Dec. 22, 1953 C. S. MILLER ET AL 2,663,654

HEAT-SENSITIVE COPYING PAPER

Filed May 15, 1952 2 Sheets-Sheet 1

Fig. 1

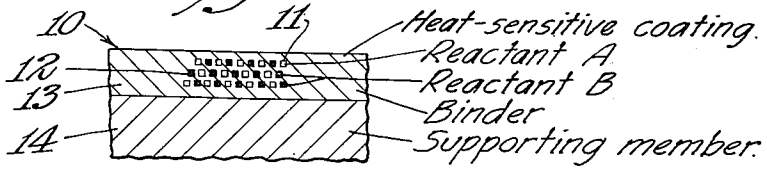


Fig. 2

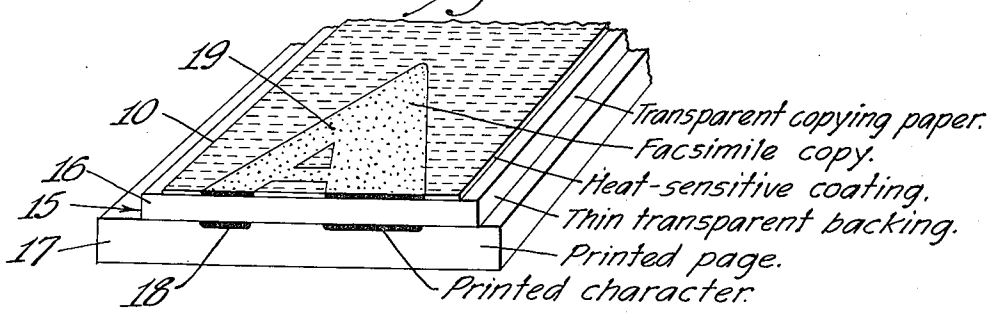


Fig. 3

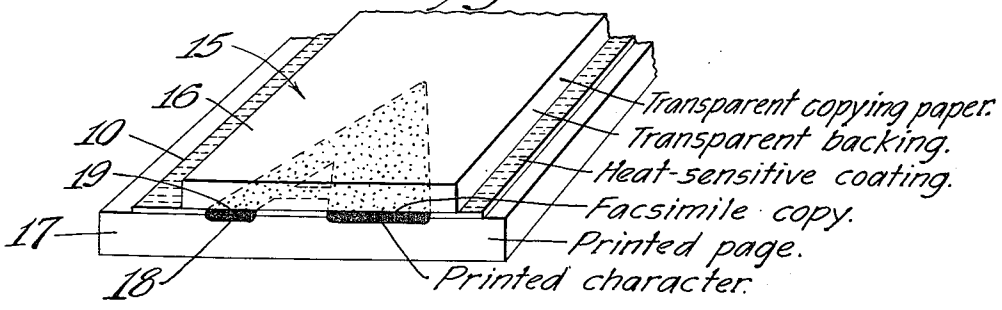
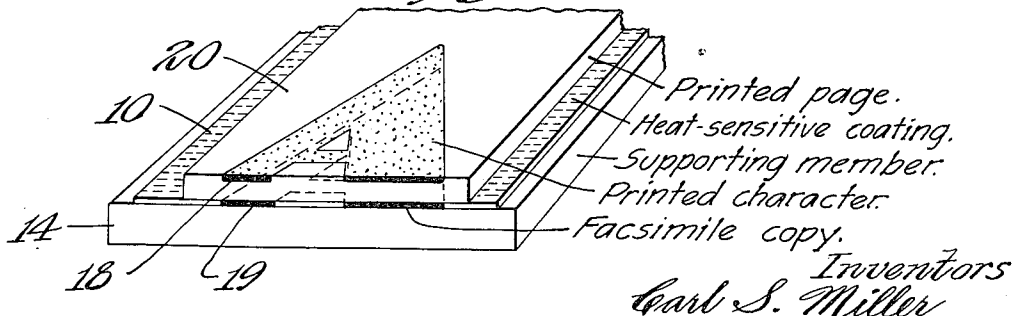


Fig. 4



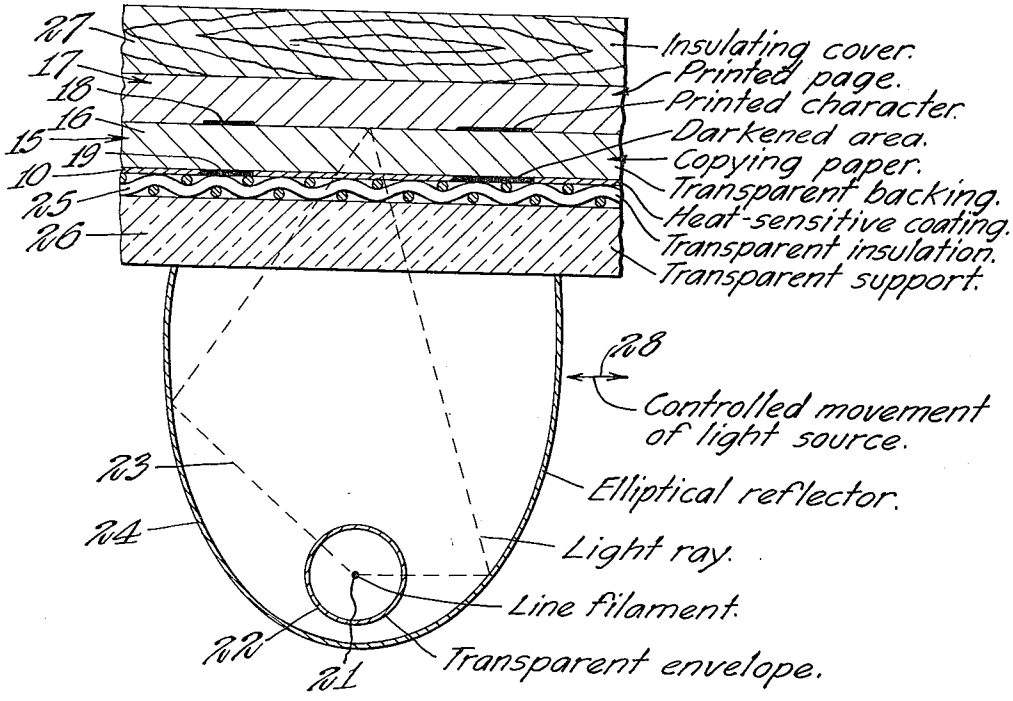
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HEAT-SENSITIVE COPYING PAPER

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. 288,003

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 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.

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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.

The heat-sensitive compositions of our invention are comprised of solid reactants which are potentially chemically capable of irreversibly and rapidly reacting at normal room temperature to produce a visibly different reaction product, but which are normally 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. The reactive components in the copying-sheet are stable at temperatures less than about 60° C. but are rapidly visibly inter-reacted when the copying-sheet is heated to 120° C.

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 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

Reactant A

To an aqueous solution of three mols of the sodium soap of commercial triple-pressed stearic acid of melting-point approximately 53° C., and which supposedly contains a minor amount of other higher fatty acids, etc., add an aqueous solution of one mol of ferric sulfate. Filter the precipitated ferric stearate, wash separately with water and alcohol, and dry at room temperature. The solid product softens or melts within the range of 70–95° C. Disperse 500 grams of the the powder in two liters of denatured ethyl alcohol, e. g. "Ponsolve," by grinding with flint pebbles in a ball mill.

Reactant B

Dissolve 1500 grams of hexamethylenetetramine in 12 liters of denatured alcohol ("Ponsolve") at 65° C.; with constant stirring, add this solution to a solution of 2000 grams of pyrogallic acid in 4 liters of the alcohol, also at 65° C. A crystalline precipitate forms. Cool to room temperature, with constant stirring to avoid lumping. Recover and dry the precipitate, which should be in the form of a fine powder. Disperse 500 grams of this powder in one and one-half liters of denatured alcohol by ball milling as for Reactant A.

Reactant C

Dissolve 10 grams of oxalic acid in 100 milliliters of ethyl alcohol.

Binder

Dissolve 150 grams of polyvinyl butyral in one liter of ethyl alcohol.

Composition in liquid form:	ml.
Reactant A	500
Reactant B	100
Reactant C (optional)	40
Binder	200

In mixing and temporarily maintaining the mixture of Reactants A and B in a volatile vehicle such as denatured ethyl alcohol, a slight discoloration may sometimes be noted. This is presumably due to solution of traces of one or both of the substantially insoluble reactants in the liquid vehicle and the resultant reaction of the dissolved materials to produce a dark-colored reaction product. The presence of a trace of oxalic acid, which forms a complex with iron and consequently may be considered to render inaccessible any dissolved or previously reacted iron, discharges and/or prevents the formation of the slight discoloration thus otherwise produced. Citric acid, which likewise forms an iron complex, is also effective. In many cases the discoloration produced, even in the absence of these modifying reactants, is so slight as not to be troublesome, particularly where adequate precautions are taken in preparing and in applying the temperature-sensitive composition.

Coated transparent sheet material

The above liquid composition is uniformly spread, as by means of a spreader bar or knive coater, over one surface of a thin transparent film of plasticized regenerated cellulose (cellophane) to a thickness of approximately 3 mils, and is allowed to dry at room temperature. The resulting visibly transparent coated sheet product rapidly darkens when heated to or above about 80° C., and is suitable for use as a temperature-sensitive copying-paper.

The darkening here obtained is thought to result from a preliminary melting or softening of the ferric stearate, making possible the mixing or co-dissolving of the two reactants and their resulting rapid reaction to form a dark-colored and opaque reaction product. This may be inferred from the fact that the darkening of the sheet is obtained on heating the copying-paper to a temperature closely approximating the melting or softening point of the particular ferric soap used. A similar color change may be produced at room temperature by adding a suitable solvent, e. g. benzol, to the otherwise non-reacting mixture of the two powders.

This reaction and rapid color change does not take place on exposure of the mixture, or of the coated sheet material, to radiant energy such as visible or infra-red light in the absence of the required temperature increase. Some darkening of the coated transparent sheet material as above prepared may be observed on prolonged exposure to light, and particularly to high intensities of actinic radiation; but this is believed to be due to the effect of certain radiations in decomposing one or both of the reactants separately, and may readily be prevented by applying a suitable filter over the temperature-sensitive coating. A thin surface coating of a mixture of 3 grams of 4,4-dihydroxy-benzalazine and 15 grams of polyvinyl butyral, applied from solution in 85 grams of alcohol, provides an effective filter for this purpose.

EXAMPLE 2

To obtain a composition having improved aging characteristics and which will react when heated to a somewhat lower temperature, similarly prepared ferric myristate, made with commercial myristic acid, is substituted for the ferric stearate of Example 1, and a reaction product of hexamethylenetetramine and gallic acid (a substituted trihydroxy benzene), is substituted for the pyrogallic acid product there described.

This second ingredient is prepared as follows: 280 grams of hexamethylenetetramine are dissolved in one liter of water, and 188 grams of gallic acid are dissolved in one liter of ethyl alcohol. One volume of the first solution is mixed with two volumes of the second, and the resulting precipitate is then recovered and dried. It is ground into heptane, by means of a ball mill, to form a 25% dispersion.

Ferric myristate softens and melts at somewhat lower temperatures than the stearate. Since the myristate is somewhat soluble in alcohol, heptane is used as the liquid vehicle, which necessitates the substitution, for the alcohol-soluble but heptane-insoluble polyvinyl butyral, of a heptane-soluble binder. In a specific example, natural rubber was used as the binder. Heptane is substantially a non-solvent for both ferric myristate and the reaction product of hexamethylenetetramine and gallic acid. There is ordinarily no visible evidence of reaction of the two materials in freshly prepared mixtures in heptane, although reaction takes place rapidly at temperatures below that required for activation of the coated copying-paper, and usually at or even below normal room temperatures, as in the case of the reactants of Example 1, in the presence of a suitable solvent such as benzene. The final composition of the fluid mass prepared according to the above description and ready for coating is approximately as follows:

	Parts by weight
Ferric myristate	100
Hexamethylenetetramine-gallic acid reaction product	25
Rubber	25
Heptane	500

This composition was coated on a thin paper, i. e. an unfilled flax paper of one mil thickness, such as is used for cigarette-paper. The mixture was applied by means of a knife-coater set to give a coating orifice of approximately 3 mils, and was dried at room temperature. The coated and at least partially impregnated sheet product was faintly tan in color and appeared semi-transparent. On heating to about 70° C. it rapidly darkened and became opaque. Exposure to light alone had substantially no effect on the appearance of the unheated material. Scribing or otherwise mechanically compacting or disrupting the surface coating did not initiate the color-developing reaction.

For improved permanence, the rubber used as binder may be protected, as by the addition of suitable antioxidants or other age-resistors; or various synthetic polymers or resins may be substituted for natural rubber where their properties, e. g. color, permanence, etc., permit or encourage such substitution.

A particularly desirable copying-paper, capable of rapidly producing a high contrast ratio when heated within a range of only 5° C., was produced by employing the hexamethylenetetramine-gallic acid reaction product in conjunction with ferric stearate prepared from highly purified stearic acid.

EXAMPLE 3

Ferric stearate in 5 times its weight of stearic acid was emulsified in a hot concentrated solution of glue in water. To the cooled solution was added a water solution of tannic acid. The resulting well-mixed composition was coated on paper and dried at room temperature. The sheet was reddish-brown, but turned black when heated as in the preparation of copies of graphic subject-matter by our novel method.

EXAMPLE 4

Ferric stearate was dispersed in acetone by ball milling as in the previous examples, and a preformed solution of ethyl cellulose was added, to a final formula of approximately 12% ferric stearate, 6% ethyl cellulose, and 82% acetone. The mixture was coated in a thin uniform layer on one mil condenser tissue, a thin, tough paper, and dried at room temperature. The weight of the dry coating of ferric stearate particles uniformly dispersed in ethyl cellulose was about 0.68 gram per square foot of surface.

Gallic acid, which is a solid at normal room temperature, was dissolved in an acetone solution of ethyl cellulose, to a final formula of approximately 5% gallic acid, 9.5% ethyl cellulose, and 85.5% acetone. This solution was coated in a thin layer over the dry ferric stearate-ethyl cellulose layer, and the sheet again dried at room temperature. The dry weight of the second coating was about 0.50 gram per square foot.

The completed sheet material was useful as a copying-paper, showing high contrast and good detail in the copy. The ferric stearate component softens or melts at 70–95° C., and at least the major portion of the color change in the copying-sheet occurs over substantially the same temperature range.

EXAMPLE 5

Fifty parts by weight of ferric stearate were dispersed in 1500 parts of acetone by ball milling. Separately, 100 parts of a phenolic resin were dispersed in 400 parts of acetone by similar procedure. The phenolic resin was a solid heat-advancing partial reaction product of para-tertiary-butylphenol and formaldehyde, melting at 144–158° F. (62–70° C.). Such a resin is soluble in drying oils and aromatic hydrocarbons but insoluble in alcohols and only slightly soluble in acetone.

Two parts of the ferric stearate dispersion were mixed with one part of the resin dispersion, and the mixture was coated on thin paper and dried at room temperature. The resulting sheet material was useful as a heat-sensitive copying-paper, but the heat-sensitive coating had a tendency to stick to contacting surfaces, particularly during the copying process. Substitution of a higher-melting heat-advancing phenolic resin for the resin hereinbefore described eliminates this tendency, resins melting above 120° C. providing fully non-sticking surfaces with, however, some reduction in contrast in the copy obtained. Sticking is also readily avoided, and with no significant reduction in contrast, by incorporating small amounts of a film-forming binder, such as ethyl cellulose, in the mixture prior to coating.

Other combinations of solid visibly inter-reactive materials which have provided effective heat-sensitive copying-papers when coated on various paper or film backings in the form of dispersions in solutions of film-forming binders include ferric stearate-triethyl sulfonium tannate; ferric stearate-cadmium tannate; and ferric stearate-ammonium salicylate. Ferric myristate, ferric palmitate, and similar salts of other organic acids softening or melting at temperatures within the range of about 60–120° C. may be substituted for the ferric stearate in these compositions.

In these examples, the visible change obtained

on activation of the coated material is the result of a combination between the iron of the ferric stearate or equivalent and the phenolic portion of pyrogallic or gallic acid, tannates, salicylates, or the like. A large number of other phenols which similarly provide colored reaction products with iron salts are listed by Wesp and Brode in the Journal of the American Chemical Society, volume 56, at pages 1039 and 1040.

The reactive compositions of the foregoing examples each comprise at least two solid sensitizing components which when placed in sufficiently intimate contact, as for example by dissolution of one or both of the components in a suitable solvent, are capable even at normal room temperature of producing an intense color or some other visible manifestation of chemical reaction. A bonding agent for conveniently supporting and bonding the reactive components is included; such a binder, or at least some reactive component thereof, may itself serve as one of the color-producing reactants. It will be apparent, from the several specific examples set forth hereinabove, that a wide variety of compositions having these qualifications may be prepared.

The reactive solid components, either individually or as a pre-formed mixture, 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 described 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 polyvinyl butyral of Example 1 or the ethylcellulose of Example 4, 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. Compositions employing a reactant or reactants which are themselves film-forming, or which have adequate adhesion to a supporting web, ordinarily require no auxiliary bonding or film-forming agent.

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 in many cases be determined, 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 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 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 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. However, 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 useful, although 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 normally 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 a support having low thermal conductivity, and a heat-sensitive layer containing, uniformly dispersed in a film-forming, transparent binder non-fusing at temperatures below about 120° C., a multitude of closely spaced particles of at least two visibly inter-reactive solids of which one is a liquid at temperatures above normal room and storage temperatures and within the range of about 60–120° C. and is an iron salt of a solid long-chain fatty acid, and the second inter-reactive particulate solid is a phenol, said inter-reactive solids 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 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, transparent binder non-fusing at temperatures below about 120° C., a multitude of closely spaced particles of at least two visibly inter-reactive solids of which one is a liquid at temperatures above normal room and storage temperatures and within the range of about 60–120° C. and is a water-insoluble iron salt of an organic acid, and the second particulate solid is a phenol, said inter-reactive solids 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.

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 comprising a film-forming, transparent binder non-fusing at temperatures below about 120° C., an iron salt of an organic acid, and a phenol which is visibly reactive therewith; said iron salt being a solid at normal room and storage temperatures and melting to a liquid within the range of about 60–120° C., and said phenol being a solid at normal room and storage temperatures; said iron salt being in the form of particles distributed substantially uniformly throughout said heat-sensitive layer; said iron salt and said phenol 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 for making direct, high contrast, clear detail copies of graphic subject-matter as herein described, said copying-sheet being non-sticking at 120° C. and comprising a support having low thermal conductivity, and a protected heat-sensitive layer comprising an iron salt of an organic acid and a phenol visibly reactive therewith, said iron salt being a solid at normal room and storage temperatures and melting to a liquid within the range of about 60–120° C., said iron salt and said phenol being firmly bonded to said support in uniform mutually closely adjacent relationship over the entire active area thereof, said iron salt and said phenol in said heat-sensitive layer being stable at temperatures less than about 60° C. and being rapidly visibly inter-reactive when said copying-sheet is heated to 120° C.

5. 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. and comprising a support having low thermal conductivity, and a protected heat-sensitive layer comprising an iron salt of an organic acid and a phenol visibly reactive therewith, said iron salt and said phenol in said heat-sensitive layer being firmly bonded to said support in mutually closely adjacent relationship, being stable at temperature less than about 60° C., and being uniformly rapidly visibly inter-reactive when said copying-sheet is heated to 120° C., both the iron salt and the phenol being solid at normal room temperatures and at least one of said iron salt and phenol melting to a liquid at a temperature within the range of about 60–120° C.

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, transparent binder non-fusing at temperatures below about 120° C., a multitude of closely spaced solid particles of materials comprising an iron salt of an organic acid and a phenol, at least one of said materials melting at a temperature within the range of about 60–120° C., said materials being capable of rapidly visibly reacting at normal room temperature, 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. The copying-sheet of claim 6 in which the support member is paper.

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No references cited.