COPY-SHEET
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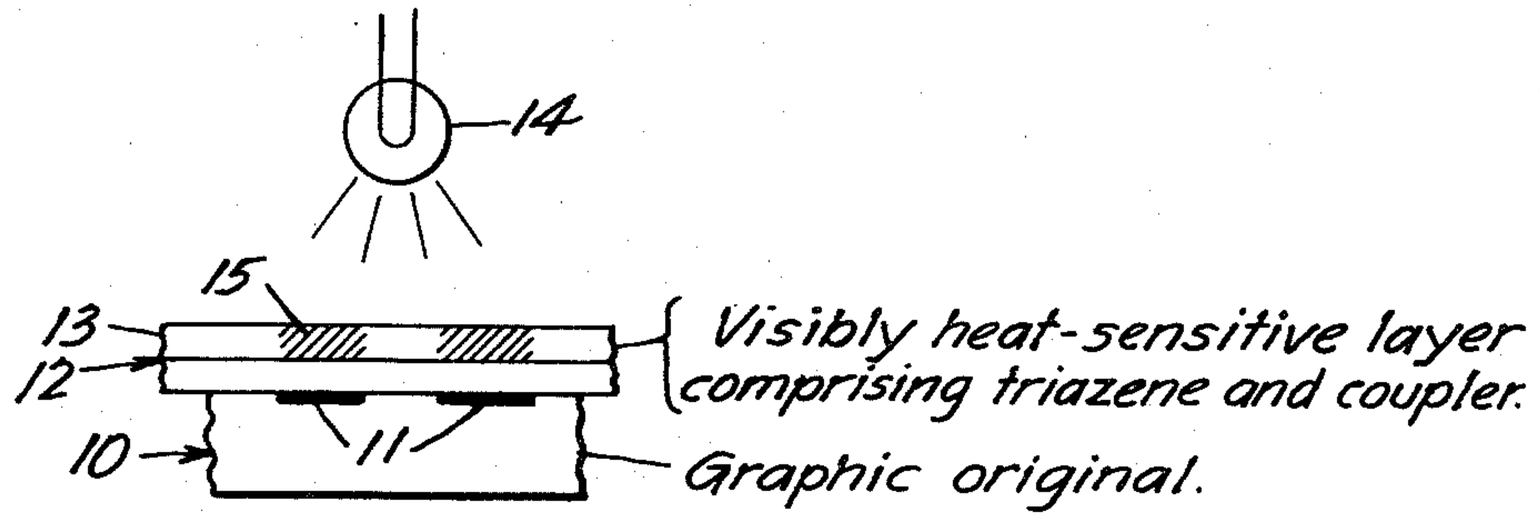

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COPY-SHEET

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This invention relates to the thermographic reproduction of graphic originals, and has particular reference to novel heat-sensitive copy-sheets for use therein.

An important thermographic reproduction process, extensively employed in reproducing office correspondence and the like, involves pressing a heat-sensitive copy-sheet into heat-conductive contact with a graphic original which is subjected to brief intense irradiation, e.g. with radiation rich in infra-red. The heat-pattern produced at the original transfers to the copy-sheet, and a corresponding visible change results. A direct reproduction of the original is obtained.

The heat-sensitive copy-sheet must be rapidly visibly reactive at the temperature attained during the reproduction process, and which is ordinarily within the approximate range of 90–150° C. as determined by indirect methods. At the same time, the copy-sheet must be capable of prolonged storage under normal handling and use conditions without observable discoloration or loss of sensitivity.

Accordingly, the present invention provides novel heat-sensitive copy-sheets which meet the foregoing requirements. The product, while ordinarily faintly colored as initially prepared, does not undergo any observable change in coloration, and remains fully heat-sensitive, under prolonged storage or during ordinary handling as encountered in normal office use. Copies are obtained immediately on exposure to the heat-image and without the use of solutions, vapors, or other additional treatment. The sheets may be designed to produce images in substantially any desired color including the usually preferred dense blue-black.

Water-soluble organic triazenes formed by the condensation of diazo compounds with primary or secondary organic amines having water-solubilizing substituent groups form a well-known class of dyestuff intermediates much used in the color-printing of cellulosic fabrics. The latter process ordinarily involves acid hydrolysis of the triazine, followed by coupling of the liberated diazo compound with an azo coupler component to form a water-insoluble color body. The required acidity and moisture are supplied by exposing the fabric, previously printed with a paste containing the triazene and coupler, to the action of steam and vaporized acetic acid. A modified process calls for the inclusion of a steam-distillable nitrogenous base in the printing paste; removal of the base by treatment with steam then reduces the alkalinity of the system and permits hydrolysis and coupling to occur.

The conventional treatment with steam, while customary and entirely acceptable in the fabric printing industry, cannot be tolerated in the reproduction of office correspondence and similar graphic originals. Use of more readily volatile nitrogenous base materials might possibly be expected to eliminate the necessity for steam distillation; but such materials will volatilize from thin layers at room temperature, and many are toxic. For these and other reasons, the successful application of triazene-coupler systems to the formulation of heat-sensitive copy-sheets useful in the thermographic reproduction of graphic originals would appear to be most unlikely; and no such application has been attempted prior to the present invention, insofar as I am aware.

Surprisingly, it has now been found that heat-sensitive copy-sheets, which are stable under normal storage and handling conditions and which permit the reproduction of graphic originals by thermographic processes in the absence of any applied steam or acid vapor, may be produced with triazene and coupler components as the sole reactants.

The appended drawing illustrates the thermographic reproduction of a graphic original **10**, having radiation-absorptive inked image areas **11**, on a heat-sensitive copy-sheet **12** in heat-conductive pressure-contact therewith. The copy-sheet includes a heat-sensitive layer **13** comprising triazene and coupler components as herein defined. The process involves brief intense irradiation of the composite from a source **14**, and results in formation of visibly distinct converted image areas **15** in the heat-sensitive layer **13**.

Although the reactive materials may be incorporated in an otherwise untreated thin fibrous sheet or in a self-supporting dried binder film, they are preferably applied, together wtih a suitable film-forming binder, as a thin surface coating on a carrier web such as paper or transparent film. Additional layers may be provided, e.g. as surface protective coatings, or to improve contrast or opacity. A preferred structure consists of thin semi-transparent paper coated with a thin heat-sensitive layer of triazene-coupler-binder composition over which is applied a thin opacifying pigment-binder layer, any color changes in the heat-sensitive layer being visible through the paper and against the opaque background.

The triazene component of the heat-sensitive layer may be represented by the formula Ar–N=N–NRR′, wherein Ar represents an aromatic radical, R is an organic radical, and R′ may be an organic radical or hydrogen. Based on the formula and on the preferred method of preparation, such compounds may properly be characterized as primary or secondary amine stabilized aromatic diazonium compounds. The triazene components employed in these copy-sheets are not highly colored, and preferred species are substantially colorless. They are stable toward actinic radiation, e.g. ultraviolet light, and are non-hygroscopic. They are solid at normal room and moderately elevated temperatures. They may or may not melt at temperatures within the conversion range of about 90–150° C. but in any event are substantially non-volatile at such temperatures. Typical illustrative compounds having the structure and characteristics thus defined, and which have been found useful in preparing the heat-sensitive copy-sheets of this invention, include 1,3-diphenyltriazene, 1,3 - diphenyl-3 - methyltriazene, 1-(2-carbomethoxyphenyl)-3-phenyltriazene, 1-(2,5-dichlorophenyl - 3 - phenyltriazene, 1 - (p-N-methylacetamidophenyl)-3 - phenyltriazene, 1-(p-diethylaminophenyl)-3-(p-acetamidophenyl)triazene, 3,3′ - dimethoxy - 4,4′ - diphenylenebis-(3 - methyl-3(sodium methylene carboxylate)-1 - triazene), and 3,3′ - dimethoxy-4,4′diphenylenebis-(3 - methyl-3(sodium betaethylenesulfonate)-1-triazene).

A wide variety of coupling components capable of coupling with diazo compounds to form color-bodies is known, and such components are generally useful in the practice of this invention. Thus many aromatic hydroxy compounds, aromatic amino compounds, and active methylene compounds, previously known to be effective azo couplers, have here been found useful as coupling components. The strongly reactive aromatic hydroxy couplers are preferred, and of these the aryl amides of 3-hydroxy-2-naphthoic acid, known commercially as the Naphtol AS series, are found to be particularly desirable. Exemplary compounds are 3-hydroxy-2-naphthanilide (Naphtol AS) and 3-hydroxy-N-2-naphthyl-2-naphthamide (Naphtol AS–SW).

Although a color-producing reaction between a triazene

compound and an azo coupling component will invariably proceed in the presence of steam and acid vapor, it is found that many of the possible specific combinations do not undergo visible reaction in the form of a thin film or bonded coating when momentarily heated for times and at temperatures available in commercial thermographic copying. However it has been found that components which will immediately visibly interreact when mixed together in a mixture of glacial acetic acid and ethanol at room or moderately elevated temperature are fully reactive in copy-sheet form also, and are eminently suitable for use in the manufacture of normally stable heat-sensitive thermographic copy-sheet products.

The test is conveniently conducted by simply adding a few crystals (roughly about 10 milligrams) of each of the reagents to 5 ml. of a solution of 10 volumes of glacial acetic acid in 90 volumes of 95% ethanol, and gently mixing. Reagents which provide an immediate and distinct color change when thus tested are found to be capable of producing useful heat-sensitive copy-sheets. When no distinct color change occurs in the test at temperatures within the range of about 70–100° F., the reagents are found to be ineffective when combined in copy-sheet form.

The reactants as thus suitably selected are preferably separately dispersed in binder solution as extremely finely divided particles, and the dispersions then combined and coated on a thin paper or transparent film. Water-resistant polymeric binders such as polystyrene, polyvinyl butyral, ethyl cellulose or the like are preferred, and appropriate inert liquid solvents for the particular polymer are easily determined. The coated web is dried at moderate temperatures so as to avoid any premature color-forming reaction.

The nature of the thermographic reproduction process hereinbefore referred to makes difficult the direct measurement of the temperatures attained in the heat-sensitive copy-sheet during said process. An indirect method of temperature determination is therefore ordinarily employed, in which a segment of the copy-sheet is momentarily pressed against a heated metal test bar at a known temperature and any visible effect on the sheet is noted. Copy-sheets which under such test are converted from colorless or weakly colored to visibly distinct and relatively intensely colored form at temperatures within the range of about 90–150° C. are found to produce excellent results in terms of the thermographic reproduction of typewritten or analogous graphic originals on thermographic copy-machines such as the "Thermo-Fax" brand "Secretary" copying machines. Copy-sheets prepared in accordance with each of the examples hereof have been found to be operable within the temperature range indicated and to produce usefully clear and distinct thermographic copies of graphic originals.

In some instances the triazene and coupler components are found to undergo slow inter-reaction, with formation of colored reaction products, when mixed together in the binder solution; and copy-sheets prepared with such materials are likewise found to discolor and lose sensitivity gradually during storage. The stability of such systems may be improved, e.g. by increasing the proportion of binder, or by selecting binder and solvent components in which the triazene and coupler are less soluble, or by forming contiguous but essentially separate coatings of triazene-binder and coupler-binder mixtures. Inert additives, such as pigments and fillers, may be added for special purposes where desired; titanium dioxide, for example, improves the stability of the sheet, increases the copying-speed of the sheet in "front-printing" thermographic reproduction processes, and provides a whiter background for the colored heated image areas. Other variations and modifications, falling within the ambit of the invention, will be apparent or will be suggested by the following illustrative but non-limiting examples.

Example 1

A binder solution was first prepared by dissolving 144 parts by weight of polystyrene resin in a mixture of 288 parts of acetone and 168 parts of commercial heptane. One part of a triazene compound, further identified as a solid water-soluble amine-stabilized tetrazotized o-dianisidine compound, decomposing at about 255° C. when tested for melting point by the capillary tube method, was dispersed in four parts of the binder solution by ball milling. Separately, one part of 3-hydroxy-2-napthoic acid anilide coupling component was similarly dispersed in four parts of the binder solution. The two dispersions were mixed together and coated on map overlay tracing paper by means of a knife-coater set at an orifice of 2 mils (0.002 inch). The sheet was dried at room temperature. It was pale yellow in color, and remained unchanged in appearance after prolonged storage at normal room temperature. Areas heated by momentary contact with a metal test bar at about 150° C. were changed to a deep blue color; the same occurred at heated image areas when the sheet was employed in the thermographic reproduction process.

The triazene component was prepared by reaction in aqueous solution of sodium methylaminoacetate and tetrazotized o-dianisidine. It separated in the form of light yellow crystals on addition of sodium hydroxide to pH 8.5, and was removed by filtration and dried. Tested for melting point (capillary tube), the product decomposed at about 235–255° C. Based on the method of preparation, on analytical tests, and on other evidence, the material is identified as 3,3-dimethoxy-4,4'-diphenylenebis (3-methyl-3-(sodium methylene carboxylate)-1-triazene).

The triazene and coupler materials were also tested by mixing together small portions in glacial acetic acid-ethanol solution as hereinbefore specified. Immediate reaction occurred, the solution becoming an intense dark blue.

Example 2

Dispersions of reactants were prepared as in Example 1 except that the amount by weight of reactant in each case was one-half the amount of binder, and the acetone and heptane were in equal amounts by weight, the total volume being sufficient to provide a coatable mixture. The mixture was coated on map overlay tracing paper at a coating orifice of 3 mils, and dried. Over this layer was then applied a further coating of a composition prepared as a smooth uniform grind of 60 lbs. of zinc oxide pigment, 2 lbs. of "Santocel C" extender, and 75 grams of phthalic anhydride in a solution of 6 lbs. of a resinous copolymer of equal parts of styrene and isobutylene in 132 lbs. of heptane, and the sheet was again dried. The resulting copy-paper appeared white and opaque. Heating at about 150° C. produced a blue coloration in the reactive central layer which was readily visible through the essentially transparent paper carrier web and against the opaque white background provided by the outer coating.

Example 3

Five grams of 3,3'-dimethoxy-4,4'-diphenylenebis (3-methyl-3-phenyl-1-triazene) were dissolved in a solution of 15 grams of polyvinyl butyral in 80 grams of ethyl alcohol. Eight grams of Naphtol AS-Supra hydroxynaphthanilide coupler compound were separately suspended in a solution of 12 grams of polyvinyl butyral in 80 grams of ethyl alcohol. Equal parts of the two were mixed together, coated on transparent "Mylar" polyester film, and dried, to provide a stable heat-sensitive copy-sheet having a faint yellowish tint and converting to a blue color when heated.

The two reactants were found to react immediately when mixed together in small amounts in glacial acetic acid-ethanol test solution, with formation of an intense blue color.

The triazene component in this example is soluble in the binder solution, whereas in Examples 1 and 2 both reactants are substantially insoluble.

The triazene component is light yellow in color. The coupler component is substantially colorless; and this component is therefore employed in excess so as to lighten rather than intensify the shade of the unreacted heat-sensitive layer. As in other examples, the amounts of either component are not critical, provided sufficient of the minor component is present to provide adequate color intensity in the converted heated areas of the copy-sheet.

Example 4

One-half part by weight of phloroglucinol was dissolved in 10 parts of a 10% solution of polyvinyl butyral resin in ethanol. One-half part of 1-(2-carbomethoxyphenyl)-3-phenyltriazene was separately dissolved in 10 parts of the same binder solution. Equal weights of the two solutions were mixed together and the mixture immediately coated on 25 lb. map overlay tracing paper at a coating orifice of 3 mils, and dried in a current of air at room temperature. The coated surface was pale yellow in appearance. It converted to a deep red-orange when pressed for not longer than two seconds against a metal test bar at 150° C., and could be used in reproducing printed originals by the thermographic process when operated at high energy levels.

The phloroglucinol coupler and triazene components were found to produce an intense red-orange color immediately on mixing in the acidified ethanol test solution hereinbefore described.

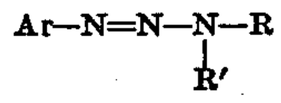
Example 5

One part of 1-(p-N-methylacetamidophenyl)-3-phenyltriazene was dissolved in 40 parts of a 10% solution of vinyl resin (Vinylite VYHH) in acetone. Separately, two parts of 1,5-diaminonaphthalene were mixed into 40 parts of a 10% solution of polyvinyl butyral resin in acetone. The coupler appeared in this example to be partially but not entirely dissolved. Map overlay tracing paper was first coated with a thin uniform layer of the first-named solution, applied by knife-coating at an orifice of 2 mils, and the coated sheet was thoroughly dried at moderately elevated temperature. A layer of the second-named solution was applied over the first layer at approximately the same coating thickness and was thoroughly dried, in this instance at room temperature. The resulting sheet was a light pink in color, turning a dark red when momentarily placed in contact with a metal test bar at 150° C., and producing effective reproductions of printed originals by thermographic procedures. The reactants immediately produced an intense deep red color when mixed together in the acetic acid-ethanol test solution.

What I claim as my invention is as follows:

1. A heat-sensitive copy-sheet adapted for making clear

and sharp reproductions of graphic originals by a thermographic process involving brief application of a heat-pattern corresponding to said original, said copy-sheet being stable under normal handling and use conditions and being rapidly permanently visibly changed on momentary contact with a metal test bar at a temperature within the range of about 90–150° C., said copy-sheet including a thin visibly heat-sensitive layer containing, in intimate association, reactants consisting of azo coupling component and solid, light-stable, non-hygroscopic triazene substantially non-volatile at temperatures up to about 150° C. and having the formula



wherein Ar is an aromatic radical, R is selected from the class of organic radicals and hydrogen, and R′ taken alone is an organic radical; and said coupling component and said triazene being further characterized as being immediately visibly inter-reactive when a few crystals, i.e. about 10 mgms., of each are gently mixed together in 5 ml. of a test solution of 10 volumes of glacial acetic acid in 90 volumes of 95% ethanol, as herein described.

2. A heat-sensitive copy-sheet as defined in claim 1 in which the triazene is an amine-stabilized tetrazotized o-dianisidine.

3. The heat-sensitive copy-sheet of claim 1 in which the visibly heat-sensitive layer includes a polymeric film-forming binder.

4. The heat-sensitive copy-sheet of claim 3 in which the heat-sensitive layer exists as a coating on a carrier web.

5. The heat-sensitive copy-sheet of claim 4 in which the carrier web is a transparent paper.

6. The heat-sensitive copy-sheet of claim 5 in which the heat-sensitive coating is further coated with an opaque protective surface coat comprising an opaque color-contrasting pigment and a binder.

7. The heat-sensitive copy-sheet of claim 1 in which the diazo coupling component is an aromatic hydroxy compound.

8. The heat-sensitive copy-sheet of claim 1 wherein the triazene is an amine-stabilized tetrazotized o-dianisidine and the coupler is an aryl amide of 3-hydroxy-2-naphthoic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,663,655	Miller et al.	Dec. 22, 1953
2,663,656	Miller et al.	Dec. 22, 1953
2,748,024	Klimkowski et al.	May 29, 1956
2,838,994	Lebl et al.	June 17, 1958
2,873,668	Klimkowski et al.	Feb. 17, 1959
2,899,334	Crevling et al.	Aug. 11, 1959