Dec. 22, 1953 C. S. MILLER ET AL 2,663,655

HEAT-SENSITIVE COPYING PAPER

Filed May 15, 1952 2 Sheets-Sheet 1

Fig. 1

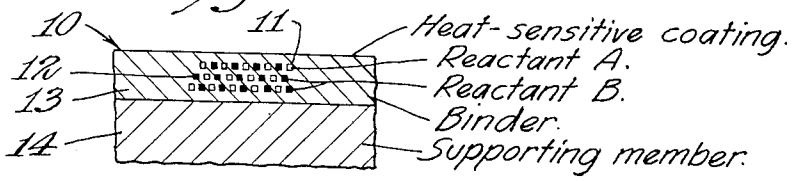


Fig. 2

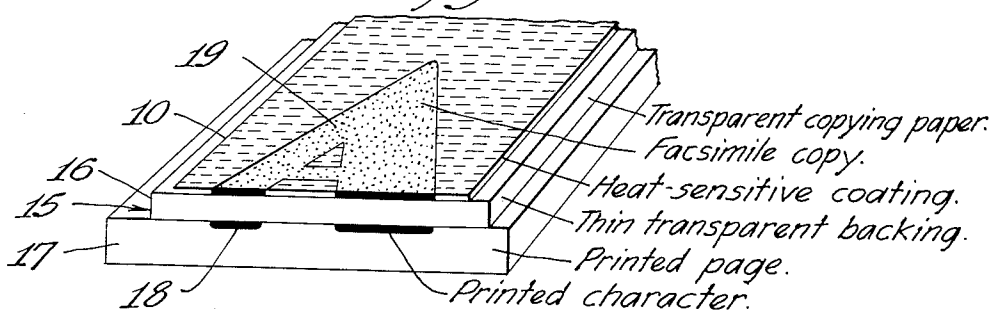


Fig. 3

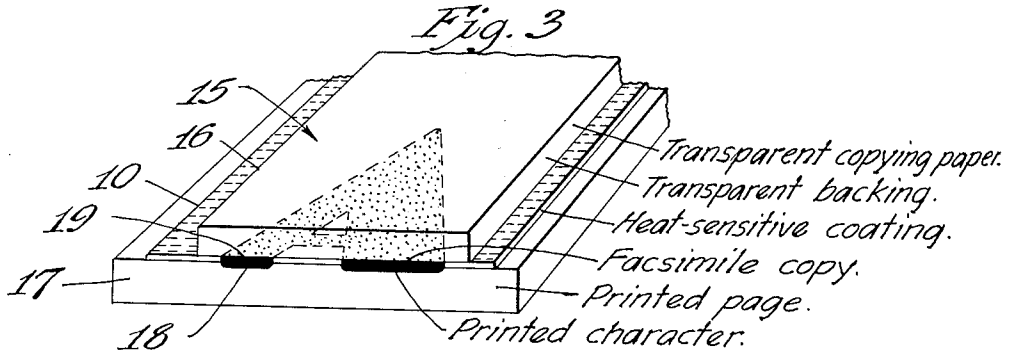
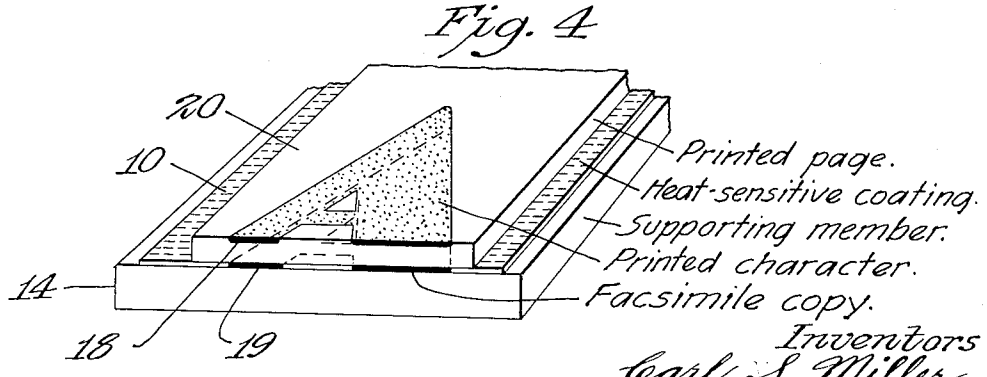


Fig. 4



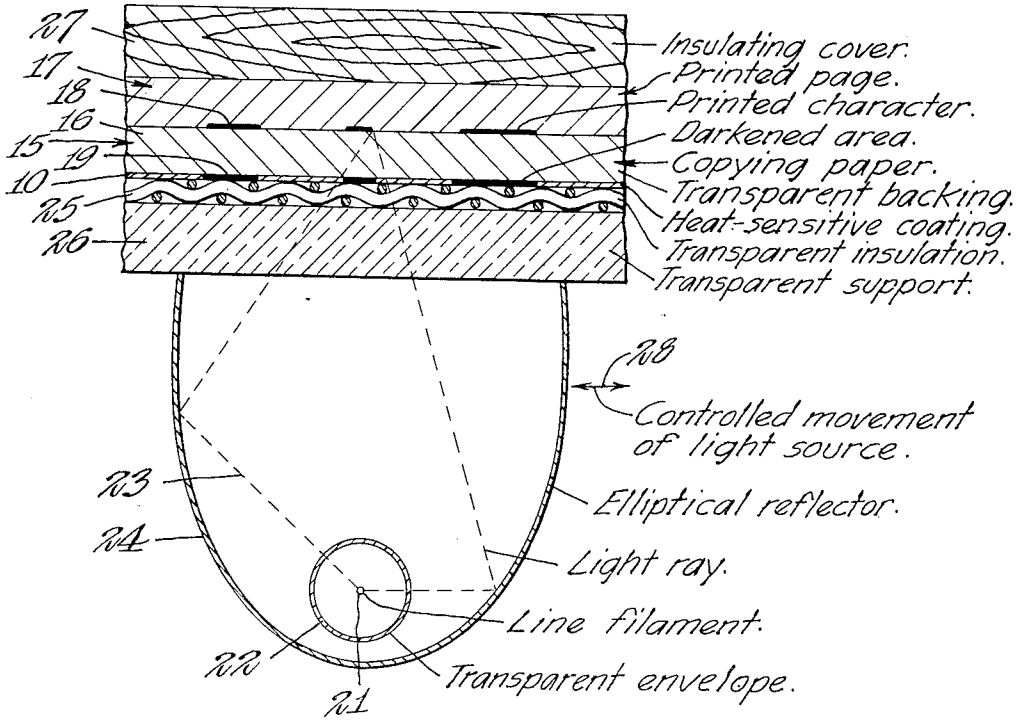
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Fig. 5



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HEAT-SENSITIVE COPYING PAPER

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Application May 15, 1952, Serial No. 288,004

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 copending application Serial No. 747,339, 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 surface, 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 composition 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

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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.

The heat-sensitive compositions of our invention are comprised of solid ionizable reactants which are potentially chemically capable of irreversibly and rapidly reacting at normal room temperature in a direct ion-exchange electron acceptor-donor chemical reaction to produce a visibly different reaction product, but which are normally maintained in physically distinct relationship and physically prevented from so reacting. The structure 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 contract 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 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

One pound of nickel acetate (tetrahydrate) was dispersed in one liter of anhydrous butyl acetate by grinding in a ball mill. Similarly, one pound of calcium sulfide was ground into one liter of anhydrous butyl acetate. A 30% solution of ½ second nitrocellulose in butyl acetate and benzol was used as the binder. The three components were proportioned as follows:

	Volumes
Nickel acetate dispersion	20
Calcium sulfide dispersion	5
Binder	30

This mixture was applied in a thin layer to various supporting surfaces, e. g. cellophane or cellulose acetate film, paper, wood, leather, etc., and dried at room temperature. The dried film was faintly greenish-white in appearance. When heated, the film rapidly became intensely black and opaque.

The reactive ingredients of Example 1 are found to be inter-reactive under proper conditions at normal room temperature, with the production of a dark-colored and opaque reaction product. For example, the addition of a small amount of water to a mixture of nickel acetate and calcium sulfide in powder form initiates the reaction between the two compounds. It is believed that the reaction obtained in the coated sheet material is due to the increased vapor pressure, at an elevated temperature, of the water present in the hydrated salt, and/or the melting of the hydrous salt to a fluid state, resulting in a reactive mingling of the nickel compound and the sulfide.

Example 2

Strontium sulfide and nickel acetate tetrahydrate were ground up in a 21% solution of 5-second nitrocellulose in butyl acetate, in the ratio of one gram each of insoluble strontium sulfide and nickel acetate tetrahydrate particles to three milliliters of nitrocellulose solution. The mixture was coated on cellophane and dried at room temperature. The sheet was light gray in color, changing to an intense black when briefly heated to 115° C. It could be used as a heat-sensitive copying-sheet by methods described herein, producing copies of good contrast and detail.

Barium sulfide and nickel acetate tetrahydrate produce similar results. In a specific formulation, 20 ml. of a dispersion of one pound of the nickel acetate in 1000 ml. of butyl acetate, 50 ml. of a 28% nitrocellulose solution in butyl acetate, and 10 ml. of a dispersion of one pound of barium sulfide in 1000 ml. of butyl acetate were mixed and coated on paper, and dried at room temperature. A protective surface sizing of a 15% solution of nitrocellulose in butyl acetate was applied over the heat-sensitive coating and dried. The finished copying-sheet was light yellowish green in color, and produced dark-colored brown-black copies when used as a heat-sensitive copying-paper by methods above indicated. Tested on a metal test block, the visible reaction was found to occur at approximately 93–105° C.

Other film-forming cellulose derivatives, as well as various non-cellulosic binders such as polyvinyl butyral, rubber, polyvinyl acetate, rubber hydrochloride and the like, may be substituted for the specific binder above mentioned, provided the volatile solvents required for such binders are at the same time non-solvents for, and non-reactive with the particulate solid components.

Example 3

Another combination of heavy metal salt and alkaline earth metal sulfide which has produced useful copies when employed in structures such as that of Examples 1 and 2 contains solid particles of nickel stearate and barium sulfide in a nitrocellulose binder. The nickel stearate, prepared by precipitation from a mixture of aqueous solutions of nickel acetate and the sodium salt of commercial stearic acid, is a waxy solid at temperatures below 60° C., and liquid at 120° C. The coated and dried sheet was dipped into a 4:1 blend of naphtha and mineral oil and again dried; the residual mineral oil improved the heat-conductivity properties of the sheet. On a metal test block, the sheet changed rapidly from light yellow to dark brown at about 113° C., and could be used in making effective facsimile copies of typewritten letters and the like by the methods herein described.

Example 4

The reaction of Example 3 can be obtained at a lower temperature by incorporating in the heat-sensitive film a small proportion of a free organic acid. The following combinations of reactants, suspended in particulate form in a 5% solution of crepe rubber in heptane, coated on flax paper, and dried at room temperatures, were each effective as heat-sensitive copying-papers and produced the indicated color change at the temperature specified.

1. Nickel palmitate-barium sulfide-stearic acid; changed from light green to intense black at 85° C. Calcium sulfide produced a light gray sheet with otherwise identical properties.
2. Nickel palmitate-barium sulfide-palmitic acid; changed from light gray to intense black at 70° C.
3. Nickel caprylate-calcium sulfide-stearic acid; changed from gray to intense black at 60° C. Crotonic acid in place of stearic acid raised the conversion temperature to 72° C.

Many other compounds in addition to the several materials previously enumerated have additionally been found to produce adequate color differences when combined as closely spaced particles in a film-forming binder as described in the above examples. Cobalt and lead salts are,

for example, equally as effective as the salts of nickel. Salts of silver, mercury, copper and iron are useful but less desirable, silver and mercury salts showing a tendency to darken on exposure of the paper to sunlight and copper and iron salts being initially undesirably dark in color and hence providing less contrast in the resulting copy. Colorless or lightly colored sulfides such as zinc sulfide, cadmium sulfide, and magnesium sulfide are effective in formulations such as those of Example 4 and for such purposes may be considered fully equivalent to the alkaline earth metal sulfides specified in that example.

The mixture of reactive solid components is 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 nitrocellulose 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, but are not necessarily most advantageous. The proportions of specific reactants shown in many of the specific examples will be found to yield useful results, but wide variations from these proportions may greatly improve the depth of color, or the contrast, or the detail, or other desired property in the case of other reactants, other proportions of the same or other binders, or other combinations of these several factors.

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 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 wavelength 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 cellophane and described under Example 1. With other wavelengths, 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 dark-

ened 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. However, many other sources of radiation, including ordinary high-intensity incandescent lamps, photoflash lamps, electric arc, infrared lamps, concentrated sunlight, etc., have been found to be useful but commercially less effective 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 comprising paper coated with a heat-sensitive layer containing, uniformly dispersed in a film-forming binder non-fusing at temperatures below about 120° C., a multitude of closely spaced solid particles of stable ionizable dissociable materials comprising a salt of a heavy metal the sulfide of which is colored, and an alkaline earth metal sulfide, at least one of said heavy metal salt and said alkaline earth metal sulfide melting 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 materials a visible change is produced in the heat-sensitive layer, said materials being

maintained in physically distinct and chemically inter-reactive relationship in said layer at normal room and storage temperatures, said materials being capable of rapidly visibly reacting at normal room temperature in a direct ion-exchange electron acceptor-donor chemical reaction in a mutual solvent capable of permitting ionization of said materials and with the formation of a stable, visibly distinct, highly polarized compound which is less dissociable than either of said materials, and said materials in said heat-sensitive layer being stable at temperatures less than about 60° C. and being rapidly visibly inter-reacted when the copying-sheet is heated to 120° C.

2. A heat-sensitive copying-sheet in accordance with claim 1 and having over the heat-sensitive layer a thin transparent protective surface sizing layer.

3. A heat-sensitive copying-sheet for making direct, high contrast, clear detail copies of graphic subject-matter as herein described, said copying-sheet comprising a support having low thermal conductivity, and a heat-sensitive layer containing, uniformly dispersed in a film-forming binder non-fusing at temperatures below about 120° C., a multitude of closely spaced solid particles of stable ionizable dissociable materials comprising a salt of a heavy metal the sulfide of which is colored, and an alkaline earth metal sulfide, at least one of said materials melting 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 materials a visible change is produced in the heat-sensitive layer, said materials being maintained in physically distinct and chemically inter-reactive relationship in said layer at normal room and storage temperatures, said materials being capable of rapidly visibly reacting at normal room temperature in a direct ion-exchange electron acceptor-donor chemical reaction in a mutual solvent capable of permitting ionization of said materials and with the formation of a stable, visibly distinct, highly polarized compound which is less dissociable than either of said materials, and said materials in said heat-sensitive layer being stable at temperatures less than about 60° C. and being rapidly visibly inter-reacted when the copying-sheet is heated to 120° C.

4. A heat-sensitive copying-sheet in accordance with claim 3 in which the heavy metal salt is a hydrated salt melting within the range of about 60–120° C.

5. A heat-sensitive copying-sheet in accordance with claim 4 in which the hydrated heavy metal salt is nickel acetate tetrahydrate.

6. A heat-sensitive copying-sheet for making direct, high contrast, clear detail copies of graphic subject-matter as herein described, said copying-sheet comprising a support having low thermal conductivity, and a heat-sensitive layer containing, uniformly dispersed in a film-forming binder non-fusing at temperatures below about 120° C., a multitude of closely spaced solid particles of stable ionizable dissociable materials comprising (1) a salt of a heavy metal the sulfide of which is colored, (2) an alkaline earth metal sulfide, and (3) an organic acid melting at a temperature within the range of about 60–120° C., said materials being present in an amount such that on heating and inter-reaction a visible change is produced in the heat-sensitive layer, said materials being maintained in physically distinct and chemically inter-reactive relationship in said layer at normal room and storage temperatures, said materials being capable of rapidly visibly reacting at normal room temperature in a direct ion-exchange electron acceptor-donor chemical reaction in a mutual solvent capable of permitting ionization of said materials and with the formation of a stable, visibly distinct, highly polarized compound which is less dissociable than either of said materials, and said materials in said heat-sensitive layer being stable at temperatures less than about 60° C. and being rapidly visibly inter-reacted when the copying-sheet is heated to 120° C.

7. A heat-sensitive copying-sheet in accordance with claim 6 in which the heavy metal salt is a nickel salt of an organic acid.

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