cut-away section) is placed against a printed page 17, with the uncoated surface of the transparent backing 16 in contact with the printed characters 18 of which a facsimile copy is desired. The transparent backing 16 of Figure 2 is a specific member of the class more generically represented in Figure 1 by supporting member 14. On exposure of the composite to intense illumination, as herein elsewhere explained, and in this case with the transparent heat-sensitive sheet 15 being between the source of light and the printed surface, a differential darkening, or other visible change, indicated by darkened area 19, is rapidly obtained in the heat-sensitive layer 10, corresponding to the printed character 18 therebelow.

The finished print obtained by the procedure outlined above in connection with Figure 2 is directly readable from the surface carrying the heat-sensitive layer. Transparency of the sheet material 15 to visible light is therefore not essential for subsequent reading of the copy obtained.

Consequently the requirement of transparency here refers to the ability of the sheet to pass radiant energy of the wave-length employed in the copying process. The use of visible light thus imposes the requirement of "visible transparency," as manifested, for example, in the construction embodying condenser-tissue and described under Example 1. With other wave-lengths, e. g. in the high-energy infra-red region, sheet material which is transparent to the infra-red but which may appear translucent or even opaque to the eye may be used and is here contemplated.

In Figure 3, the heat-sensitive layer 10 of the (visibly) transparent heat-sensitive copying-paper 15 is placed directly in contact with the printed characters 18 of the printed page 17. High intensity radiation directed against the transparent backing 16 results in a visible change, in the sensitive layer 10, corresponding to the printed characters 18, indicated by the darkened area 19 (partially concealed in the drawing). The resulting copy is a direct facsimile of the printed original when viewed through the visibly transparent backing 16.

In Figure 4, the heat-sensitive coating 10 is disposed, as shown in cut-away section, on a supporting member 14, which may be either transparent, translucent or opaque, but which should be at least reasonably non-conductive to heat. A thin opaque printed page 20, which may or may not carry printed characters on the under side, but which has printed characters 18, of which a copy is desired, on the outer side, is placed against the sensitive layer 10. Proper irradiation of the outer printed side of the printed page 20 results in the formation of a visible facsimile copy or darkened area 19, on the sensitive layer 10, corresponding to the printed characters 18, with no undesirable blurring or "ghost-image" formation being obtained from any similar printed characters which may be present on the under side of the page 20.

In Figure 5, which illustrates in cross-section one means by which reproductions of printed matter may conveniently be made according to the principles set forth in connection with Figure 2, an electrically-activated high-intensity source of useful radiation such as light rays 23, comprising an incandescent line filament 21 in transparent evacuated envelope 22, is shown supported within a movable trough-like reflector 24 of elliptical cross-section. Filament 21 is located at one focal line of the elliptical reflector; consequently light rays 23, emanating therefrom, are focused at the other focal line, which is caused to coincide with the printed surface of printed page 17, carrying printed or other graphic characters 18 of which a facsimile copy is desired.

Page 17 rests on the uncoated surface of a sheet of transparent heat-sensitive copying-paper 15, consisting of a transparent backing 16 and a heat-sensitive coating 10. The copying-paper rests on a transparent heat-insulating sheet material 25, which may be an open-mesh screen such as silk bolting-cloth, and this screen in turn rests on a transparent support 26, which may be a glass plate, preferably of heat-resistant glass. (Where support 26 is inherently sufficiently heat-non-conductive or is suitably roughened or otherwise treated at the surface so as to present a non-conductive surface to the copying-paper 15, the separate thickness of insulation 25 may be eliminated.) The copy-paper 15 and page 17 are held in close and heat-conductive contact by means of a heat-insulating cover 27, which may be a wooden cover, as shown in Figure 5, or may be constructed of any other suitable material including a soft and flexible material such as a pneumatic or hydraulic pressure-bag. If desired, the cover 27, and the underlying printed page 17, may be maintained at any desired temperature below the printing temperature of the copying-paper 15, by suitable temperature control means. The elliptical reflector 24, with its enclosed light source, is movable across the surface of the thermographic assembly, as indicated by the double arrow 28, by suitable means (not shown), in a plane such that the light rays 23 are continuously focused at the printed surface of the printed page 17. The rate of movement of the reflector assembly is adjustable, to compensate for differences in the thickness and heat conductivity of the page to be copied, here shown as printed page 17, and also to compensate for differences in the sensitivity

of the temperature-sensitive layer 10, the intensity of light output, and various other factors.

For rapid copying of text-book pages, letters, or the like with the apparatus of Figure 5, it has been found convenient to use a 2000-watt coiled tungsten line-filament incandescent lamp, 10 inches long, with "Pyrex" glass envelope, mounted in an elliptical reflector 24. The resulting concentration of radiation is of such high intensity as to cause charring or burning if allowed to remain focused on the same section of paper for more than about one second. With this light source, and with temperature-sensitive copying-paper such as that described under the various examples, clear unfogged facsimiles may be obtained. Many other sources of radiation, including ordinary high-intensity incandescent lamps, photoflash lamps, electric arc, infra-red lamps, concentrated sunlight, etc., have been found to be effective, although of more restricted commercial utility, in various thermographic assemblies using our heat-sensitive copying-papers.

Many modifications, both in preparing the reactive compositions and the coated materials, and in utilizing the products in the direct reproduction of graphic subject-matter, have been described. While the importance of each of these and other modifications in the commercial application of the principles involved will become obvious in view of the foregoing description, it will be even more apparent that the underlying principle, on which the novel phenomena herein presented are based, remains the same in all of the applications and modifications thereof. This principle involves the selection and blending of two or more solid reactants in such a manner that the reactants are prevented from combining or reacting with each other until the blend is heated to or above a predetermined range of temperature. When such a temperature is reached, however, the reactants are enabled rapidly to combine or react, whereupon there is produced a visible indication of such action, e. g. a color change. While the action thus obtained is of value under a wide variety of conditions, it has been shown to be particularly valuable in making available, as a new article of manufacture, a heat-sensitive copying-paper suitable for the preparation of visible light-stable copies of graphic subject-matter by methods involving only the exposure of such matter to intense irradiation while in heat-conductive relationship with the heat-sensitive material.

Having now described our invention in terms of specific examples and embodiments, but without intent to be limited thereto, what we claim is as follows:

1. A heat-sensitive copying-sheet for making direct, high contrast, clear detail copies of graphic subject-matter as herein described, said copying-sheet being non-sticking at 120° C., being stable at normal room and storage temperature,

and being rapidly and permanently visibly changed when heated from room temperature to 120° C.; said copying-sheet comprising a support having low thermal conductivity, and a heat-sensitive layer firmly bonded thereto and containing a plurality of stable ionizable dissociable normally solid reactant materials including at least one electron donor component and at least one electron acceptor component disposed in contiguity with each other in said layer, at least one of said components being fusible at a temperature within the range of about 60–120° C. and being present in an amount such that on fusion and reaction with other components a visible change is produced in the heat-sensitive layer, said components being maintained in physically distinct and chemically inter-reactive relationship in said layer at normal room and storage temperatures, and said components being so selected as to be inter-reactive in a direct ion-exchange electron acceptor-donor chemical reaction at room temperature in a mutual solvent capable of permitting ionization of said components and with the formation of a stable, visibly distinct, highly polarized compound which is less dissociable than either of said components; and said reactant materials being further characterized in that an electron acceptor component is an ionizable compound of an anion and a polyvalent metal cation, and an electron donor component is an ionizable organic chelating agent.

2. A heat-sensitive copying-sheet according to claim 1 in which the heat-sensitive layer contains the reactant materials in the form of a multitude of closely spaced particles uniformly dispersed in a film-forming binder non-fusing at temperatures below about 120° C.

3. The heat-sensitive copying-sheet of claim 1 in which the polyvalent metal compound melts at a temperature within the range of about 60–120° C. and is a polyvalent soap of a fatty acid.

4. The heat-sensitive copying-sheet of claim 2 in which the polyvalent metal compound melts at a temperature within the range of about 60–120° C. and is a polyvalent soap of a fatty acid.

5. The heat-sensitive copying-sheet of claim 4 in which the organic chelating agent is an oxime.

6. The heat-sensitive copying-sheet of claim 4 in which the organic chelating agent is a carbazone.

7. The heat-sensitive copying-sheet of claim 4 in which the organic chelating agent is a carbazide.

CARL S. MILLER.
BRYCE L. CLARK.

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