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Jan. 22, 1963 R. OWEN 3,074,809

HEAT-SENSITIVE COPYING-PAPER

Filed Oct. 26, 1959

FIG. 1

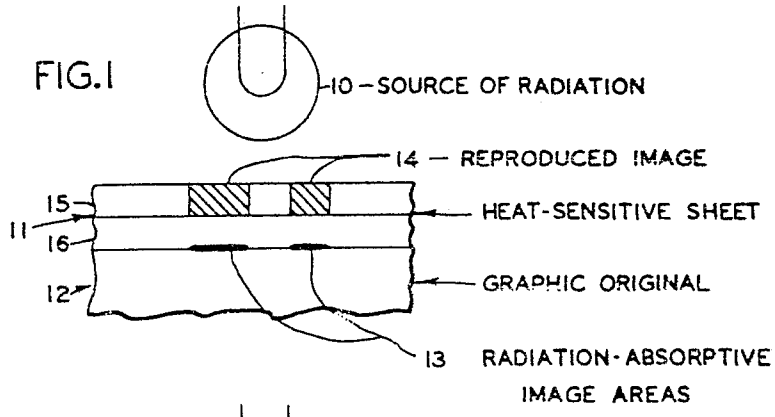


FIG. 2

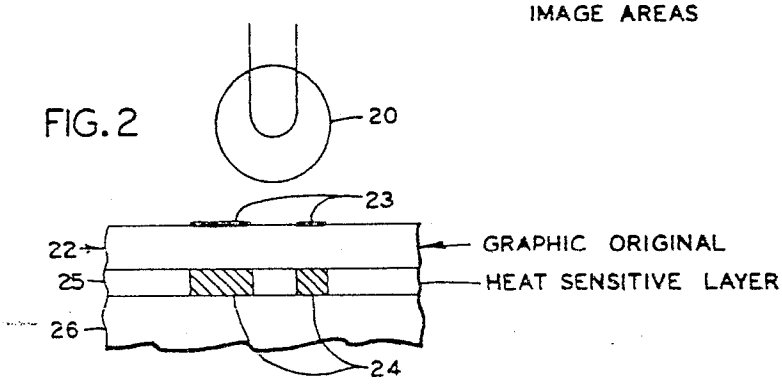
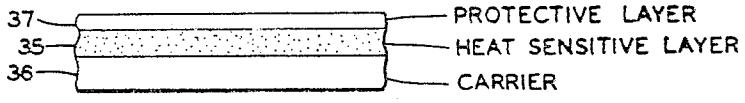


FIG. 3



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HEAT-SENSITIVE COPYING-PAPER

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12 Claims. (Cl. 117—36.8)

This application is based on my copending application Serial No. 594,540, filed June 28, 1956, now U.S. Patent No. 2,910,377.

This invention is concerned with improvements in heat-sensitive copying-paper useful in preparing copies of printed matter by procedures, such as those described in Miller Patent No. 2,740,896, involving placing a printed or other graphic original in heat-conductive association with the heat-sensitive copying-paper and then briefly exposing the graphic original to intense radiant energy. The resulting elevated-temperature pattern produces in the copying-paper a visible direct copy of the graphic original. The present invention provides a stable heat-sensitive copying-paper capable of providing duplicate copies having improved contrast between image and background areas, as well as improved esthetic appearance.

For convenience in describing the novel copying-paper and its application to the copying of documents, typical products and procedures are illustrated in the accompanying drawing, in which:

FIGURE 1 schematically illustrates in cross-section one method of copying a graphic original;

FIGURE 2 similarly illustrates an alternative method; and

FIGURE 3 illustrates in cross-section a preferred form of heat-sensitive copying-paper.

A commercially available thermo-copying machine widely employed for copying office records on heat-sensitive copying-paper includes as the source of radiant energy a high-intensity infrared lamp such as a GE "T-3" lamp having a linear coiled filament supported within a reflector which focuses the radiation in a narrow beam accross the sheet as the latter is moved past the lamp assembly. Such a lamp draws 1350 watts at 280 volts to provide a color temperature of about 2800° K. Irradiation and copying of a conventional letter-size sheet requires about 1–6 seconds. A non-fading copy is directly produced by such irradiation and without any subsequent processing such as developing, fixing, washing, treatment with fumes or vapors, or any other treatment.

In FIGURE 1, radiant energy from source 10 is directed through heat-sensitive copying-paper 11 to printed original 12. Energy is selectively absorbed in printed areas 13 and released in the form of heat energy, causing the occurrence of a visible change in corresponding areas 14 of the heat-sensitive layer 15 of sheet 11. The procedure is known as "front-printing."

In FIGURE 2 the radiant energy from source 20 impinges directly on the printed surface of the graphic original 22, and the resulting release of heat energy causes visible change in the heat-sensitive layer 25 on support 26 at areas 24 corresponding to the printed and radiation-absorptive areas 23 of the original. The procedure has been termed "back-printing."

The copying-sheet 11 of FIGURE 1 consists of a heat-sensitive layer 15 on a carrier 16, which may be a thin paper. The sheet must transmit sufficient of the radiant energy to provide the required release of heat at the printed areas 13 but is preferably sufficiently visibly opaque to provide high contrast in the copy.

Still greater accuracy of copy is obtained by inverting the copying-paper 11 so that the heat-sensitive layer 15

is more closely associated with the printed surface of the graphic original 12. In this case a visibly transparent carrier 16 permits viewing of the copy areas 14 through the carrier and in the same direction as the original.

The "front-printing" process of FIGURE 1 is applicable to a wide variety of originals and to radiation-transmissive copy-paper, whereas "back-printing" is most effective with originals printed on relatively thin heat-transmissive paper and the copy-paper may be fully opaque to the radiation employed.

FIGURE 3 illustrates a further variation in heat-sensitive copying-papers in which the heat-sensitive layer 35 is applied to a carrier web 36 and is covered with a protective layer 37. Either or both of web 36 and layer 37 may be visibly transparent, but in a preferred construction for "front-printing" operations the web 36 is transparent while the thin protective layer 37 is visibly opaque and provides high visual contrast for the visibly changed areas of the heat-sensitive layer.

The actual temperatures developed in such heat-sensitive papers by these various techniques have not been directly measured. However it has been observed that papers which change visibly when momentarily pressed against a metal test bar heated to about 100–120° C., or at most to about 150° C., become similarly altered under the irradiation techniques just described. On the other hand, papers which do not change on brief pressure contact with the test bar at temperatures much greater than about 150° C. are found to be ineffective as heat-sensitive copying-papers when tested in copying-machines as described hereinbefore. Since heating to such high temperatures, particularly when prolonged or frequently repeated, is likely to cause degradation or deterioration of the printed page forming the original of which a copy is desired, copy-sheets are ordinarily required to be visibly heat-sensitive at temperatures below about 150° C. and preferably at temperatures below about 120° C.

Heat-sensitive copying papers suitable for the copying of printed and other graphic originals by methods just described have previously been developed, and such products are described in Miller et al. Patents Nos. 2,663,654–2,663,657, in Taylor et al. Patent No. 2,668,126, and in Clark et al. Patent No. 2,710,263. The sheet materials of the present invention operate through a different mechanism, involving the reduction of certain metallic ions and precipitation of the metal in a pattern corresponding to the heat-pattern established in the copying procedure. The invention is more specifically concerned with the precipitation or formation of the metal in a form providing maximum image opacity and contrast, and a pleasing appearance.

Like the earlier heat-sensitive copying-papers, those of the present invention are suitable for making direct, high contrast, clear detail, permanent copies of typewritten, printed, and other graphic subject-matter. The copy-paper does not adhere to nor deface the graphic original or the thermoprinting apparatus. It is stable at normal room and storage temperatures, and in particular may be stored in the light without visible change either before or after heat-copying. In addition, the product hereof produces copies of typewritten originals which resemble the said originals much more closely than do those copies prepared with copy-sheets not containing the improvements herein described.

These and other advantageous properties are secured, in accordance with the principles of the present invention, by incorporating with the metal salt and reducing agent of the heat-sensitive coating certain additional components which have been found to darken and to increase the apparent opacity of the image-forming areas and in many instances to promote the formation of lustrous black

or blue-black images from compositions normally providing dull brownish or other less attractive and less pleasing image areas. The effect may be compared with that obtained in the photographic art through the addition of "toners"; and the materials here employed will likewise be characterized as toners or toning compounds.

Typical formulations employed in heat-sensitive copy-sheets in which image formation occurs through an oxidation-reduction reaction involving precipitation of a metal are those comprising silver salts and aromatic reducing agents, of which silver behenate and hydroquinone are illustrative. These specific reactants, suitably maintained in physically distinct relationship in a film-forming binder in a heat-sensitive layer, undergo visible reaction when the layer or sheet is heated momentarily to the required temperature. There is formed a yellowish-brown colored area which is visibly distinct against the essentially white background provided by the adjacent unreacted areas. Other formulations produce image areas of other specific color or appearance; but in all instances, although the reproduction is fully legible, it is deficient in image density, or in contrast, or in color. Thus, silver behenate and spiroindane produce a golden brown image; gold stearate and 2,5-dihydroxybenzoic acid produce a purplish black image. The image areas are formed, at least in part, of particles of the reduced metal.

It has now been found that the image areas thus formed may be given a more pleasing appearance, generally darker color, and increased apparent density and contrast, by incorporating with the mixture of noble metal salt and organic reducing agent a significant small amount of an organic carboxylic acid toning compound, which compound preferably contains at least one additional functional group reactive with the carboxyl radical by elimination of the elements of water to form a 5 or 6 member cyclic structure.

These components, and other additives as desired, are normally employed in conjunction with a water-resistant film-forming binder, the combination being in the form of either a self-supporting thin film or a thin coating on a suitable paper or other carrier web. The reactants are present in amounts sufficient to provide adequate visible change on heating, and the binder maintains the reactants in the required intimate association and in position on the paper backing. In some instances the reactants may be maintained in the required relationships within a fibrous sheet structure in the substantial absence of a binder.

The following specific examples further illustrate the invention.

Example 1

A mixture of equal mol percent of silver behenate and behenic acid is prepared by mixing together one mol of silver nitrate and two mols of sodium behenate in aqueous medium and under slightly acidic conditions. The resulting water-insoluble precipitate is recovered, washed and dried. The product fuses at about 135° C. and melts to a liquid at about 175° C.

Ten grams of the product mixture is intimately dispersed in 90 grams of a 2% solution of polystyrene resin binder in methylethylketone, by milling for sixteen hours in a ball mill. Separately, four grams of hydroquinone is dissolved in 100 grams of a 10% solution of the resin in a mixture of equal parts by weight of acetone and commercial heptane. A mixture is prepared of ten grams of the dispersion with ten grams of the solution, and is applied in a thin uniform coating to map overlay tracing paper and the coating dried in a current of air at room temperature. The resulting "control" sheet is white in appearance, and converts to yellowish-brown on brief contact with a metal test bar at 120° C. The sheet produces good legible copies of differentially radiation-absorptive originals in the thermographic reproduction process; the image areas are yellowish-brown.

To another mixture of ten grams of the silver soap dispersion and ten grams of the hydroquinone solution is added 0.06 gram of gluconic acid, and the mixture is similarly applied as a dried surface coating on the transparent paper. Image areas produced by localized heating of the sheet, either by thermographic copying or with the test bar at 120° C., are brownish black and present a much more pleasing appearance than those formed on the control sheet.

Example 2

With a mixture of ten grams of the silver soap dispersion and ten grams of the hydroquinone solution of Example 1 there is admixed 0.04 gram of succinic anhydride. The resulting mixture is coated on transparent paper, dried, and tested as described in connection with Example 1. A copy is produced in which the image areas are substantially black and show still further improvement in contrast. In reproducing a typewritten original, the reproduction does not differ substantially from the original in appearance, whereas the control sheet of Example 1, while providing fully legible copy, is easily distinguished from the original.

Example 3

A suspension of six parts by weight of the silver behenate: behenic acid mixture of Example 1 is dispersed in a solution of 1.5 parts of polystyrene resin in a mixture of 16 parts heptane and 26.5 parts acetone by ball milling to a smooth dispersion. Separately, 1.5 parts of methyl gallate, 0.1 part of 2,3-dihydroxybenzoic acid, and 0.2 part of phthalic anhydride are stirred into a solution of 11.6 parts of polystyrene resin in 13.6 parts heptane and 23 parts acetone. The two solutions are blended together and the blend coated smoothly on map overlay tracing paper, the dried coating weighing 0.5 gram per square foot, equivalent to about 21 milligrams of silver.

Trace amounts of inhibitors, e.g., citric acid, are preferably included with the phthalic anhydride to prevent reaction and darkening of the solution prior to coating.

The sheet is then further coated with 0.5–1.5 grams per square foot dry weight, of a smooth dispersion of 30 parts of zinc oxide, 3 parts of "Parapol S–50" resin, 1 part of "Santocel C" filler, and 0.08 part of phthalic anhydride, in 66 parts of heptane.

The product is white in appearance. It does not discolor on prolonged storage at normal room and storage temperatures, nor on exposure to sunlight. When pressed against a printed page and the latter intensely irradiated as hereinbefore described, the sheet darkens to a lustrous black appearance at the heated areas and provides a clear, sharp duplicate of the original printed matter.

Silver behenate, either alone or in conjunction with free behenic acid, is a preferred example of an organic acid salt of a reducible metal which, as has been shown by analysis of the resulting image areas, is reduced to the free metal during the oxidation-reduction reaction. The silver content is readily reduced to metallic silver. The compound is colorless, visibly stable toward light, insoluble in many volatile liquid vehicles, and moisture-resistant. It is produced in the desired physical form without difficulty and at reasonable cost. The free behenic acid content improves the moisture-resistance of the sheet but is not essential and may be omitted or replaced.

Silver stearate has been successfully substituted for silver behenate, and silver salts of many other organic acids have also been found useful in these heat-sensitive compositions and copying-papers. A partial list of such organic acids includes oleic, lauric, hydroxystearic, acetic, phthalic, terephthalic, butyric, m-nitrobenzoic, salicyclic, phenylacetic, pyromellitic, p-phenylbenzoic, undecylenic, camphoric, furoic, acetamidobenzoic and o-aminobenzoic. Water-insoluble salts of higher weight acids, particularly the higher fatty acids, are preferred.

Similarly, other reducing agents have been substituted for the specific materials of the examples. Such materials

include the following: pyrogallol; 4-azeloyl-bis-pyrogallol; 4-stearoyl pyrogallol; galloacetophenone; di-tertiary-butyl pyrogallol; gallic acid anilide; methyl gallate; ethyl gallate; normal and iso-propyl gallate; butyl gallate; dodecyl gallate; gallic acid; ammonium gallate; ethyl protocatechuate; cetyl protocatechuate; 2,5-dihydroxy benzoic acid; 1-hydroxy-2-naphthoic acid; 2-hydroxy, 3-naphthoic acid; phloroglucinol; catechol; 2,3-naphthalene diol; 4-lauroyl catechol; sodium gallate; protocatechualdehyde; 4-methyl esculetin; 3,4-dihydroxy benzoic acid; 2,3-dihydroxy benzoic acid: hydroquinone; 4,4'-dihydroxy biphenyl; 3,4-dihydroxyphenylacetic acid; 4(3',4'-dihydroxyphenylazo)-benzoic acid; 2,2'-methylene bis-3,4,5-trihydroxybenzoic acid; ortho- and para-phenylene diamine; tetramethyl benzidine; 4,4',4''-diethylamino triphenylmethane; o-, m-, and p-aminobenzoic acids; alpha and beta naphthols; 4-methoxy, 1-hydroxy-dihydronaphthalene; and tetrahydroquinoline.

Although the specific effect observable with the various components and combinations hereinbefore tabulated will vary with the particular reactants employed as well as with the specific toning material selected, significant improvement in the appearance of the thermographic reproduction has been observed on the addition to representative metal-image forming oxidation-reduction copy-sheet formulations of each of the following representative toning compounds: maleic acid or anhydride; succinic acid or anhydride; gluconic acid; oxalic acid; 2-hydroxycinnamic acid; 2-hydroxy-1-naphthoic acid; glycolic acid; anthranilic acid; malic acid; phthalic acid; and gamma-hydroxybutyric acid. During image formation at least some of the toner is presumably present in acid form whether added as the acid or as the cyclic condensation product thereof. Accordingly, where the acid is specified it will be appreciated that equivalent cyclic condensation derivatives thereof are also to be included.

The action of these and other equivalent toners is not fully understood. However it has been observed that silver particles precipitated from a solution in water and acetone, of silver nitrate and organic reducing agent, and containing the toner component, are of significantly more complicated shape, when viewed under the microscope, than particles precipitated in the absence of the toner. The precipitate is also significantly more voluminous. Surprisingly, the same volume increase is observed if the toning agent is added subsequent to precipitation. The size of the silver particles obtained in the image areas of the copy-sheet has been shown by electron micrographs to be increased under the influence of the toning agent.

The amount of toning agent required is not critical but can be varied within rather wide limits. In each instance the optimum proportion will depend not only on the specific toner compound or mixture but also on the specific metal salt and reducing agent, and, to a lesser extent, on other variables such as the amount and nature of the binder, the thickness of the heat-sensitive layer, the presence or absence of various additives, the temperature of conversion, and perhaps others. Insufficient toning agent will not produce sufficient change in the appearance of the image. Excessive amounts will dilute the image, and in some instances may prevent its formation. The presence of more than trace amounts of oxalic acid, for example, is found to prevent the formation of a visible image, whereas in the smaller amounts this toner causes effective darkening of the silver image areas. In general, the optimum amount will be found to be within the approximate proportions of one to ten percent based on the total weight of reactants and binder, as exemplified by the proportions of the specific examples.

Stability of the heat-sensitive composition is influenced adversely by the presence of water. It is therefore desirable to employ resinous binders which are substantially non-absorptive of moisture and offer maximum protection to the reactive components. Polystyrene resins are particularly effective. Less moisture-resistant binders may frequently be improved by the incorporation of small amounts of waxes or other moisture-proofing materials. Moisture-resistant surface coatings are also helpful.

Within the limitations imposed by the requirements of water and moisture resistance, transparency or opacity, permanence, handleability, light stability, operating temperatures, flexibility, etc., as hereinbefore indicated, it will be apparent that a considerable number of specifically different but fully equivalent film-forming binder materials, pigments and fillers, solvents and diluents, resins, plasticizers, fibrous and non-fibrous supporting webs, and various other auxiliary materials may equally well be employed.

Specifically, the map overlay tracing paper has been replaced by other fibrous and non-fibrous sheet materials such as "Monarco" paper and cellophane, and the coatings are found to be operable also when applied to wood, leather, fabrics, and many other substrates, or as self-supporting films. Ethyl cellulose is useful as a film-forming binder material although somewhat less moisture-resistant than polystyrene resin. Where plasticizers for the resinous binder are found to be desirable, phosphates and phthalates, having low water absorption properties, are superior to glycols and their esters. Zinc sulfide, titanium dioxide, diatomaceous earth, and numerous other pigments and fillers are useful in conjunction with the protective surface coating; metal powders and carbon black, for example, may be used in substantial proportions in back-printing copying-papers, and have been found useful in very small proportions in the surface coatings of front-printing papers, e.g., to provide somewhat higher sheet temperatures. Pigments and other particulate materials such as glass cullet or spherides may also be added to the heat-sensitive coating for special purposes where desired.

Silver behenate, and silver stearate to a somewhat lesser extent, is substantially insoluble in ethyl acetate and in heptane-acetone mixtures at normal room temperatures and is mixed with the other components of the heat-sensitive coating in the form of a dispersion or suspension in such solvents or mixtures, as indicated in the examples. Most salts having a relatively high degree of solubility in a particular vehicle have been found to react with the reducing agent to an extent sufficient to cause undesirable darkening of the liquid mixture and of the dried coating. In such cases it is ordinarily possible to select for the vehicle a volatile liquid in which either the oxidizing agent, or the reducing agent, or both are substantially completely insoluble. In other instances the components may be dissolved together in a mutual solvent held at reduced temperature, and then coated and dried without heating, to provide useful heat-sensitive copying-paper.

What I claim is:

1. A heat-sensitive copy-sheet useful in providing dense dark-colored image areas of pleasing appearance in the thermographic copying of differentially radiation-absorptive graphic originals, said copy-sheet including a visibly heat-sensitive layer comprising: a normally solid organic acid salt of a noble metal; a cyclic organic reducing agent for the noble metal ions, which reducing agent has an active hydrogen atom attached to an atom, selected from the class of oxygen, nitrogen and carbon atoms, directly attached to an atom of the cyclic ring; and, as a third significant component and in significant small amount within the approximate proportions of one to ten percent of the composition, an organic carboxylic acid toner compound having a carboxyl group and at least one other group, from the clas consisting of carboxyl and hydroxyl groups, in position to permit condensation reaction with said carboxyl group and with formation of a heterocyclic ring structure having 5–6 members in said ring.

2. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of a

silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount within the approximate proportions of 1 to 10 percent of the weight of said composition, of malic acid.

3. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of a silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image improving toning agent, a significant small amount, within the approximate proportions of 1 to 10 percent of the weight of said composition, of phthalic acid.

4. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of a silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image improving toning agent, a significant small amount, within the approximate proportions of 1 to 10 percent of the weight of said composition, of oxalic acid.

5. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of a silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image improving toning agent, a significant small amount, within the approximate proportions of 1 to 10 percent of the weight of said composition, of 2-hydroxy-1-naphthoic acid.

6. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of a silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount, within the approximate proportions of 1 to 10 percent of the weight of said composition, of anthranilic acid as a third significant component.

7. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount within the approximate proportions of 1 to 10 percent of the weight of said composition of maleic acid.

8. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount within the approximate proportions of 1 to 10 percent of the weight of said composition of succinic acid.

9. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount within the approximate proportions of 1 to 10 percent of the weight of said composition of gluconic acid.

10. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount within the approximate proportions of 1 to 10 percent of the weight of said composition of 2-hydroxycinnamic acid.

11. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount within the approximate proportions of 1 to 10 percent of the weight of said composition of glycolic acid.

12. A heat-sensitive copy-paper including a visibly heat-sensitive layer comprising a heat-sensitive mixture of silver salt of an organic acid and an organic reducing agent for the silver ions and, as an image-improving toning agent, a significant small amount within the approximate proportions of 1 to 10 percent of the weight of said composition of gamma-hydroxybutyric acid.

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