

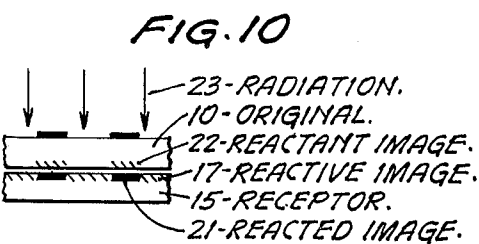
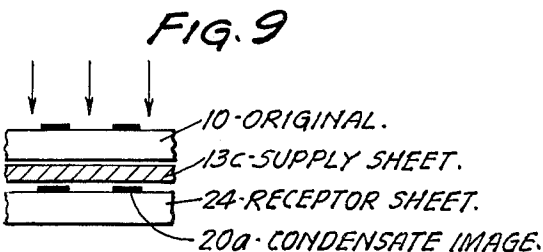
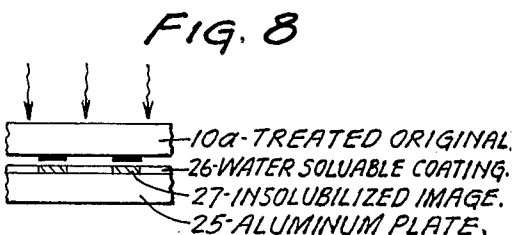
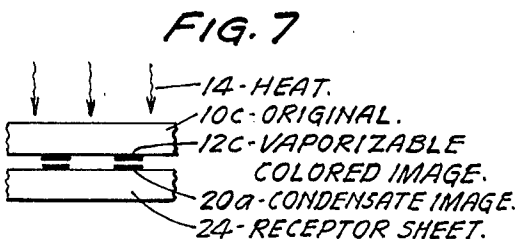
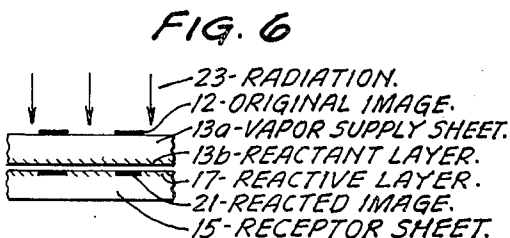
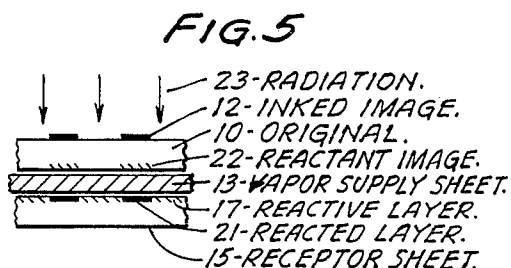
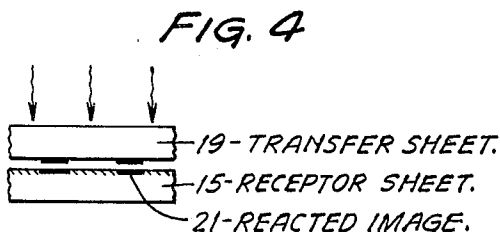
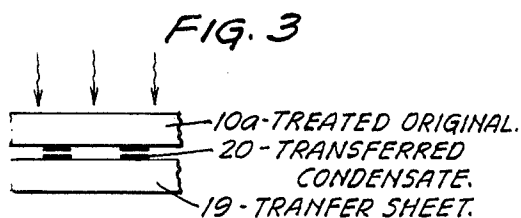
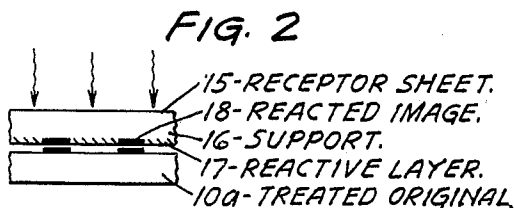
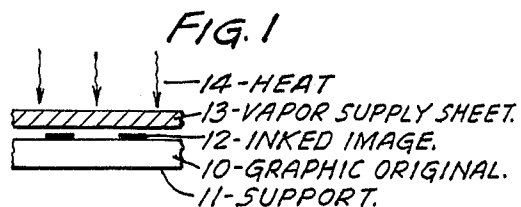
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3,481,760

THERMOGRAPHIC COPYING SHEETS

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3,481,760

## THERMOGRAPHIC COPYING SHEETS

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4 Claims

### ABSTRACT OF THE DISCLOSURE

Volatilizable image-forming material is transferred at predetermined image areas from a source sheet to a receptor sheet by heating and condensation to produce a visible image.

This is a continuation of our co-pending application Ser. No. 359,246, filed Apr. 13, 1964, now abandoned, as a continuation-in-part of Ser. No. 843,161, filed Sept. 29, 1959, and now abandoned.

This invention relates to the thermally induced reproduction of graphic originals and to materials employed therein, and is particularly directed to novel procedures involving heat-induced transfer of image forming components, and to novel products employed therein.

Chemically reactive heat-sensitive copy-papers and thermographic reproduction processes in which such papers are employed have become widely known, for example in the reproduction of typewritten correspondence and other office records. In one commercial application, the copy-paper is placed in heat-conductive pressure-contact with the original which is then briefly intensely irradiated, e.g. with radiation rich in infra-red. Heating occurs at the radiation-absorptive image areas of the original, accompanied by a visible reaction at corresponding areas of the copy-paper. A direct or positive copy is produced immediately, without further chemical or other processing.

Physically heat-sensitive copy-papers useful in thermographic copying are also known. One form consists of a dark-colored paper or film base provided with an opaque surface coating of a transparent fusible material in particulate form. Fusion of the particles at the heated areas renders the coating permanently transparent, permitting the dark background to be seen. Another form depends on flow of the fused and liquefied coating, e.g. into the absorbent carrier web, to provide a visible change at the heated area. As with the chemical paper, the applied heat-pattern causes the formation of a reproduction of the graphic original without further chemical or other processing.

The present invention likewise makes possible the formation of reproductions of graphic originals in a single-step simplified process requiring no subsequent chemical or other treatment. The resultant copy is not susceptible to further coloration on subsequent heating, so that background darkening is avoided. Simplified procedure for providing the necessary temperature are made possible. Other distinctions and advantages will be made apparent hereinafter.

The invention broadly involves the transfer of a normally stably solid image-forming material in vapor form from a supply sheet to a suitable receptor surface in a pattern determined by the graphic representations of the original. In one form of the invention the image-forming material is transferred to a receptor sheet containing a color-forming reactant for said material, the two then reacting to form visibly distinct image areas. Where the vaporizable material is itself strongly colored, no reactant is required on the receptor sheet. The va-

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porizable material may be incorporated in the ink with which the graphic original is printed, either prior to or after printing; or it may be supplied as a component of the printed sheet or of a separate vapor supply sheet.

The invention will now be further described in connection with the accompanying drawing in which the several figures indicate in partial cross-section various combinations and composites of components as employed in producing copies or reproductions of graphic originals by the various processes indicated.

In FIGURE 1 there is provided a graphic original 10 comprising a support 11 on which has been printed or otherwise deposited inked image areas 12. A page of a book printed with an oil base carbon ink on a white paper is one example of such an original. Another example is a lithographic printing plate, having oil-receptive image areas and water-receptive background areas on a treated aluminum panel. Typically, the image areas may include a hardened gelatin substrate and a resinous or oleaginous oil-receptive surface coating.

Against the printed surface of the original 10 there is placed a vapor supply sheet 13, one form of which consists of a thin porous paper partially impregnated with a vaporizable phenolic compound, e.g. pyrogallol. Heat is applied to the composite, as indicated by the wavy arrows 14, typically by passing the composite through a heated mangle or ironing machine. Vapors from the vapor supply sheet 13 are condensed, presumably by absorption, on the inked image areas of the printed original. The thus treated original is identified in FIGURES 2 and 3 as treated original 10a and itself serves as a vapor supply sheet in subsequent processing.

It will be understood that the spacing between sheets indicated in the several figures of the drawing is for purposes of clarification and that in practice the sheets are in surface-to-surface contact.

The vapor supply sheet 13 is next replaced by a receptor sheet 15, as shown in FIGURE 2, and the new composite is again heated, for example by passing through the heated mangle. The receptor sheet 15 comprises a support 16 having a reactive layer 17 within or on the surface thereof. Where pyrogallol is employed as the vaporizable material, the layer 17 may suitably comprise ferric stearate.

When the receptor 15 is removed from the surface of the treated original 10a, it is found to have a visible image pattern corresponding to the image areas of the graphic original and indicated as reacted image areas 18 in FIGURE 2. The reproduction appears as a mirror image as viewed from the treated side of the sheet 15, i.e. from the surface previously in contact with the image area of the original. Alternatively, the image may be viewed as a direct image from the reverse side of the receptor 15 when the support member 16 is transparent.

In FIGURE 3 the treated original 10a, prepared as described in connection with FIGURE 1, is placed in contact with an intermediate transfer sheet 19 and the composite is again heated. During this process the reactive material, which was originally transferred from the vapor supply sheet 13 to the inked areas of the graphic original 10 as described in connection with FIGURE 1 is again vaporized and transferred to the transfer sheet 19, where it is retained in condensed or absorbed form as indicated at 20. The transfer sheet 19 is then removed from the graphic original. The image areas 20 are clearly visible when a strongly colored vaporizable component is used, and form a visible direct positive or right-reading copy of the original as viewed through the transfer sheet 19, which for this purpose must therefore be transparent.

Where a reactant vaporizable material is employed, the imaged surface is next placed in contiguity with the

treated surface of a co-reactive receptor sheet 15 as illustrated in FIGURE 4, and the composite is heated as before, causing re-transfer of vaporized reactant from the transfer sheet 19 to the receptor 15, with formation of reacted visible image areas 21 corresponding directly to the image areas of the graphic original 10. In the latter procedure the transfer sheet need not be transparent and the mirror image formed thereon need not be a visible image. The same procedure is applicable with non-reactive, directly visible vaporizable image-forming material except that in this instance a non-reactive receptor sheet may be employed.

Where the graphic original is as described in connection with the process of FIGURE 1, and the vapor supply sheet 13 contains pyrogallol, also as described under FIGURE 1, the transfer sheet 19 may conveniently be a waxed or paraffined paper, and the receptor sheet 15 will then suitably comprise a normally stable layer or coating of ferric stearate.

The procedure indicated in FIGURE 5 employs radiation with high intensity light rays, preferably rich in infrared, in place of direct heating. As shown in the figure, the graphic original 10 having printed image areas 12 is placed with its unprinted surface against the vapor supply sheet 13 which is in contact with the reactive layer 17 of the receptor sheet 15. The image and background areas of the surface of the original 10 are differentially absorptive of radiation 23, which as previously indicated may be largely infrared radiation. The composite is briefly subjected to intense irradiation, resulting in a preferential heating effect at the printed image areas, causing the transfer of vaporized reactant from the supply sheet 13 to the co-reactive treated surface layer 17 of the receptor sheet 15 and resulting in formation of reacted image areas 21 corresponding directly with the printed image areas 12 of the original. Some of the reactant is simultaneously transferred to the unprinted surface of the original where it condenses to form reactant image areas 22 and from whence it may subsequently be transferred to form visible image areas 21 on a receptor sheet 17 as shown in FIGURE 10.

Apparatus suitable for momentarily intensely irradiating the composite as just described may conveniently consist of a line source of light including a tubular lamp having a linear filament and mounted within a focused reflective housing for progressive exposure of the printed surface of the original, all as described in Miller United States Patent No. 2,740,895. Another suitable form of apparatus is described in Kuhrmeyer et al. United States Patent No. 2,891,165.

In a simplified version of the foregoing, the vapor supply sheet and graphic original are combined in a single sheet material, e.g. by surface-treating the rear or unprinted surface of the original with pyrogallol or other vaporizable component, or by printing or otherwise applying an original graphic representation to a previously impregnated vapor supply sheet. The procedure is illustrated in FIGURE 6. The radiation-absorptive inked image areas 12 are inscribed on the vapor supply sheet 13a, the opposite surface of which carries a layer 13b of volatilizable normally solid reactant. The sheet is placed against the reactive surface 17 of a receptor sheet 15 and is briefly exposed to intense radiation 23, causing vaporization and transfer of reactant and formation of visible image areas 21. The procedure is repeated with additional receptor sheets 15 in making a number of copies.

FIGURE 7 indicates a modification in which the image areas 12c of the graphic original 10c are initially formed of an ink which contains a vaporizable strongly colored image-forming material. The sheet is placed with the inked surface against a receptor sheet 24. The application of heat, as with a heated mangle or flatiron, causes transfer of the colored material in vapor form from the inked areas to the corresponding areas of the surface of the copy-paper, and results in the formation of image areas

20a. In this instance the resulting reproduction will occur as a mirror image of the original when viewed from the treated surface, but may be viewed as a direct (right-reading) reproduction in the case of a transparent receptor sheet, or may be produced as a direct reproduction on an opaque receptor sheet by a two-step transfer procedure as previously described.

The use of inter-reactive volatilizable component and receptor sheet will be seen to make possible the selection of a wide variety of volatilizable components which may be either intensely colored or colorless. Reactants may be selected so as to provide intensely colored and permanent image areas. Effective images may be produced with extremely slight amounts of vaporizable reactant, so that large numbers of copies may be produced from a single treated original. Simple and readily available sources of heat may be effectively employed. The receptor sheet coating may be applied to paper, film, fabric, wood or various other surfaces, for reproduction thereon of handwritten or printed intelligence, engineering drawings or designs, etc.

Ferric stearate is a preferred compound for use in the reactive receptor sheet or copy-paper in conjunction with volatilizable phenolic image-forming materials such as pyrogallol. A suitable form of ferric stearate is prepared as follows: 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 water-insoluble 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. The compound is dispersed in a solution of nitrocellulose in a mixture of toluene and acetone, the amount of nitrocellulose being one-fourth the amount of ferric stearate by weight, by grinding in a ball mill until a smooth coatable dispersion is obtained. The dispersion is applied to the surface of the paper by any convenient coating procedure, for example with a knife coater, and dried. The coated sheet is stable towards heat and light, at least to substantially the same extent as the untreated paper.

Nitrocellulose is a preferred inert, heat-resistant binder, but other binder materials, e.g. ethylcellulose, polyvinyl acetate, polystyrene, and polyvinyl butyral are also useful. Relative amounts of binder and reactants may be widely varied. In some instances the binder may be omitted and the reactant retained within the copy-sheet, being bonded and protected by the paper fibers. With larger amounts of binder it is found desirable to employ such combinations of volatile solvents as will produce a porous "blushed" binder film, thereby providing for easy access of the reactant vapor to the co-reactive ferric stearate or other reactant material.

Pyrogallol and ferric stearate employed as hereinabove described produce intensely colored high contrast image areas on a substantially white background, with desirably high reaction speed, and at readily available temperatures of the order of about 80–150° C. Ferric soaps of other long-chain fatty acids are equally effective. For best results, these materials should be water-insoluble, and will ordinarily be found to have a melting point within the approximate range of 70–120° C. Other vaporizable, normally stably solid phenolic reactant materials may similarly be substituted for the pyrogallol; catechol is one such compound.

The phenolic-ferric combinations will normally be found to provide a deep black or blue-black image, and therefore are highly effective for the copying of typewritten or printed originals having a black image on a white background. For certain purposes it may be desirable to provide various colors of images; and appropriate combinations of reactants are available for such purposes. For example, nickel salts, e.g. nickel acetate, in the copy-

paper may be reacted at image areas with vapors from a vapor supply sheet containing dimethylglyoxime or thiourea to produce respectively red or black image areas. Cobalt acetate copy-paper treated with vapors from ammonium thiocyanate produces a blue image; ammonium molybdate and 8-hydroxyquinoline provide a yellow image; methyl orange and vapors from heated oxalic acid in image areas provide an orange-red image; and a copy-paper containing a colorless reaction product of malachite green and octadecyl amine when subjected to vapors from a heated oxalic acid-containing image provides a green image. Particularly effective results have also been attained using protocatechuic acid in an image vapor supply sheet and silver behenate, or a mixture of silver behenate and behenic acid, in the co-reactive receptor sheet.

In some of the foregoing, for example the pyrogallol acid and ferric stearate combination, the volatilizable reactant is transferred unchanged on heating and is directly reactive with the co-reactant in the copy-paper, at least at suitably elevated temperatures. In other cases, such for example as the combinations including oxalic acid, gallic acid or thiourea, the volatilizable component may result from the heat decomposition of the material initially present in the ink or in the vapor supply sheet. In all instances, however, the one reactant is transferred in vapor form to the copy-sheet where the visible image is then produced by condensation and co-reaction as indicated.

In a further modification, illustrated in FIGURE 8, an emulsion of ferric stearate was prepared in a solution of gelatin in water and was coated on an aluminum plate 25, and the coating dried to form a water-soluble layer 26. A printed page in which the printed areas were composed of a pigment and a non-volatile oily binder, viz ordinary printing ink, was sensitized with pyrogallol vapor by heating in contact with a vapor supply sheet as described in connection with FIGURE 1. The thus treated original 10a was then placed against the dry gelatin surface 26 and again heated. The pyrogallol vapor from the image areas entered the gelatin coating and reacted with the ferric stearate, producing water-soluble materials which then reacted with the gelatin to provide a comparatively water-insoluble reaction product. The remaining areas of the gelatin coating were then removed by washing with water, leaving the insoluble portions which corresponded with the image portions of the printed graphic original. The plate could then be processed as a lithographic plate for direct printing on untreated paper.

In FIGURE 9 the irradiation of graphic original 10 causes transfer of strongly colored vaporizable material from vapor supply sheet 13c to untreated receptor sheet 24, which may conveniently be a white bond paper, to produce image-duplicating areas 20a of transferred condensate and form a right-reading reproduction of the original. Quinalizarine green dye is one example of a strongly colored, vaporizable, normally stably solid image-forming material suitable for this use. The process is further simplified and improved by inscribing the graphic intelligence directly on the vapor supply sheet.

The use of inherently readily visible vaporizable material as described hereinbefore in connection with FIGURE 3, and more particularly in connection with FIGURE 9, permits the formation of reproductions of a graphic original on untreated receptor sheets or surfaces and without chemical reaction. Useful receptor sheets include untreated paper, fabric, nonwoven fibrous webs, polymeric films, and metal foil. The receptor sheet may be treated or coated, as with pigments, fillers, binders, etc., to provide a background of increased contrast, or to assist in retaining the colored image-forming material, or for other purposes. The copy may also be treated or coated, e.g. with small amounts of solvents or fixatives or the like to aid in retaining the colored material. No chemical reactant is necessary, however, to produce the desired visible image; and background areas therefore remain non-reactive.

In addition to quinalizarine green, the following dyes have been found particularly effective in producing reproductions of typewritten originals on untreated paper receptor sheets by the method described in connection with FIGURE 9; alizarine Irisole N; chrysoidine R; Du Pont Oil Blue A; Rhodamine B Extra; Ethyl Violet AX; Auramine Base; Du Pont Oil Orange; Du Pont Oil Yellow; Du Pont Oil Brown N; Du Pont Oil Red; Latyl Violet BN Crude; Acetamine Scarlet B; Methyl Violet 2B Base Conc.; National Indigo NACCO Pdr.; Azosol Brilliant Yellow 8 GF; Sudan Red BBA; Sudan Green 4B; and Victoria Green Base. Various mixtures and combinations of these and other suitable dyes may also be used. Reactive and non-reactive vaporizable components may likewise be employed in admixture if desired.

The dyestuff has been effectively applied to a paper base by simply swabbing the dry powder over the slightly porous surface with a cotton swab, to produce either an intermediate transfer sheet or a coated original. A preferred method involves coating one entire surface of a suitable paper with a solution of the dye in a volatile solvent, since improved penetration and uniformity are thereby attained. Typically, Du Pont Oil Orange is dissolved in acetone to a 10% concentration and is uniformly coated on the soft unglazed surface of thin "Yankee finish" paper, which is then useful either as an intermediate vapor supply sheet or as a vapor-supplying base on which to print or type the graphic original.

The following specific illustrative examples will serve further to describe the invention, which however is not to be construed as limited thereto.

#### EXAMPLE 1

A used lithographic plate having inked oleophilic image areas on a hydrophilic treated aluminum base is placed in contact with a dry sheet of paper which has been uniformly lightly coated with pyrogallol acid. The composite is passed through a heated mangle. The paper sheet is removed and replaced with a paper receptor sheet having a thin surface coating of ferric stearate, and the composite again passed through the mangle. A mirror image of the inked image areas of the lithographic plate is visible on the coated surface and may be seen as a direct or right-reading image from the reverse surface of the semi-transparent receptor sheet.

The same results are obtained on substituting a page of a book printed on dense white paper for the lithographic plate.

#### EXAMPLE 2

The lithographic plate of Example 1 after being heated in contact with the pyrogallol acid paper is again heated in the mangle in contact with waxed paper, a heavily paraffined paper commonly used as a waterproof wrapping material. The waxed paper is then placed against the ferric stearate coated paper and again heated. A right-reading reproduction of the original is obtained on the receptor sheet.

#### EXAMPLE 3

A sheet of thin "Mylar" polyester film is coated at 0.6 gram per square foot with a layer of a mixture of silver behenate and an excess of protocatechuic acid, together with methyl methacrylate binder, applied as a dispersion in acetone. The sheet is placed against a printed original which is then briefly irradiated with intense radiant energy rich in infra-red, forming a reproduction of the black image areas in the heat-sensitive coating. The process is well known as "front-printing."

The copy is then placed with its coated surface in contact with a receptor sheet prepared by coating white paper with silver behenate in a polymeric binder. Pigments such as zinc oxide, fusible resins such as "Piccolyte S-135" polyterpene resin, and other additives are desirably included but are not essential in the receptor-sheet coating. The copy is again irradiated as for thermographic copying. Controlled brief intense irradiation produces on the

receptor sheet a "latent image" which is thereafter made visible by heating in an oven or over a hot-plate; there is produced a direct reproduction of the printed original. Somewhat more drastic irradiation causes immediate formation of the visible image on the receptor sheet while still in contact with the intermediate or vapor-supply sheet.

#### EXAMPLE 4

Thin porous paper is sparingly coated on both sides with a solution of about 20 parts of methyl gallate and one part of polyvinyl acetate binder in a solvent mixture of methylisobutylketone and alcohol. Corn starch in amount by weight equal to the methyl gallate is desirably dispersed in the coating solution to overcome any tendency of the coating to offset, but is not essential. The dry sheet is first printed, e.g. with a typewriter, from movable type, or in handwriting, using an ink which is infra-red-absorptive. The resulting graphic original, which is also a vapor supply sheet, is placed against a co-reactive receptor sheet and subjected to the thermographic copying procedure, as described under Example 3. Up to 50 or more copies of the same original are prepared in this way.

#### EXAMPLE 5

Quinalizarine green base is added to a volatile liquid vehicle in amount sufficient to form a strongly colored ink which is then used to prepare a handwritten graphic original on white paper. The dried sheet is placed with the printed surface in contact with a blank sheet of paper and the composite passed through a mangle, the back surface of the original contacting the heated shoe of the machine. A mirror image of the inked areas is obtained on the receptor sheet.

#### EXAMPLE 6

A sheet of paper is coated over a portion of one surface with a one percent solution in acetone of Du Pont Oil Orange, and over the remainder of the same surface with a similar solution of Du Pont Oil Blue A. A message is printed with a typewriter on the uncoated surface. The resulting original is placed with its coated surface in contact with an untreated sheet of paper, and subjected to thermographic irradiation. A copy of the message is obtained, but in colors corresponding to the location of the dye coatings.

#### EXAMPLE 7

Thin paper is saturated with a dilute solution of Du Pont Oil Orange and dried. The resulting supply sheet is placed between an untreated paper receptor sheet and the back surface of a thin printed original. The printed surface is briefly intensely irradiated with light rich in infra-red, producing a copy on the receptor sheet. Upwards of 75-100 copies are produced from the same supply sheet by repeating the process.

#### EXAMPLE 8

Paper is smoothly coated with a composition containing five parts Oil Blue A, ten parts ethyl cellulose, and five parts silica gel in acetone. The sheet is dried and placed with the coated surface in contact with a printed page, and the composite is held under moderate tension against a smooth metal surface heated to a temperature of 175° C. for five seconds. The coated sheet is replaced by a sheet of bond paper and the heating is repeated. A distinct mirror image copy of the printed characters is reproduced in blue on the paper.

#### EXAMPLE 9

A page of a magazine, having black letters printed in varnish base ink on a glossy white paper, is dipped in a dilute solution of 8-hydroxyquinoline in acetone, drained, dried, placed on a ferric stearate receptor sheet, and ironed with a heated flat-iron. A colored reproduction of the inked areas is obtained as a reverse or mirror image on the receptor sheet. Using the same procedure but with

the 8-hydroxyquinoline applied from dilute solution in carbon tetrachloride or toluene, a negative image is obtained, the colored areas of the copy corresponding to the unprinted background areas of the original.

Correspondingly, a dilute solution of "Autol Brilliant Red BND" dye in toluene applied to a printed original results in the formation of a reversed negative image on ironing the treated original against a sheet of white paper.

#### EXAMPLE 10

Thin paper is supplied on one surface with a thin coating of isopropyl catechol and a polymeric binder. The resulting vapor supply sheet is placed with its coated surface in contact with a sheet of paper which has previously been printed on the opposite surface by typewriting, and the printed surface is briefly intensely irradiated as in thermographic reproduction procedures. The coated supply sheet is then replaced with a receptor sheet having a surface layer of silver behenate and polymeric binder, and the composite is again irradiated from the printed surface. The printed sheet now serves as a vapor source or supply sheet, the vapor previously condensed therein opposite the irradiated print areas being transferred to the receptor sheet and there condensing with the silver soap to provide corresponding visible image areas.

In place of the untreated printed original there may be employed an ink-receptive paper or other thin carrier web having on the reverse surface a thin waxy, resinous or other oleophilic coating which, like the paraffin coating of the transfer sheet of Example 2, serves as a temporary reservoir for the phenolic or other vaporizable image-forming material.

It will be appreciated that the vaporizable image-forming materials employed in the practice of this invention, whether of the reactive or non-reactive type, should be essentially non-vaporizing at normal room and storage conditions, as indicated by the description of these materials as "normally stably solid." At the operating temperatures employed, vaporization occurs at a rate sufficient to produce the desired effect within the limited time available in the procedures described. In further illustration of the vaporizability of compounds useful in the practice of the invention, it is noted that usefully vaporizable materials will rapidly provide sufficient vapor to actuate a test sheet when heated to a vaporizing temperature not higher than about 160° C. For example, a small quantity of Du Pont Oil Orange in an aluminum weighing-dish about 3/4 inch deep covered with a piece of white filter paper produced an orange-red stain on the paper when the dish was placed for a few minutes on a metal test panel heated to 100° C.

Where the appended claims call for condensing the image-forming vapor at the receptor surface, it is to be understood that the term is employed in its broad sense, to encompass both chemical reaction resulting in a new compound, and physical conversion to a denser form of the same compound.

There have thus been provided novel products and processes for the reproduction of printed, typed or other graphic originals involving the heat-induced transfer of normally stably solid vaporizable image-forming material in vapor form to a receptor sheet in a pattern determined by said original. In one embodiment, the invention involves the transferring of a reactant vaporizable material in a pattern corresponding to the pattern of the graphic original, and the subsequent reaction of the reactant material with a treated or coated reactive receptor copy-sheet with which the vapor material is visibly reactive. In another embodiment the vaporizable material is itself image-forming, so that pre-treatment of the receptor sheet is rendered unnecessary. In all cases there results a visible pattern on the receptor sheet which is identical, either as a direct copy or as a mirror image, with the pattern of the graphic original. In addition to its application in the copying of graphic originals having radiation-absorptive

image areas, the process is applicable to the reproduction of originals prepared with special inks or the like containing vaporizable coloring agents or reactants, as well as to the reproduction of originals printed with resinous, oily or other image-forming ink residues and capable of selectively accepting and at least temporarily retaining the vaporizable material.

What is claimed is as follows:

1. For use in the thermographic copying of differentially radiation-absorptive graphic originals, in combination as a two-ply composite, a receptor copy-sheet having a surface coating comprising a fusible non-volatile reactant material in a porous blushed lacquer binder, and a vapor source sheet, including a co-reactant for said reactant material which is volatile at 70-120° C., in contact with said coating.

2. The combination of claim 1 wherein the fusible non-volatile reactant material is a water-insoluble ferric soap melting at 70-120° C. and the volatile co-reactant is a normally stably solid phenol.

3. The combination of claim 2 wherein the ferric soap

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is ferric stearate and the phenol is pyrogallol or catechol.

4. The combination of claim 1 wherein the amount by weight of said lacquer binder is greater than one-fourth the amount of said reactant material.

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