

Sept. 17, 1963

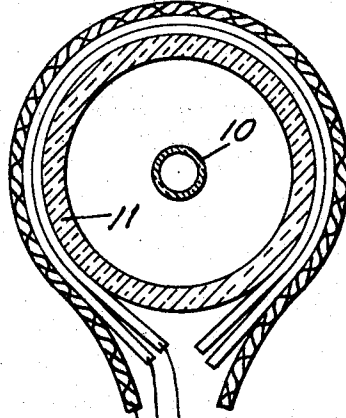
E. W. GRIESHABER

3,103,881

METHOD OF COPYING

Filed Oct. 20, 1958

FIG. 1



12-COPY SHEET
13-ORIGINAL
14-PRESSURE COVER

FIG. 2

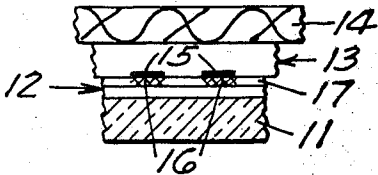


FIG. 5

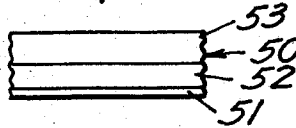
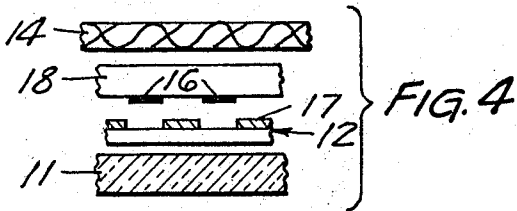


FIG. 3



FIG. 6



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3,103,881

METHOD OF COPYING

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3 Claims. (Cl. 101—149.2)

This invention relates to the thermographic reproduction of graphic originals. In one significant aspect it provides for the visible reproduction on untreated paper or other receptor surfaces of printed or other graphic originals, either black-and-white or colored, by methods involving brief intense irradiation of the graphic subject-matter. In another aspect the invention provides for the preparation, by simple irradiation, of intermediate reproductions of graphic originals, from which duplicates may subsequently be produced by known techniques. The invention also provides novel sheet materials in the form of heat-sensitive copy-sheets having application in the attainment of these and other useful and advantageous results.

The reproduction of typewritten or printed documents or other graphic originals by thermographic methods has recently become of widespread commercial importance. One method involves subjecting the printed surface to brief intense irradiation, for example from a heated tungsten filament, through a transparent heat-sensitive copy-sheet held in heat-conductive contact against said surface. The resulting selective heating effect at the inked areas causes a visible change to occur in corresponding areas of the heat-sensitive sheet, thus producing the desired reproduction. The process is ordinarily carried out with radiation high in infra-red, and is most effective with black-and-white originals, the carbon of the ink being highly absorptive of infra-red. Colored inks are absorptive of other radiation, and sources are known which provide adequate intensity of such radiation to produce the desired selective heating effect with colored image areas also. It has been found, however, that many heat-sensitive copy-sheets which are fully effective with black-and-white originals do not produce effective reproductions of images printed in colored inks. Again, the unchanged areas of the exposed copy-sheet remain sensitive to heat and hence a copy produced on such sheet may be over-printed or otherwise altered. Thus, although thermographic copying procedures offer rapid and convenient reproduction of graphic originals, and avoid such prior art requirements as protection from light-exposure, or solution or fume image-development, and hence have become commercially widely adopted, they have not thus far been found fully effective for certain specific applications.

The present invention offers means for enlarging the scope of thermographic copying in the respects hereinbefore indicated as well as in other ways, as will hereinafter become apparent or will be specifically pointed out. Clear and sharp reproduction of graphic originals having colored as well as black image areas is provided. The reproduction may be obtained on untreated support members such as paper, glass, plastics, fabric, wood, metal, and various other materials. The reproductions may in some instances be further employed in the production of additional duplicates.

These and other advantages are attained, in accordance with the principles of this invention, by a two-stage irradiation procedure in which a thermographic reproduction of the graphic original is first produced on an intermediate heat-sensitive copy-sheet by an initial irradiation, and the visibly altered image-forming portions thus provided are then transferred to a white paper or other receptor sheet by a further irradiation, preferably at a higher intensity.

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Exemplary materials employed and procedural details followed will now be further set forth in terms of specific illustrative but non-limitative examples.

Example 1

An intermediate heat-sensitive copy-sheet is first prepared, using as a flexible backing or support web a one-mil oriented polyester film, such for example as "Mylar" polyester film. The web is coated on one surface with a three-mil uniform layer of a liquid coating composition, and dried at room temperature. The formulation of the coating composition is as follows, proportions being given in parts by weight:

Ferric stearate	192
Spiroindane	20
Ethyl cellulose	91
Triphenyl phosphate	29
Acetone	1527

The ferric stearate is ground, with a portion of the ethyl cellulose and acetone, in a ball mill until a smooth dispersion is obtained. Typically, a 200 gram charge is ground for 72 hours in a one pint capacity mill two-thirds filled with glass balls. The ferric stearate is thereby reduced to a minimum particle size, no further reduction observable on microscopic examination being obtained on further grinding.

The spiroindane employed is a polyhydroxy phenol and is a polymeric reaction product of acetone and pyrogallol formed by reaction at approximately room temperature in the presence of phosphorus oxychloride catalyst, having a moderately high molecular weight of about 900-1600, melting within approximately the range 220-230° C., and completely soluble in acetone. It is combined with the triphenyl phosphate and the remaining ethyl cellulose and acetone to form a homogeneous solution which is then mixed with the ferric stearate dispersion.

The coated film is light buff in color and smooth, shiny and opalescent in appearance. When heated briefly, for example to 100° C., as by brief contact with a heated metal rod or in the thermographic copying process hereinbefore noted, the heated area immediately converts to a dense opaque blue-black.

A reproduction of a graphic original such as a printed page of a book, newspaper, or other black-and-white printed page, is next produced on the coated film. For this purpose there is preferably employed a thermographic printing apparatus having as the support for the original and copy-sheet a transparent glass cylinder with an outside diameter of 1½ inches. A gas flash tube with a uniform internal diameter of 2 mm. is supported within and along the axis of said tube. The flash tube is filled with xenon under a pressure of 600 mm. Hg and contains two electrodes spaced 10 inches apart and enclosed in suitable terminal bulbs. The lamp is actuated from a capacitor having a capacity of 100 mfd. which may be charged at any desired voltage. Means for initiating the discharge through the lamp are also provided. Other specific dimensions are equally applicable, but those given here have proven useful in practice and further description will therefore for convenience be in terms of such lamp system.

The heat-sensitive coated film is first wrapped around the glass cylinder with the polyester surface toward the glass. The printed original is then placed over the film and with the printed surface, of which a copy is desired, in contact with the outwardly positioned sensitive coating. A further wrapping of conformable film, fabric or the like may be employed to hold the original and copy-paper together under pressure. The capacitor is then charged to about 2300 volts and discharged through the flash tube,

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producing an intense brief irradiation of the composite of paper and film. The resulting heating of inked areas of the graphic original produces heating and darkening of corresponding portions of the heat-sensitive coating. The background areas remain unchanged.

The printed page or other graphic original is next removed and replaced by a sheet of plain white paper, and the irradiation is repeated, in this case at a voltage of about 2800. The previously unaffected background areas of the copy-paper are now found to be drastically darkened but to remain affixed to the support film. The previously darkened image portions of the heat-sensitive layer are found at the same time to be substantially completely transferred to the white paper, forming a permanent reproduction of the graphic original on the paper and a corresponding negative transparency in the copy-sheet.

Formation of the image areas in the heat-sensitive surface may be accomplished in the apparatus described at light intensities and exposure times obtained at voltages in the approximate range of 2000-3000 volts, and transfer of image likewise may be accomplished within the range of about 2500-3500 volts. However it is necessary that the irradiation employed for image transfer be at least as intense as that used in making the intermediate copy, if effective transfer is to be attained.

The amount of phenol (spiroindane) employed in the coating composition of Example 1 is much less than the amount required for optimum darkening of the composition and which would normally be employed in heat-sensitive copy-papers using these reactants, being only about 35-40% of said optimum amount. Surprisingly, it is found that this decrease in phenol component results in an increase rather than a decrease in the optical density of the resulting copy when transferred to the white paper. This result is due to the substantially complete transfer of the coating containing the reduced amount of phenol, as compared to the limited transfer occurring at the higher proportions.

Effective transfer of the image portions is likewise improved by selection of low molecular weight ethyl cellulose or other binder, care being taken to avoid the stickiness encountered with certain classes of polymeric binders at the very low molecular weight levels.

The degree of milling of the ferric stearate is not particularly critical for copy-papers designed for reproduction from black-on-white originals. In the foregoing example, effective reproductions of such originals have been produced with compositions prepared with only 6-12 hours of grinding in the ball mill. The reproduction of originals printed in colored inks requires somewhat higher intensity radiation, and under these conditions it is found that even slight surface roughness may result in blotchiness or irregular darkening of background areas. It is therefore preferred to grind or otherwise reduce the particle size of the ferric soap or equivalent component to minimum size.

Another means of improving the ability of the copy-paper to form reproductions of colored originals is demonstrated in the following example.

Example 2

	Parts by weight
Ferric stearate.....	100
Ethyl cellulose.....	61
Tertiary-butyl catechol.....	15
Triphenyl phosphate.....	12
Acetone.....	1064

A smooth dispersion is formed as described in connection with Example 1, the soap component being ground to minimum particle size. The mixture is coated at 3 mils on a lightly plasticized 1½ mil polyvinyl chloride film and dried at room temperature. The smooth glossy coating is opalescent. It is next coated with a minimum transparentizing coating of liquid polydimethylsiloxane ("DC-200" silicone liquid) by sponging with an excess of the

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liquid and then removing the excess by rubbing with an absorbent towel. The surface is rendered transparent but not greasy.

The copy-sheet thus treated is placed around the exposure cylinder of the apparatus described in Example 1, and a test sheet printed with a variety of colored inks is held with the printed surface in pressure-contact with the heat-sensitive coating. With the capacitor charged at 2800 volts, the resulting irradiation causes darkening of the heat-sensitive coating in areas corresponding to each of the inked areas, including black, blue, green, red, and yellow areas.

The printed original is then replaced by a receptor sheet of plain white paper and the flash repeated but at an initial voltage of about 3200 volts. The previously darkened portions are substantially completely transferred to the receptor sheet. The background areas of the copy-sheet are darkened but no transfer occurs in these areas. Both the printed original and the image-coated receptor sheet are easily separated from the intermediate heat-sensitive copy-sheet.

When the copy-sheet of Example 1, or that of Example 2 prior to application of the silicone coating, is tested as above described, effective reproduction of the darker images is obtained, but the lighter colors do not give complete reproduction, and no legible reproduction whatever is produced at the yellow image area. Attempts to improve the reproduction of the lighter colored images by increasing the intensity of irradiation are not successful because of excessive background darkening.

Liquid silicone materials are effective in extremely small amounts and are presently preferred for the purpose indicated; but other mobile, heat-conductive, radiation-transmitting, void-filling liquids or pastes which are inert toward the coatings and films with which employed and do not cause softening or stickiness or other difficulties are likewise contemplated. These include fluorocarbon oils and, in some instances, light petroleum oils.

Resinous phenolic materials are known which are readily visibly reactive with ferric soaps under the conditions described, and such materials have been found useful both as reactants and at the same time as binders, replacing the ethyl cellulose or other binder in whole or in part.

Heat-sensitive coatings based on ferric-phenolic compositions have been found highly effective for the purpose of this invention and are preferred; but other heat-sensitive coatings have also proven useful for thermographic reproduction and may be employed, as illustrated by the following example.

Example 3

	Parts by weight
Silver behenate.....	160
Polyethyl methacrylate ("Lucite 42").....	240
Tricresyl phosphate.....	24
Acetone.....	1200

The silver behenate is formed by precipitation from aqueous sodium behenate with one-half the molar quantity of silver nitrate added in solution sufficiently acidic to precipitate the remainder of the behenic acid.

The listed components are ground together in a ball mill to minimum particle size. Separately there is prepared a solution of 25 parts of protocatechuic acid in 75 parts of acetone. Four parts of this solution are then mixed with 20 parts of the dispersion to form the coating composition. The latter is coated at a 3 mil orifice on 1 mil oriented polyester film, dried, and overcoated with "DC-200" silicon applied as a 20% solution in heptane by roll coating in an amount just sufficient to transparentize the initially opalescent surface.

The heat-sensitive film is pre-printed from a graphic original in the apparatus of Example 1 operated at a voltage of 2800, and the resulting image transferred to

a plain white paper receptor sheet using a voltage of 3200.

The heat-sensitive copy-sheet, after transfer of the initial image portion, remains as a stencil having transparent image areas in an opaque background. As such, it can be employed for producing additional duplicates by photographic means, e.g. by light-sensitizing of blueprint paper through the transparent areas followed by developing or intensifying with water or chemical solutions as required. Somewhat analogously, the reproductions produced on the paper receptor sheets may serve as graphic originals for the preparation of further reproductions by thermographic or other methods. In both instances, any desired number of duplicates can be produced. A further means of providing duplicates is described in the following example.

Example 4

A receptor sheet is provided by coating the smooth, clay-loaded and heavily calendered surface of a paper web with a thin layer of polyvinyl alcohol, applied from aqueous solution. The resulting surface is hydrophilic. Products of this character are commercially available, being used in the preparation of "Multilith" lithographic copy-sheet material.

A reproduction of a printed graphic original is produced on the heat-sensitive copy-sheet of Example 1 by thermographic copying procedures, in this case by brief intense irradiation of the original through the copy-sheet in pressure-contact therewith and with radiation obtained from an incandescent filament and concentrated at the printed surface.

The printed portions are next transferred from the copy-sheet to the hydrophilic surface of the receptor sheet by methods as described under Example 1, using a voltage of 2500 in the specific apparatus there described. There is provided an organophilic image pattern on a hydrophilic background. The resulting sheet is then swabbed with aqueous fountain solution, and used for making multiple prints with oil base inks on plain paper by lithographic techniques commonly employed in "Multilith" duplicating.

The successful reproduction of colored originals requires close and continuous contact between original and heat-sensitive layer. Fine grinding of dispersed particles has been shown to be of assistance in this respect, the size of voids between particles being thereby diminished. Improved contact between copy-surface and original may also be secured by providing a compressible or conformable sub-layer between heat-sensitive layer and transparent support web. For example, a thin added layer of relatively soft vinyl resin has been found to be of assistance; presumably the particles of the heat sensitive layer are partially pressed into such layer under the pressure-contact between copy-sheet and original. Application of a mobile transparent filler material such as silicone oil, as hereinbefore described, similarly reduces the size of surface voids and ensures more complete contact, and at the same time assists in preventing any slight tackiness or adhesion between copy-paper and original, particularly where the two are firmly pressed together while being irradiated.

Surprisingly, the presence of the silicone is not observed to have any deleterious effect on the subsequent transfer of the image-forming portions of the heat-sensitive layer, or on the ability of these portions to be permanently bonded to the receptor sheet. As a possible explanation for this effect, it is suggested that the transfer of image-forming material is accomplished by what amounts to volatilization of such material, with subsequent condensation at and within the surface pores of the contiguous receptor sheet, rather than by simple fusion and bulk transfer of molten material. In any event, and regardless of theory, the sheet materials and processes here described have now made possible the

economical and rapid permanent reproduction of both colored and black-on-white graphic originals on a wide variety of receptor surfaces by strictly thermographic techniques requiring no chemical or other image-development.

An additional advantageous feature of this invention, inherent in the foregoing examples, is the ability to intensify partial images formed at less than optimum irradiation by "front-printing" on heat-sensitive copy-paper. In Example 1 it is observed that the initially unaffected background areas of the copy-paper are drastically darkened during the second irradiation which transfers the previously darkened image-forming portions to the receptor-sheet. Although the background areas show no observable darkening during the initial irradiation, there is apparently produced sufficient change in these heat-sensitive areas so that they become substantially more absorptive of the radiation. Subsequent irradiation then produces at least a moderate heating effect within these background areas, resulting in the drastic darkening observed in such areas during transfer of the previously fully darkened image-forming areas. The phenomenon may be utilized in producing fully visible reproductions of graphic originals which cannot safely be subjected to the otherwise indicated high intensity of radiation. For example, irradiation of a black-on-white original through the heat-sensitive copy-paper is carried out at an intensity sufficient to produce only a barely visible darkening of the image areas. In the apparatus described in connection with Example 1, such an irradiation might be accomplished by charging the capacitor to about 1500 volts or less, rather than to 2000-3000 volts as indicated in connection with the example. The original is then removed, and the copy-paper further irradiated with one or more additional flashes at the indicated low intensity. It is found that the differential in radiation absorptivity between the partially darkened image areas and the visibly unchanged background areas is sufficient under these conditions to result in maximum darkening of the image areas with substantially no visible change in the background areas. The resulting intermediate is then employed in forming a reproduction on plain white paper or other receptor-sheet by further flash irradiation at required high intensity as hereinbefore described.

In the accompanying drawing, FIGURE 1 is a schematic representation, in cross-section, of the apparatus described in connection with Example 1; FIGURES 2, 3 and 4 are fragmentary views showing the progress of the reproduction process; and FIGURES 5 and 6 are representations of portions of alternative forms of heat-sensitive copy-sheets.

In FIGURE 1, a copy-sheet 12 and an original 13 are held in position against a transparent cylinder 11 by means of an outer fabric cover 14. Irradiation is supplied from flash tube 10 through the cylinder 11 and the copy-sheet 12 to the differentially radiation-absorptive graphic original 13. As illustrated in more detail in FIGURE 2, the heating effect thus produced at the radiation-absorptive image areas 15 of the original 13 causes a darkening at corresponding areas 16 of the heat-sensitive layer 17 of the copy-sheet 12. The visibly darkened areas 16 are radiation-absorptive. The remaining areas of the heat-sensitive layer 17 remain essentially visibly unchanged.

Where the radiation absorptivity of the areas 16 is inadequate or undesirably low, the copy-sheet may be subjected to the application of further radiation sufficient to cause substantially complete darkening of the image-producing areas 16, as illustrated in FIGURE 3, without making any significant or objectionable change in the remaining areas of the heat-sensitive layer 17. In most cases, this intermediate step is unnecessary.

As illustrated in the exploded view of FIGURE 4, the original 13 is next replaced by a sheet of plain white

paper 18, or other receptor sheet, and the composite again subjected to flash irradiation. The radiation-absorptive image-reproducing areas 16 are transferred from the copy-sheet 12 to the receptor sheet 18, producing a permanent reproduction of the graphic original. The remaining heat-sensitive areas of the layer 17 of the copy-sheet 12 are at the same time partially darkened, the copy-sheet thereby forming a negative transparency corresponding to the graphic original.

The heat-sensitive copy-sheet 50 of FIGURE 5 includes a thin inert surface coating 51 over the heat-sensitive layer 52 on the transparent carrier web 53. The copy-sheet 60 of FIGURE 6, on the other hand, is provided with a thin soft sub-layer 61 intermediate the heat-sensitive layer 62 and the carrier web 63.

What is claimed is as follows:

1. The method of making a thermographic reproduction, on a receptor sheet having a surface, of a graphic original, comprising (1) exposing the original to brief intense irradiation through a radiation-transmitting heat-sensitive copy-sheet in heat-conductive contact with said original for producing in said copy-sheet a radiation-absorptive and visibly distinct image portion corresponding to the radiation-absorptive image-forming area of said original, and (2) exposing the thus converted copy-sheet to further brief irradiation at an intensity at least equal to that used in (1) while holding the copy-sheet with its heat-sensitive surface in intimate contact with the receptor sheet surface, for selectively transferring said visibly distinct image portion permanently onto the receptor sheet surface, said copy-sheet consisting essentially of a radiation-transmissive base sheet and a visibly heat-sensitive radiation-transmissive coating thereon, said coating being rendered visibly distinct and radiation-absorbent on being briefly heated in the thermographic copying process, the thus heated portions being readily transferable from said base sheet on heating to substantially higher temperature.

2. The method of preparing the surface of a hydrophilic printing-plate for lithographic printing of reproductions of a graphic original, comprising (1) exposing said graphic original to brief intense irradiation through a radiation-transmitting copy-sheet having an organophilic visibly heat-sensitive layer in heat-conductive contact with said original for producing in said layer a radiation-absorptive and visibly distinct image portion corresponding to the radiation-absorptive image-forming area of said original, and (2) exposing the thus converted copy-sheet to further brief irradiation at an intensity at least equal to that used in (1) while holding the copy-sheet with its organophilic layer in intimate contact with said printing-plate surface, for selectively transferring the organophilic image portion to the hydrophilic printing-plate surface; said copy-sheet being further characterized as consisting essentially of a radiation-transmissive base sheet and a

visibly heat-sensitive organophilic radiation-transmissive coating thereon, said coating being rendered visibly distinct and radiation-absorptive on being briefly heated to conversion temperature in the thermographic copying process, the thus converted portions being readily transferable from said base sheet on heating to a temperature substantially higher than said conversion temperature.

3. The method of making a thermographic reproduction, on a receptor sheet having a surface, of a graphic original, comprising (1) exposing the original to brief intense irradiation through a radiation-transmitting heat-sensitive copy-sheet in heat-conductive contact with said original for producing in said copy-sheet a radiation-absorptive and visibly distinct image portion corresponding to the radiation-absorptive image-forming area of said original and at less than maximum image density while avoiding any visible change in the background portion, (2) exposing the partially converted copy-sheet to further brief intense irradiation sufficient to increase the density of the partially radiation-absorptive image areas while avoiding any significant discoloration of said background, and (3) exposing the thus converted copy-sheet to further brief irradiation at an intensity at least equal to that used in (1) while holding the copy-sheet with its heat-sensitive surface in intimate contact with the receptor sheet surface, for selectively transferring said visibly distinct image portion permanently onto the receptor sheet surface; said copy-sheet being further characterized as consisting essentially of a radiation-transmissive base sheet and a visibly heat-sensitive radiation-transmissive coating thereon, said coating being rendered visibly distinct and radiation-absorptive on being briefly heated to conversion temperature in the thermographic copying process, the thus converted portions being readily transferable from said base sheet on heating to a temperature substantially higher than said conversion temperature.

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