

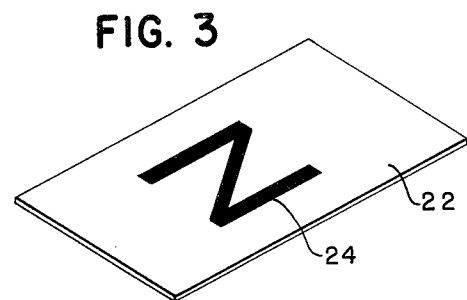
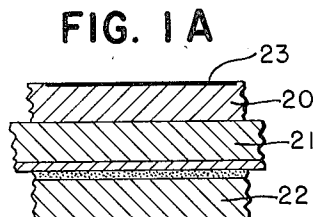
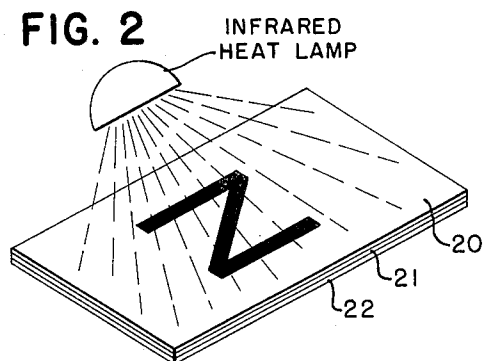
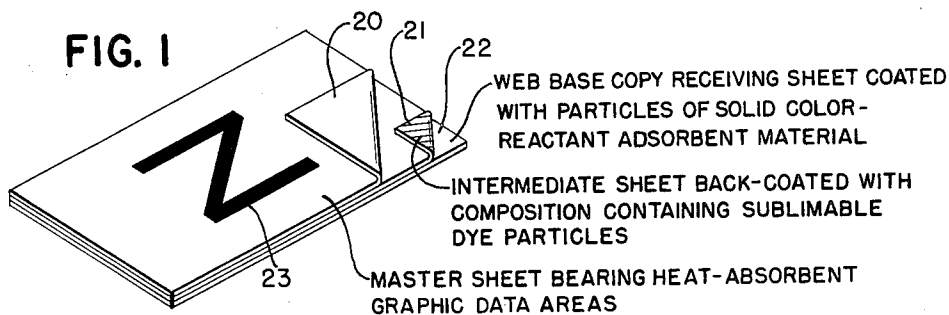
March 8, 1966

R. E. MILLER ETAL
THERMOTRANSFER SHEET MATERIAL AND COPYING
SYSTEMS UTILIZING SAME

3,239,366

Filed Nov. 21, 1961

3 Sheets-Sheet 1



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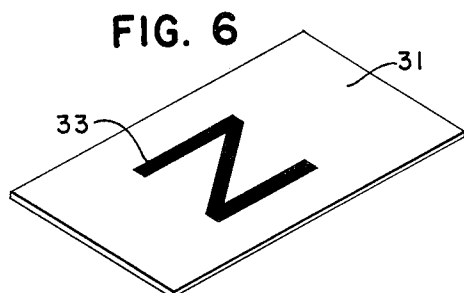
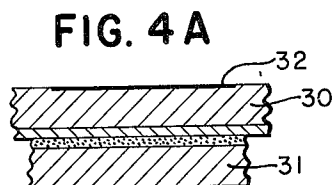
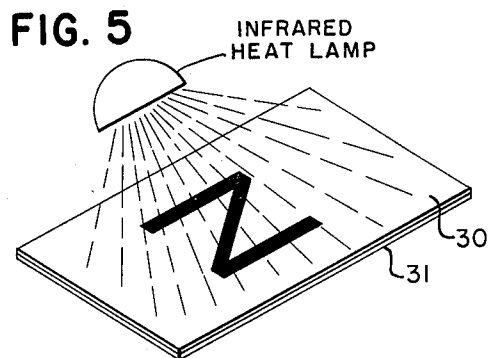
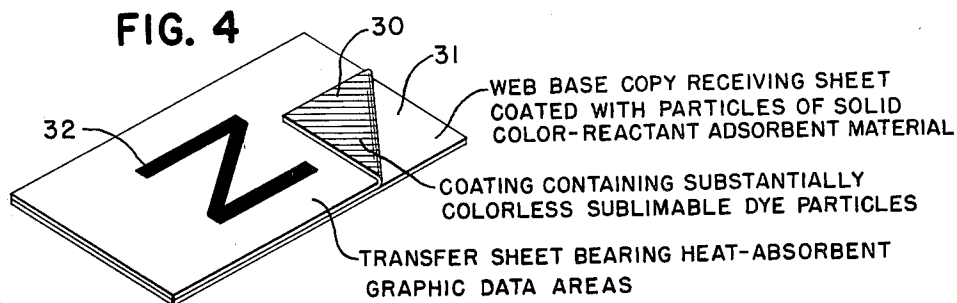
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3 Sheets-Sheet 2



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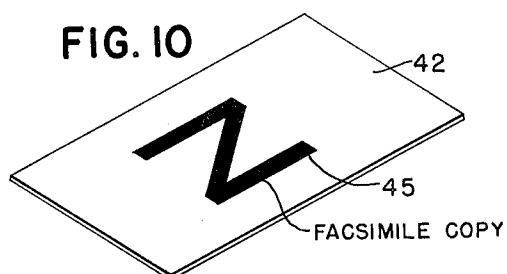
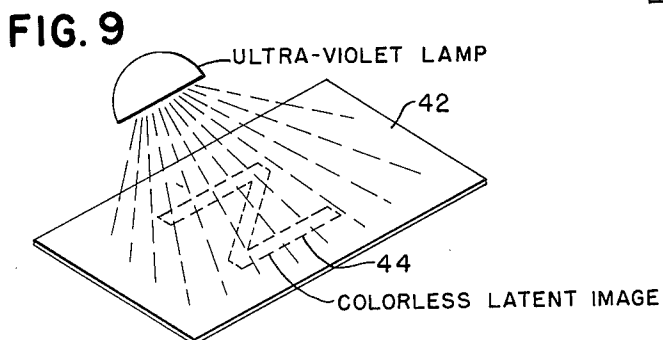
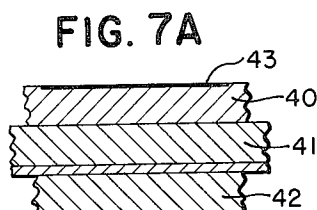
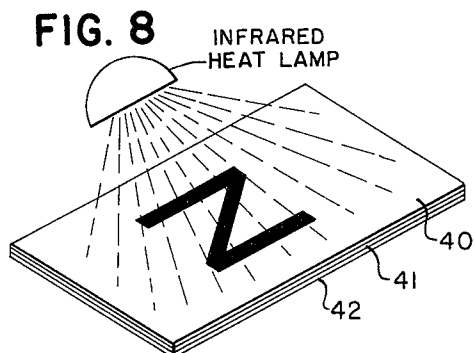
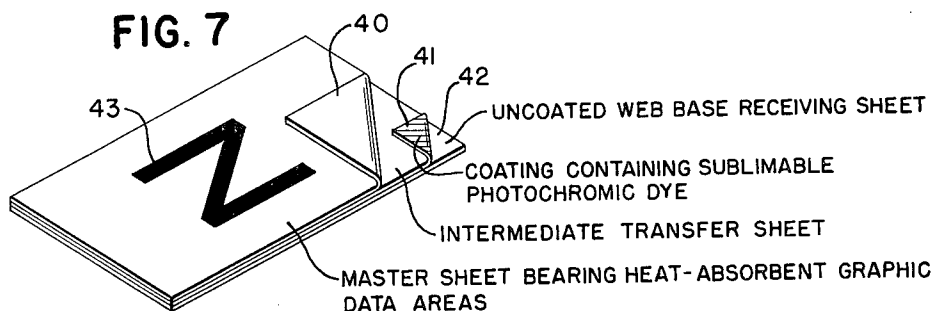
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3 Sheets-Sheet 3



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3,239,366

**THERMOTRANSFER SHEET MATERIAL AND
COPYING SYSTEMS UTILIZING SAME****Robert E. Miller and James Ke-Jen Cheng, Dayton, Ohio,
assignors to The National Cash Register Company,
Dayton, Ohio, a corporation of Maryland****Filed Nov. 21, 1961, Ser. No. 153,806****24 Claims. (Cl. 117—36.1)**

This invention relates to thermotransfer record copying sheet material, to compositions containing sublimable color-forming compounds useful therewith, and to graphic data-copying systems utilizing said sheet material.

More particularly, it relates to thermotransfer sheets and to the use of such thermotransfer sheet material coated with sublimable dye, whereby a large number of duplicate or facsimile copies of a graphic original may be produced by thermographic means when the thermotransfer dye material on said transfer sheet is placed in heat-conductive relation with both the graphic original and a suitable receiving sheet and the combination is briefly exposed to intense infra-red irradiation obtained with suitable conventional means.

More specifically, the thermotransfer sheet of this invention is utilized in a copying system in which a master sheet having high heat-absorbent areas containing graphic data and low heat-absorbent areas is irradiated with infra-red radiation to control the formation of an image on a copy-receiving sheet, the image being formed as a colored image in the form of a condensed sublimate of normally colorless or slightly colored organic dyes which lead themselves to development to a visibly colored form, in some instances by adsorption reaction in the vapor or solid state with acidic surface active adsorbent material, and in other instances by subjecting the condensed sublimate to light predominantly in the ultra-violet region of the spectrum, depending on the organic compound in use.

Thermographic copying papers and processes have heretofore been disclosed, such as the heat-sensitive papers disclosed in United States Patent No. 2,710,263, issued to Bryce L. Clark and Carl S. Miller on June 7, 1955, and the thermographic process disclosed by Carl S. Miller in United States Patent No. 2,740,896, issued April 3, 1956. In these and similar disclosures, however, there is no disclosure of transfer of color-forming material from a thermotransfer dye-containing material to a receiving sheet as disclosed herein; rather, in such prior-art methods copies are made on heat-sensitive sheets which are coated with or contain the color-forming ingredients, by placing a printed or graphic original in heat-conductive contact with said heat-sensitive sheet and then briefly exposing the graphic original to intense infra-red radiation, thus creating an elevated-temperature pattern in the heat-absorbent graphic matter which is directly conducted to the heat-sensitive layer of the copy sheet to develop a visible copy of the graphic original on said copy sheet.

More recently, there has been disclosed, in United States Patent No. 2,939,009, granted to Jack M. Tien on May 31, 1960, a thermal copying process which utilizes the method of making a copy of a graphic original by thermaltransfer of color-forming compounds coated on a transfer sheet to the surface of a suitably-coated copy-receiving sheet. In general, one disadvantage associated with the use of such prior-art thermotransfer sheets is the relatively small number of copies which can be made with any one transfer sheet. In contrast with the principal disadvantage inherent in such prior-art thermotransfer sheets, the novel thermotransfer materials of the invention provide an unexpectedly large number of copies by repeated transfers from the same sheet. From forty to sixty copies of original data may readily be made with the thermotransfer materials of this invention, the last

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copy being essentially of the same quality as the first. As will be made more apparent hereinafter, the unexpected advantages obtained with the thermotransfer sheet materials of this invention inhere principally in the thermotransfer composition coated on said sheet material, and particularly in the thermotransferable sublimable dyes and organic compounds and mixtures thereof present in said coated compositions. Typical classes of sublimable dyes and organic compounds having the necessary physical and chemical characteristics to be useful for purposes of this invention include the following: (1) leuco methylene blue dyes, (2) leucauramine compounds, and (3) indolino benzo spiro pyran compounds. As used herein, in the specification and claims, the term dye(s) represents and includes any and all of the sublimable color-forming compounds disclosed herein. Even though some of the mentioned compounds may not normally be considered as dyes, they are color-producing, and therefore, from a functional standpoint, they are similar to dyes. It has been found that the dyes comprised in the coating compositions of this invention are transferred or transported from said coating to the surface of the juxtaposed receiving sheet by true sublimation. In part, this phenomenon accounts for the large number of copies obtainable with the novel sheet material, as compared to the limited number obtainable with related prior-art thermotransfer materials, in which the color-producing compounds are first melted or fused, so that transport of said prior-art compounds to the receiving sheet surface is effected while the compounds are in the liquid state. Manifestly, a greater number of facsimile copies can be made with the thermotransfer sheet material coated with the sublimable dye compositions described herein than with prior materials coated with color-forming compounds which are transferred in the liquid state, since, for each copy made, other factors being equal, a much smaller fraction of the total available dye or color-forming material is transferred to the receiving sheet by the mechanism of sublimation than is transferred by liquid transport.

Although the thermotransfer materials of this invention are suitable for use in a number of different copying systems and arrangements, they are preferably used in either a two-sheet or a three-sheet arrangement. In the two-sheet arrangement, the top sheet consists of a thin flexible sheet of infra-red-transmitting, base web material bearing on one surface the graphic data to be copied, the data being present as substantially heat-absorbent characters, such as black heat-absorbent type-written, drawn, or written characters; and having disposed on the other surface of said sheet a thermotransfer coating including one or more sublimable color-forming dyes. In the production of facsimile copies, this top sheet is superimposed upon a non-infra-red-absorptive copy-receiving sheet, and the combination, while held in close heat-conductive contact, is moved past a source of heat-producing irradiation, such as an infra-red lamp, so that radiant energy is made to fall on the master sheet at such a rate and at such energy level as to preferentially heat the heat-absorbent printed areas in relation to the light-reflecting areas having no graphic data. The amount of heat generated by absorption of radiant energy by the heat-absorbent graphic data areas is much greater than the amount absorbed by areas where no graphic data is present, so that the heat so absorbed results in a heat pattern corresponding to the graphic data. Heat from said heated areas, in the form and outline of said heat pattern, is transferred by conduction through the intervening base web to the dye coating in areas contiguous and corresponding to said graphic data, causing the dye or dyes contained therein to sublime in small quantity, the sublimate so produced con-

densing in the form of said heat pattern on the receiving sheet as a colored or latent image, depending on the type of dye and receiver sheet being used. The color of the image so produced ranges from blue to red, the color being determined by the particular color-forming compounds and the receiving sheet surface characteristics.

The three-sheet arrangement is similar to the two-sheet arrangement except that the heat-absorbent graphic data is carried on an individual master sheet instead of being disposed on the side opposite the dye-coated side of the transfer sheet, as in the two-sheet arrangement. The transfer sheet in the three-sheet arrangement is used as an intermediate sheet between the master sheet and the receiver sheet, said transfer sheet being coated on one side with sublimable dye, the coated side being held in heat-conductive contact with the receiving sheet during the copying operation.

It is therefore an object of this invention to provide a novel thermotransfer sheet material having on one side a coating comprising at least one sublimable dye.

Another object of this invention is to provide a novel composition comprising at least one color-forming compound useful for coating thermotransfer sheet material, said compound being sublimable from a coated sheet used for copying purposes with thermographic copying means.

Another object of the invention is to provide a thermographic copying system comprising an array of (1) an infra-red-transmitting, low-heat-conductivity master sheet bearing heat-absorbing graphic data on one surface thereof; (2) an infra-red-transmitting sheet coated on one side with a composition including sublimable color-forming material, and (3) a copy-receiving sheet.

Yet another object of the invention is to provide a thermographic copying system consisting of two sheets in combination: a first, infra-red-transmitting, sheet having disposed thereon a coating containing a sublimable color-forming compound on one side and heat-absorbent graphic data on the other, and, as a second sheet, a copying-receiving sheet having acidic absorbent particles coated on one side, which side is in heat-conductive contact with the coated side of said first sheet.

Still another object of the invention is to provide a thermographic copying system consisting of either a two-sheet arrangement or a three-sheet arrangement, wherein said arrangements include one of two species of receiving sheet; that is, either a sheet coated with particles of acid clay absorbent material or like materials, or one which consists of a plain sheet of paper with no absorbent coated thereon, the choice depending on the sublimable dye coated on the transfer sheet and on the end result desired.

Other objects of the invention will become apparent from the following description and claims and by reference to the accompanying drawings, which disclose the principle of the invention and the best mode of carrying out that principle, the drawings and the examples to follow being merely illustrative and not limitative of the invention.

In the drawings:

FIGS. 1, 2, and 3 represent views, in perspective, of sheet arrangements for copying graphic data wherein a three-ply stack having an intermediate transfer sheet is subjected to infra-red radiation in making a copy.

FIGS. 4, 5, and 6 represent a related arrangement of sheets for copying graphic data, except that a two-sheet system, instead of the three-sheet arrangement of FIGS. 1, 2, and 3, is shown.

FIGS. 7, 8, 9, and 10 show another system consisting of a three-ply array of sheets wherein an intermediate sheet coated with a photochromic dye transfers a latent image of graphic data onto a receiving sheet when said graphic data is subjected to infra-red radiation, the latent image being developed to a substantially stable visibly

colored image by subsequent exposure to ultra-violet radiation.

FIGS. 1A, 4A, and 7A represent cross-sections of the sheet arrangements of FIGS. 1, 4, and 7, respectively. These figures, showing the cross-section of sheet arrangements in proper relation for conducting the copying operation, are included to clearly identify the separate sheets with their associated coated layers, and to aid in differentiating one from the other.

Referring to FIG. 1, there is shown a three-sheet system for copying heat-absorbent graphic data, consisting of an intermediate sheet 21, held in heat-conductive contact between a master sheet 20 and a receiving sheet 22. The master sheet 20 is an infra-red-transmitting paper web base having disposed on its surface heat-absorbent graphic data areas 23, such as carbon ink characters, said master sheet being overlaid in heat-conductive contact with the uncoated surface of the intermediate sheet 21. The sheet 21 is back-coated with a sublimable dye or a composition containing a sublimable dye, this coating in turn being held in contact with the coated side of the receiving sheet 22, which is coated with clay particles or equivalent, which particles are acid relative to the sublimable dyes transferred to said sheet. The mode of providing graphic copies by utilizing a heat pattern as the means for transferring sublimable dye to a coated receiving sheet using the arrangement of FIG. 1 was described in detail above.

FIG. 2 shows the three-sheet arrangement of FIG. 1 being briefly irradiated with an intense source of infra-red heat-producing rays provided by a suitable heat lamp. It should be understood that means for providing suitable infra-red radiation necessary for the practice of this invention are now well known in the art and hence need not be described herein.

FIG. 3 represents the copy-receiving sheet 22 with an exact facsimile copy 24 of the original graphic data 23 disposed on the master sheet 20, the copy having been produced by irradiation of the three-sheet arrangement of FIG. 2.

In FIG. 4, there is shown a combination of two sheets useful for copying and duplicating graphic originals, consisting of a receiving sheet 31 overlaid with a transfer sheet 30. The transfer sheet 30 comprises a thin pliable infra-red-transmitting web base material having heat-absorbent indicia 32 disposed on its top surface and a thin layer of sublimable dye coated on its bottom surface. This transfer sheet is superposed in heat-conductive contact relation with the receiving sheet 31, the contacting surface of which is coated with minute particles of surface active adsorbent material, such as that previously described in connection with FIG. 1.

FIG. 5 shows the two-sheet system being exposed to intense infra-red radiation in the manner described in connection with FIG. 2.

FIG. 6 represents a facsimile copy 33 of graphic original 32 similar to that described under FIG. 3, except that the copy is made with a two-sheet system instead of the three-sheet system of FIG. 3.

Referring now to FIG. 7, there is shown, in perspective, a three-sheet copying system which is identical with the arrangement shown in FIG. 1 except that the receiving sheet 42 consists of plain uncoated web base material, and the intermediate transfer sheet 41 is coated with a thin layer including a sublimable photochromic dye. The sheet 41 is held in heat-conductive contact between said receiving sheet and a master sheet 40, which master sheet has heat-absorbent graphic data 43 disposed on its surface.

FIG. 8 shows the three-sheet combination of FIG. 7 being subjected to high-intensity heat rays, such as infra-red rays, generated by the heat lamp shown in the figure.

In FIG. 9, the uncoated receiving sheet 42 is shown with a latent image 44 of the graphic original on its surface in position for irradiation with an ultra-violet light

source, said latent image having been obtained by infra-red irradiation of the three-sheet arrangement as shown in FIG. 8. Thus, the latent image 44 represents an invisible sublimate of photochromic dye transferred to the receiving sheet 42 from the intermediate transfer sheet. The latent image is in the form of the heat pattern generated within the graphic original by irradiation of said original with infra-red rays.

FIG. 10 shows the receiving sheet 42 after exposure to ultra-violet light, the exposure having transformed the latent image 44 to a visibly blue colored facsimile copy 45 of the graphic original.

It will be apparent that systems which utilize an uncoated receiving sheet are especially useful when used in conjunction with a sublimable-photochromic-dye-coated transfer sheet, since one of the principal features of this arrangement is to form a latent image of said photochromic dye on the surface of the uncoated receiving sheet, which image may subsequently be developed to a visibly colored copy of the original graphic data by subjecting the latent image to short wave-length radiation, such as ultra-violet radiation. A two-sheet system utilizing an uncoated receiving sheet in conjunction with a sublimable-photochromic-dye-coated master sheet gives essentially the same result as the three-sheet system and can be substituted therefor.

Other modifications of the arrangement shown in FIGS. 7, 8, 9, and 10 are also within the purview of this invention. For example, when a sublimable-photochromic-dye-coated transfer sheet is used with a clay-coated receiving sheet, a visibly colored reddish image of the graphic original is directly obtained on the receiving sheet, instead of a latent image, which is obtained with the uncoated receiving sheet arrangement above described. It is thus possible to obtain facsimile copies of graphic data in contrasting colors on the same receiving sheet by the transfer of photochromic dye to clay-coated sheet areas and to uncoated sheet areas, the former areas providing a reddish-colored image directly and the latter providing a latent image which develops a blue color when subjected to ultra-violet radiation.

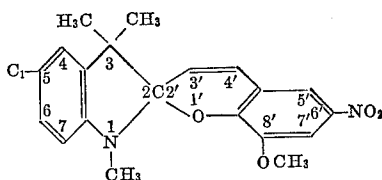
Other variations include the use of sublimable dye compositions comprising sublimable photochromic dyes and one or more of the other sublimable dyes of this invention in a copying system including either an uncoated receiving sheet or a clay-coated receiving sheet to obtain graphic copies of varying color composition.

The following examples are presented in order to provide specific embodiments of compositions comprising sublimable dyes and to set forth the best mode of preparing thermotransfer sheet material including such compositions.

EXAMPLE I

A preferred composition for coating thermotransfer sheet material of this invention comprises three dyes or color-forming compounds and is prepared as follows: An aqueous dispersion is prepared by ball-milling a composition consisting of, in parts by weight:

- 6 parts of 10-isovaleryl-3,7-bis-(dimethylamino) phenothiazine, also known as N-isovaleryl leuco methylene blue, and herein abbreviated as IVLMB,
- 2.4 parts of N-(2,5 dichlorophenyl) leucauramine,
- 1.6 parts of a photochromic dye, 1,3,3-trimethyl-5 chloro, 6'-nitro, 8' methoxy-spiro[(2'H-1'-benzopyran) - 2,2'-indoline] having the structure



3%, based on the combined weight of the dyes, of a nonylphenoxyethanol surfactant; i.e., Triton N-100, a non-ionic surface active agent, and 31 parts of water.

- 5 This composition is ball-milled for about eighteen hours or until the dye particles have been reduced to an average size of five microns or smaller. The final transfer coating emulsion is prepared by blending the above-described dye dispersion with a binder composition consisting of a mixture of 2.1 parts (dry weight basis) of a 20% aqueous solution of Elvanol 50-42, a high-viscosity, highly-hydrolyzed polyvinyl alcohol, having a viscosity of 35-45 centipoises when measured with a 4% aqueous solution at 20 degrees centigrade by the Hoesppler falling ball method and in which the degree of hydrolysis varies from 97.7 to 98.4%, and 1.05 parts (dry weight basis) of Dow Latex 630, which is a 48% solids styrene-butadiene copolymer latex. The so-prepared blend is then adjusted to about 20% total solids, and, after thorough mixing, the dispersion is ready for coating.

A sheet of paper coated with 2.5 pounds per ream (25" x 38" x 500 sheets) of the above composition was used as the thermotransfer sheet in both a three-sheet system and a two-sheet system in accordance with this invention, and, when so utilized with thermographic copying means, each novel thermotransfer sheet readily provided at least sixty and in many instances a greater number of legible and clear facsimile copies of a graphic original on individual attapulgitic-clay-coated receiving sheets.

EXAMPLE II

The composition of this example consists of two color-producing compounds instead of the three shown in Example I. An aqueous dispersion is prepared by ball-milling the following ingredients, the amounts given as parts by weight:

- 6.0 parts of 10-isovaleryl-3,7-bis-(dimethylamino) phenothiazine, also designated by the trivial name N-isovaleryl leuco methylene blue,
- 4.0 parts of 1,3,3-trimethyl-5-chloro, 6' nitro, 8' methoxy-spiro [(2'H-1'-benzopyran)-2,2'-indoline],
- 3% based on the combined weight of dyes, of Triton N-100, a nonylphenoxyethanol surfactant, the latter being a non-ionic surface active agent, and
- 31 parts of water

After the so-prepared emulsion has been ball-milled for about eighteen hours, or until the dye particles have been reduced to about five microns, the final coating composition is made by blending therewith the binder composition of Example I in the manner described therein.

EXAMPLE III

In Examples I and II, the coloring materials are dispersed in an aqueous system. In this example, a thermotransfer coating composition consisting of the following materials is prepared, in which the materials are dispersed and/or dissolved in an organic vehicle as follows, all parts being by weight:

- 150 parts of 10-isovaleryl-3,7-bis-(dimethylamino) phenothiazine,
- 5 parts of N-(2,5 dichlorophenyl) leucauramine,
- 4 parts of natural rubber,
- 0.1 part of lecithin (dispersing agent),
- 0.03 part of azo-oil Blue Black "B," a polyazo alkylated naphthol dye, disclosed in United States Patent No. 2,090,938, issued to Karl F. Conrad on August 24, 1937,
- 200 parts of straight-chain aliphatic petroleum distillate (boiling range 205 to 240 degrees Fahrenheit).

Four parts of milled natural rubber is first dissolved in 200 parts of the petroleum solvent, to which have been added the given amounts of lecithin, a dispersing agent,

and azo oil Blue Black "B," which serves as a tinting agent by incorporating a slight color to the coating and thus aids in distinguishing coated areas from uncoated areas of the base sheet. The coloring compounds or dyes are then added, and, after thorough mixing, the dispersion is applied as a coating on suitable web stock, such as Nekoosa bond paper, in an amount ranging from about two to three pounds per ream of 25" x 38" x 500 sheets. The coating is applied to the transfer base by any suitable conventional technique, and the applied coating then is dried by passing the coated medium through a heated tunnel or the like to evaporate the solvent.

EXAMPLE IV

A transfer coating emulsion containing a photochromic dye is prepared by ball-milling a 3% aqueous dispersion of the photochromic dye of Example I with a 2% aqueous binder solution of DX843-11, a polyethylenemaleic anhydride copolymer having a specific viscosity of 1.0 as a 1% solution in dimethyl formamide at 25 degrees centigrade as measured by Ostwald method "B," the binder solution containing a few drops of Triton-100, a non-ionic nonylphenoxyethanol, as a dispersing agent. The transfer emulsion is coated at the rate of 2.5 pounds per ream of 500 sheets (25" x 38") by conventional means and dried in a heated tunnel.

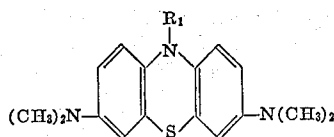
EXAMPLE V

A thermotransfer composition containing the photochromic dye of Example I but having no binder is prepared by evaporating the acetone solvent from a paper base transfer medium coated with a saturated acetone solution of said photochromic dye.

Because of the lower coating weight normally associated with transfer sheets prepared in this manner, it is not generally possible to obtain as many copies with these sheets as are obtained with emulsion-coated binder-containing sheets. In all other respects, however, sheets coated in the manner of this example perform in the same manner, with equal adaptability and sensitivity, as the emulsion-coated sheets.

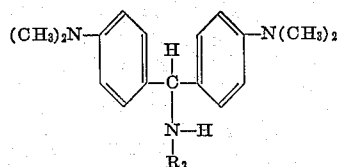
The preferred dyes or color-forming compounds disclosed in the foregoing examples may be substituted with other compounds selected from the same or related class of compounds. Examples of compounds from each class which have been found to be particularly suitable include the following:

(I) Leuco methylene blue compounds of the formula



wherein R_1 is selected from the group consisting of isobutyl, isovaleryl, pivalyl, acetyl, propionyl, and phenyl acetyl;

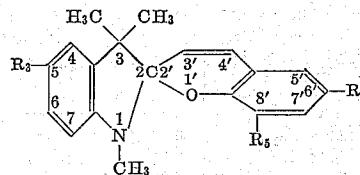
(II) Leucauramine compounds of the formula



wherein R_2 is selected from the group consisting of

2,5-dichlorophenyl
3,4-chlorophthaloyl
5-chloro-2-methylphenyl
p-nitrophenyl
phenyl, and

(III) Photochromic compound of the formula



wherein R_3 , R_4 , and R_5 are selected from the group consisting of (a) R_4 is NO_2 and R_3 and R_5 are hydrogen, (b) R_3 and R_4 are hydrogen and R_5 is NO_2 , (c) R_3 and R_4 are hydrogen and R_5 is OCH_3 , (d) R_3 is hydrogen, R_4 is NO_2 , R_5 is OCH_3 , (e) R_3 is Cl, R_4 and R_5 are both NO_2 , (f) R_3 is hydrogen, R_4 is Br, and R_5 is NO_2 , (g) R_3 is Cl, R_4 is hydrogen, and R_5 is NO_2 , (h) R_3 is Cl, R_4 is NO_2 , and R_5 is hydrogen, (i) R_3 is Cl, R_4 is Br, and R_5 is NO_2 , and (j) R_3 is Cl, R_4 is NO_2 , and R_5 is OCH_3 .

From the foregoing examples, it is thus apparent that thermotransferable compositions of this invention may comprise one or more dyes from each of the dyes of Groups I, II, and III above, one or more dyes selected from each of the dyes of Groups I and II or Groups I and III, or one or more dyes from Group III.

Although leuco methylene blue compounds substituted in the 10 position with 4 and 5 carbon iso-alkyl substituents are not common and well known in commerce, such compounds may be prepared according to the process described in United States Patent No. 2,909,520, which issued October 20, 1959, and United States Patents Nos. 2,783,227 and 2,783,228, both of which issued February 26, 1957. The process described in the latter two patents is preferred. As is obvious to one skilled in the art, the desired iso-alkyl leuco methylene blue compound may be prepared by substituting the selected iso-alkyl acyl halide for the acyl halides in the process of the above-identified patents.

Compounds of the type shown in Group II, the leucauramine group, are disclosed in United States Letters Patent Nos. 2,828,341 and 2,828,342, issued to Clyde S. Adams et al. on March 25, 1958, and those of Group III, the indolino benzospiropyran compounds, are disclosed in the United States patent application of Elliot Berman Serial No. 108,710, filed May 9, 1961, now U.S. Patent No. 3,100,778 which is a continuation-in-part of United States patent application Serial No. 803,836, filed April 3, 1959, and now abandoned.

The acidic adsorbent particles coated on the receiving sheets utilized with this invention are well known and comprise, preferably, attapulgite clays and zeolite materials, as well as many less preferred adsorbents. Examples of such clays and other adsorbent materials, and sheet materials coated therewith, are disclosed in United States Patents No. 2,581,186, issued to Barrett K. Green on January 1, 1952; No. 2,641,557, issued to Barrett K. Green on June 9, 1953; and No. 2,777,780, issued to Marjorie J. Cormack and Ned A. Thacker on January 15, 1957.

Preferably, the polymeric binder material of this invention comprise a blend of a hydrophilic synthetic polymer and a rubbery copolymer latex, such as the polymer blend of Examples I and II. However, other polymeric materials may be substituted for the preferred binder compositions. Examples of such other materials include hydrophilic polyvinyl alcohol without the added copolymer latex, and hydrophilic copolymers of polyethylenemaleic anhydride, as well as other known copolymers having similar characteristics. The binder may also comprise polymers of natural origin, such as gelatin, gum arabic, and the like.

The proportions of the three classes of dyes may be varied over a considerable range.

Preferably, the ratio, on a weight basis, of the amount of leuco methylene blue dye to the amount of dye from

either of the other two classes of dyes may vary from about 1.5:1 to 4:1.

From the foregoing, it is manifest that, although the dye proportions of the examples are the preferred proportions and yield optimum results, excellent copies are obtainable when the proportions of individual dyes are varied over a wide range.

It should be understood that no criticality lies in the use of any particular binder materials or blends thereof, or in any solvent or dispersing agent, and that suitable substitutes and equivalents for the above classes of materials will be readily suggested to those skilled in the art. It will also be apparent to skilled artisans that the proportions of these non-critical materials, as well as other variables such as coating weight, percent total solids in the coating emulsions and dispersions, etc., may be adjusted and modified in a manner consistent with the desired end result without departing from the scope of this invention.

Although, in general, all of the dyes enumerated above are stable to heat, only the derivatives of leuco methylene blue are stable to light and to the effects produced by prolonged exposure to atmospheric conditions. Accordingly, the preferred transfer compositions include a leuco methylene blue derivative, preferably an iso alkyl derivative having four or five carbon atoms attached to the 10 position on the phenothiazine group, in combination with one or more dyes from the other previously-disclosed classes of dyes. Thermotransfer compositions containing such leuco methylene blue derivatives provide permanent copies of graphic matter; i.e., which remain stable indefinitely against the effects of heat and light. Some tendency of the graphic copy to fade, however, is observed in copies prepared with sublimable dye compositions in which leuco methylene blue derivatives have been excluded, the degree of fading, of course, varying with the dye and the type of receiving sheet.

It has been found that graphic copies made on clay-coated receiving sheets with thermotransfer sheets coated with the preferred composition of Example I are clear and legible and exhibit only very slight color fade even after fifty hours' exposure in a standard Fadometer machine.

It will be noted from the foregoing examples that, with the exception of the compositions of Examples IV and V, in both of which the only color-forming compound is a photochromic dye, the other compositions all contain the preferred isovaleryl derivative of leuco methylene blue. Even though this compound is preferred in the compositions of this invention, it has been found that a limited number of other derivatives of leuco methylene blue, particularly the 10-isobutyryl and 10-pivalyl derivatives, have the proper balance of physical and other characteristics, such as melting point and sublimation point, which, when combined in a composition containing at least one other dye selected from the leucauramine and photochromic dyes of this invention, cooperate with the latter to also provide an unexpectedly large number of copies when utilized in accordance with the invention.

Although the large number of copies obtainable with transfer sheets containing the preferred leuco methylene blue derivatives above mentioned is of great value from a practical and economic standpoint, it has also been found that other advantages of nearly equal importance are inherent in the use of said derivatives.

For example, a large number of trials have shown that, although the characteristic large number of colored facsimile copies of good quality may be produced with thermotransfer sheets in which the preferred leuco methylene blue derivatives—i.e., 10-isovaleryl, 10-isobutyryl, and 10-pivalyl—have been replaced by the other derivatives of this class specified above—i.e., the 10-acetyl, 10-propionyl, and 10-phenyl acetyl derivatives—copies made with sheets containing the former preferred derivatives have much greater stability to color change,

show reduced tendency to smudging, and display a more homogeneous and even distribution of the sublimed dyes than do copies made with sheets containing the latter less preferred derivatives.

While the invention has been described with respect to certain preferred embodiments of copying systems and thermotransferable dyes, it should be understood that changes in various details of the disclosed invention may be made by those skilled in the art without departing from either the spirit or the scope of the invention.

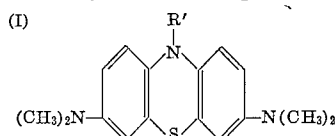
What is claimed is:

1. Thermotransfer record sheet material adapted for making copies of heat-absorbing graphic data onto receiving sheet material by subjecting said graphic data to heat-producing irradiation while said data is held in heat-conductive relation with said thermotransfer and receiving sheet materials, the thermotransfer sheet material comprising

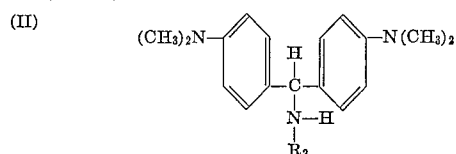
(1) a flexible infra-red-transmitting supporting web base, and

(2) a thin layer containing sublimable dye coated on one side of said base, said layer comprising a mixture of sublimable fine solid particles of (a) a leuco methylene blue dye, (b) a leucauramine compound, and (c) a 1,3,3-trimethyl - spiro - [(2'H'1'-benzopyran)-2,2'-indoline] compound.

2. The thermotransfer sheet of claim 1 wherein (1) the base material is a thin infra-red-transmitting flexible paper web and (2) the thin layer on said base material comprises a polymeric binder having homogeneously dispersed therein a sublimable mixture of fine particles of (a) a leuco methylene blue compound of the formula



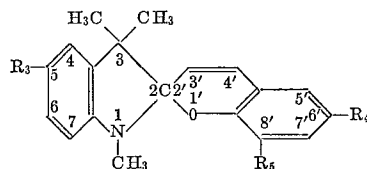
wherein R₁ is selected from the group consisting of isobutyryl, isovaleryl, pivalyl, acetyl, propionyl, and phenyl acetyl; (b) a leucauramine compound of the formula



wherein R₂ is selected from the group consisting of:

2,5-dichlorophenyl
3,4-chlorophthaloyl
5-chloro-2-methylphenyl
p-nitrophenyl
phenyl

and (c) a photochromic spiro-pyran compound of the formula

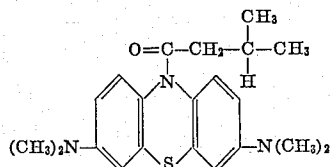


wherein R₃, R₄, and R₅ are selected from the group consisting of (a) R₄ is NO₂ and R₃ and R₅ are hydrogen, (b) R₃ and R₄ are hydrogen and R₅ is NO₂, (c) R₃ and R₄ are hydrogen and R₅ is OCH₃, (d) R₃ is hydrogen, R₄ is NO₂, R₅ is OCH₃, (e) R₃ is Cl, R₄ and R₅ are both NO₂, (f) R₃ is hydrogen, R₄ is Br, and R₅ is NO₂, (g) R₃ is Cl, R₄ is hydrogen and R₅ is NO₂, (h) R₃ is Cl, R₄ is NO₂, and R₅ is hydrogen, (i) R₃ is Cl, R₄ is Br, and R₅ is NO₂, and (j) R₃ is Cl, R₄ is NO₂, and R₅ is OCH₃.

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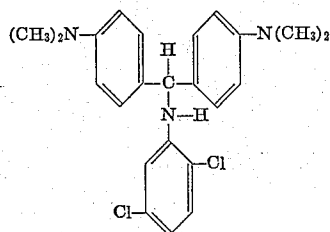
3. The thermotransfer sheet material of claim 2 wherein (a) the leuco methylene blue compound is a compound of the formula

(I)

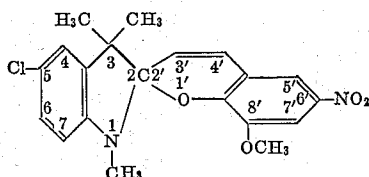


(b) the leucauramine compound has the formula

(II)



and (c) the photochromic compound has the formula

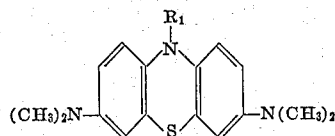


4. Thermotransfer record sheet material adapted for making copies of heat-absorbing graphic data onto receiving sheet material by subjecting said graphic data to heat-producing irradiation while said data is held in heat-conductive relation with said thermotransfer and receiving sheet materials, the thermotransfer sheet material comprising

- (1) A flexible infra-red-transmitting supporting web base, and
- (2) A thin layer containing sublimable dye coated on one side of said base, said layer comprising a mixture of sublimable fine particles of (a) a leuco methylene blue dye, and (b) a 1,3,3-trimethyl-spiro-[(2'H-1'-benzopyran)-2,2'-indoline] compound homogeneously dispersed in a binder.

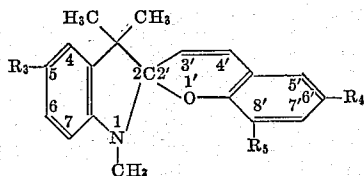
5. The thermotransfer sheet of claim 4 wherein the layer coated on the base material comprises a mixture of fine particles of (a) a leuco methylene blue compound of the formula

(I)



where R_1 is selected from the group consisting of isobutyl, isovaleryl, pivalyl, acetyl, propionyl, and phenyl acetyl; and (b) a photochromic compound of the formula

(III)



wherein R_3 , R_4 , and R_5 are selected from the group consisting of (a) R_4 is NO_2 and R_3 and R_5 are hydrogen, (b) R_3 and R_4 are hydrogen and R_5 is NO_2 , (c) R_3 and R_4 are hydrogen and R_5 is OCH_3 , (d) R_3 is NO_2 , R_5 is OCH_3 , (e) R_3 is Cl, R_4 and R_5 are both NO_2 , (f) R_3 is hydrogen, R_4 is Br, and R_5 is NO_2 , (g) R_3 is Cl, R_4 is hydrogen and R_5 is NO_2 , and (h) R_3 is Cl, R_4 is NO_2 , and R_5 is hydrogen, (i) R_3 is Cl, R_4 is

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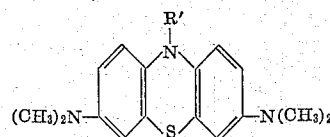
Br and R_5 is NO_2 , and (j) R_3 is Cl, R_4 is NO_2 , and R_5 is OCH_3 .

6. Thermotransfer record sheet material adapted for making copies of heat-absorbing graphic data onto receiving sheet material by subjecting said graphic data to heat-producing irradiation while said data is held in heat-conductive relation with said thermotransfer and receiving sheet materials, the thermotransfer sheet material comprising

- (1) A flexible infra-red-transmitting supporting web base, and
- (2) A thin layer containing sublimable dye coated on one side of said base, said layer comprising a mixture of sublimable fine particles of (a) a leuco methylene blue dye, and (b) a leucauramine compound, said sublimable fine particles being homogeneously dispersed in a binder.

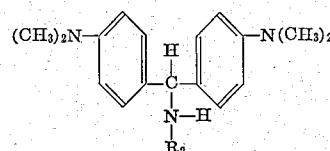
7. The thermotransfer sheet of claim 6 wherein the layer coated on the base material comprises a mixture of fine particles of (a) a leuco-methylene blue dye of the formula:

(I)



wherein R_1 is selected from the group consisting of isobutyl, isovaleryl, pivalyl, acetyl, propionyl, and phenyl acetyl; and (b) a leucauramine compound of the formula:

(II)

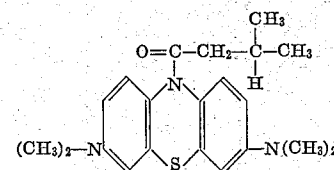


wherein R_2 is selected from the group consisting of:

- 2,5-dichlorophenyl
- 3,4-chlorophthaloyl
- 5-chloro-2-methylphenyl
- p-nitrophenyl
- phenyl

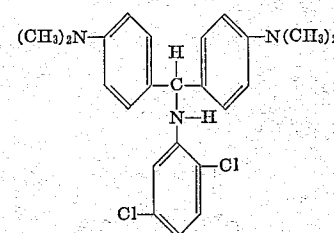
8. The thermotransfer sheet material of claim 7 in which the leuco methylene blue compound has the formula:

50



and the leucauramine compound has the formula

55



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9. A thermotransfer copying system consisting of a three-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic matter, comprising, in order,

- (1) an infra-red-transmitting master sheet having heat-absorptive graphic data areas on one surface thereof,
- (2) a flexible non-infra-red-absorptive thermotransfer sheet consisting of a web base coated on one side with

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a thin layer comprising sublimable dye, said layer comprising a mixture of sublimable fine solid particles of (a) a leuco methylene blue dye, (b) a leucauramine compound, and (c) a 1,3,3-trimethyl-spiro-[2'H-1'-benzopyran)-2,2'-indoline] compound, and

(3) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,

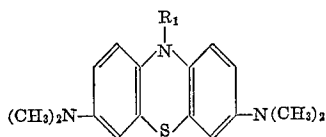
said layer of sublimable dye overlaying said particles of adsorbent material, so that irradiation of the graphic data areas with infra-red rays of suitable duration and energy generates heat in said graphic data areas and, by heat conduction through the supporting web base of sheets 1 and 2 above, forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

10. The thermotransfer copying system of claim 9 in which the coating containing sublimable dye consists of

(1) a polymeric binder, and, homogeneously dispersed therein,

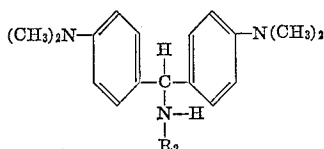
(2) a sublimable mixture of fine particles of (a) a leuco methylene blue compound of the formula

(I)



wherein R_1 is selected from the group consisting of isobutyryl, isovaleryl, pivalyl, acetyl, propionyl, and phenyl acetyl; (b) a leucauramine compound of the formula

(II)

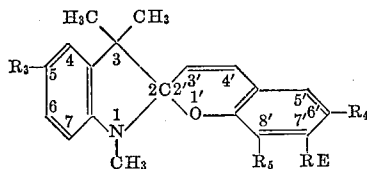


wherein R_2 is selected from the group consisting of:

2,5-dichlorophenyl
3,4-chlorophthaloyl
5-chloro-2-methylphenyl
p-nitrophenyl
phenyl

and (c) a photochromic spiro-pyran compound of the formula

(III)



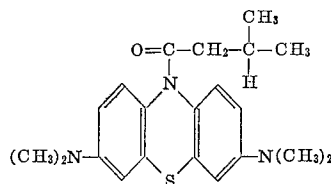
wherein R_3 , R_4 , and R_5 are selected from the group consisting of (a) R_4 is NO_2 and R_3 and R_5 are hydrogen, (b) R_3 and R_4 are hydrogen and R_5 is NO_2 , (c) R_3 and R_4 are hydrogen and R_5 is OCH_3 , (d) R_3 is hydrogen, R_4 is NO_2 , R_5 is OCH_3 , (e) R_3 is Cl, R_4 and R_5 are both NO_2 , (f) R_3 is hydrogen, R_4 is Br, and R_5 is NO_2 , (g) R_3 is Cl, R_4 is hydrogen and R_5 is NO_2 , (h) R_3 is Cl, R_4 is NO_2 , and R_5 is hydrogen, (i) R_3 is Cl, R_4 is Br, and R_5 is NO_2 , and (j) R_3 is Cl, R_4 is NO_2 , and R_5 is OCH_3 .

11. The thermotransfer copying system of claim 10 in which the coating containing sublimable dye consists of (1) a polymeric binder, and, homogeneously dispersed therein,

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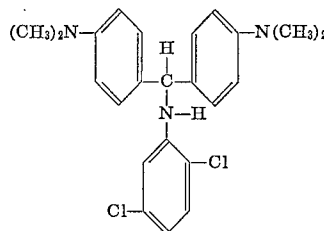
(2) a sublimable mixture of fine particles of (a) the leuco methylene blue compound is a compound of the formula

(I)



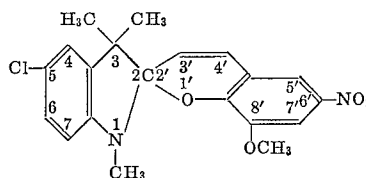
(b) the leucauramine compound has the formula

(II)



and (c) the photochromic compound has the formula

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12. A thermotransfer copying system consisting of a two-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic data, comprising, in order,

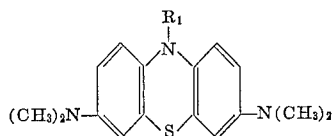
(1) a flexible master sheet consisting of an infra-red-transmitting web base having heat-absorbent graphic data areas disposed on its outer surface, and a thin layer comprising sublimable dye coated on the opposite surface, said layer comprising a mixture of sublimable fine solid particles of (a) a leuco methylene blue dye, (b) a leucauramine compound, and (c) a 1,3,3-trimethyl-spiro-[2'H-1'-benzopyran)-2,2'-indoline] compound, and

(2) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,

said adsorbent material held in contact with said sublimable dye, so that irradiation of said graphic areas with infra-red rays of suitable duration and energy generates heat in said graphic areas and by heat conduction through the master sheet supporting web base 1 forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

13. The thermotransfer copying system of claim 12 wherein the thin sublimable dye layer comprises a polymeric binder having homogeneously dispersed therein a sublimable mixture of fine particles of (a) a leuco methylene blue compound of the formula

(I)

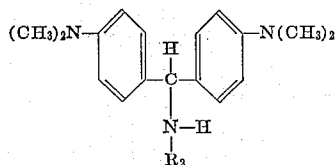


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wherein R_1 is selected from the group consisting of isobutyryl, isovaleryl, pivalyl, acetyl, propionyl, and phenyl acetyl; (b) a leucauramine compound of the formula

(II)

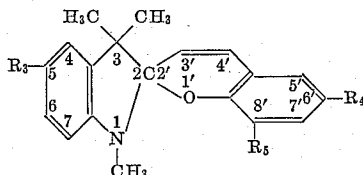


wherein R_2 is selected from the group consisting of:

2,5-dichlorophenyl
3,4-chlorophthaloyl
5-chloro-2-methylphenyl
p-nitrophenyl
phenyl

and (c) a photochromic spiro-pyran compound of the formula

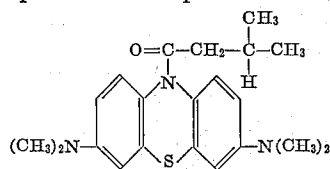
(III)



wherein R_3 , R_4 , and R_5 are selected from the group consisting of (a) R_4 is NO_2 and R_3 and R_5 are hydrogen, (b) R_3 and R_4 are hydrogen and R_5 is NO_2 , (c) R_3 and R_4 are hydrogen and R_5 is OCH_3 , (d) R_3 is hydrogen, R_4 is NO_2 , R_5 is OCH_3 , (e) R_3 is Cl, R_4 and R_5 are both NO_2 , (f) R_3 is hydrogen, R_4 is Br, and R_5 is NO_2 , (g) R_3 is Cl, R_4 is hydrogen and R_5 is NO_2 , (h) R_3 is Cl, R_4 is NO_2 and R_5 is hydrogen, (i) R_3 is Cl, R_4 is Br, and R_5 is NO_2 , and (j) R_3 is Cl, R_4 is NO_2 , and R_5 is OCH_3 .

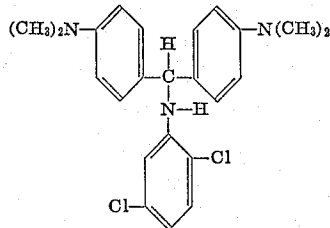
14. The thermotransfer copying system of claim 12 wherein the sublimable dye layer comprises a polymeric binder having homogeneously dispersed therein a sublimable mixture of fine particles of (a) the leuco methylene blue compound is a compound of the formula

(I)

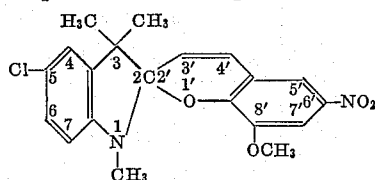


(b) the leucauramine compound has the formula

(II)



and (c) the photochromic compound has the formula



15. A thermotransfer copying system consisting of a three-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic matter, comprising, in order,

(1) an infra-red-transmitting master sheet having heat-absorptive graphic data areas on one surface thereof,

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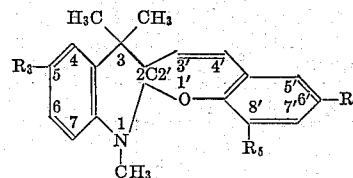
(2) a flexible non-infra-red-absorptive thermotransfer sheet consisting of a web base coated on one side with a thin layer comprising a sublimable indolino benzo spiro pyran dye, and

(3) a flexible base web receiving sheet,

said layer of sublimable dye overlying said base web receiving sheet, so that irradiation of the graphic data areas with infra-red rays of suitable duration and energy generates heat in said graphic areas and by heat conduction through the supporting web base of sheets 1 and 2 forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet as an invisible latent image of said graphic data, said latent image being developed to a distinctive color by brief exposure to ultra-violet light.

16. The thermotransfer copying system of claim 15 wherein the sublimable dye is homogeneously dispersed in a polymeric binder coated on said base, and said dye is a compound having the formula

(III)



wherein R_3 , R_4 , and R_5 are selected from the group consisting of (a) R_4 is NO_2 and R_3 and R_5 are hydrogen, (b) R_3 and R_4 are hydrogen and R_5 is NO_2 , (c) R_3 and R_4 are hydrogen and R_5 is OCH_3 , (d) R_3 is hydrogen, R_4 is NO_2 , R_5 is OCH_3 , (e) R_3 is Cl, R_4 and R_5 are both NO_2 , (f) R_3 is hydrogen, R_4 is Br, and R_5 is NO_2 , (g) R_3 is Cl, R_4 is hydrogen and R_5 is NO_2 , (h) R_3 is Cl, R_4 is NO_2 and R_5 is hydrogen, (i) R_3 is Cl, R_4 is Br, and R_5 is NO_2 , and (j) R_3 is Cl, R_4 is NO_2 , and R_5 is OCH_3 .

17. A thermotransfer copying system consisting of a two-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic data, comprising, in order,

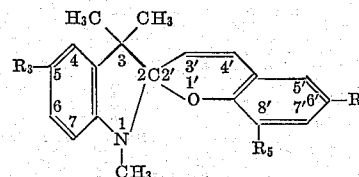
(1) a flexible master sheet consisting of an infra-red-transmitting web base having heat-absorptive graphic data areas disposed on its outer surface, and a thin layer comprising a sublimable indolino benzo spiro pyran dye coated on the opposite surface, and

(2) a flexible base web receiving sheet,

said layer of sublimable dye overlying said base web receiving sheet, so that irradiation of said graphic areas with infra-red rays of suitable duration and energy generates heat in said graphic areas and by heat conduction through the master sheet supporting web base 1 forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet as an invisible latent image of said graphic data, said latent image being developed a distinctive color by brief exposure to ultra-violet light.

18. The thermotransfer copying system of claim 17 wherein the sublimable dye is homogeneously dispersed in a polymeric binder coated on said base, and said dye is a compound having the formula

(III)



wherein R_3 , R_4 , and R_5 are selected from the group consisting of (a) R_4 is NO_2 and R_3 and R_5 are hydrogen, (b)

R₃ and R₄ are hydrogen and R₅ is NO₂, (c) R₃ and R₄ are hydrogen and R₅ is OCH₃, (d) R₃ is hydrogen, R₄ is NO₂, R₅ is OCH₃, (e) R₃ is Cl, R₄ and R₅ are both NO₂, (f) R₃ is hydrogen, R₄ is Br, and R₅ is NO₂, (g) R₃ is Cl, R₄ is hydrogen and R₅ is NO₂, (h) R₃ is Cl, R₄ is NO₂, and R₅ is hydrogen, (i) R₃ is Cl, R₄ is Br, and R₅ is NO₂, and (j) R₃ is Cl, R₄ is NO₂, and R₅ is OCH₃.

19. A thermotransfer copying system consisting of a three-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic matter, comprising, in order,

- (1) an infra-red-transmitting master sheet having heat-absorptive graphic data areas on one surface thereof;
- (2) a flexible non-infra-red-absorptive thermotransfer sheet consisting of a web base coated on one side with a thin layer comprising sublimable dye, said layer consisting of a mixture of sublimable fine particles of (a) a leuco methylene blue dye, and (b) a leucauramine dye, said sublimable fine particles being homogeneously dispersed in a binder, and
- (3) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,

said layer of sublimable dye overlaying said particles of adsorbent material, so that irradiation of the graphic data areas with infra-red rays of suitable duration and energy generates heat in said graphic data areas and, by heat conduction through the supporting web base of sheets 1 and 2 above, forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

20. A thermotransfer copying system consisting of a three-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic matter, comprising, in order,

- (1) an infra-red-transmitting master sheet having heat-absorptive graphic data areas on one surface thereof,
- (2) a flexible non-infra-red-absorptive thermotransfer sheet consisting of a web base coated on one side with a thin layer comprising sublimable dye, said layer consisting of a mixture of sublimable fine particles of (a) a leuco methylene blue dye, and (b) a 1,3,3 - trimethyl - spiro - [(2'H-1'-benzopyran)-2,2'-indoline] compound, said sublimable fine particles being homogeneously dispersed in a binder, and
- (3) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,

said layer of sublimable dye overlaying said particles of adsorbent material, so that irradiation of the graphic data areas with infra-red rays of suitable duration and energy generates heat in said graphic data areas and, by heat conduction through the supporting web base of sheets 1 and 2 above, forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

21. A thermotransfer copying system consisting of a three-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic matter, comprising, in order,

- (1) an infra-red transmitting master sheet having heat-absorptive graphic data areas on one surface thereof,
- (2) a flexible non-infra-red-absorptive thermotransfer sheet consisting of a web base coated on one side with a thin layer comprising sublimable dye, said layer consisting of fine solid particles of a 1,3,3-

trimethyl - spiro-[(2'H-1'-benzopyran)-2,2'-indoline] compound homogeneously dispersed in a binder, and

- (3) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,

said layer of sublimable dye overlaying said particles of adsorbent material, so that irradiation of the graphic data areas with infra-red rays of suitable duration and energy generates heat in said graphic data areas and, by heat conduction through the supporting web base of sheets 1 and 2 above, forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

22. A thermotransfer copying system consisting of a two-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic data, comprising, in order,

- (1) a flexible master sheet consisting of an infra-red-transmitting web base having heat-absorbent graphic data areas disposed on its outer surface, and a thin layer comprising sublimable dye coated on the opposite surface, said layer comprising a mixture of fine particles of (a) a sublimable leuco methylene blue dye, and (b) a sublimable leucauramine compound, said particles being homogeneously dispersed in a binder, and
- (2) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,

said adsorbent material held in contact with said sublimable dye, so that irradiation of said graphic areas with infra-red rays of suitable duration and energy generates heat in said graphic areas and by heat conduction through the master sheet supporting web base 1 forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

23. A thermotransfer copying system consisting of a two-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic data, comprising, in order,

- (1) a flexible master sheet consisting of an infra-red-transmitting web base having heat-absorbent graphic data areas disposed on its outer surface, and a thin layer comprising sublimable dye coated on the opposite surface, said layer comprising a mixture of fine solid particles of (a) a leuco methylene blue dye, and (b) a 1,3,3-trimethyl - spiro - [(2'H-1'-benzopyran)-2,2'-indoline] compound, said particles being homogeneously dispersed in a binder, and
- (2) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,

said adsorbent material held in contact with said sublimable dye, so that irradiation of said graphic areas with infra-red rays of suitable duration and energy generates heat in said graphic areas and by heat conduction through the master sheet supporting web base 1 forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

24. A thermotransfer copying system consisting of a two-sheet array in heat-conductive relation adapted for making colored copies of heat-absorptive graphic data, comprising, in order,

- (1) a flexible master sheet consisting of an infra-red-transmitting web base having heat-absorbent graphic data areas disposed on its outer surface, and a thin layer comprising sublimable dye coated on the opposite surface, in which the coating containing sublimable dye consists of fine solid particles of a 1,3,3-trimethyl - spiro-[(2'H-1'-benzopyran)-2,2'-indoline] compound, said particles being homogeneously dispersed in a binder, and
- (2) a flexible non-infra-red-absorptive web base receiving sheet coated on one side with fine particles of acidic adsorbent material,
- said adsorbent material held in contact with said sublimable dye, so that irradiation of said graphic areas with infra-red rays of suitable duration and energy generates heat in said graphic areas and by heat conduction through the master sheet supporting web base 1 forms a heat pattern in an area of the dye layer corresponding to the heat-energy-absorbing areas of said graphic data, whereupon said heat causes a small fraction of sublimable dye

in the heated area to sublime and then condense on the receiving sheet acidic particles as a visible colored facsimile of the original graphic data.

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