

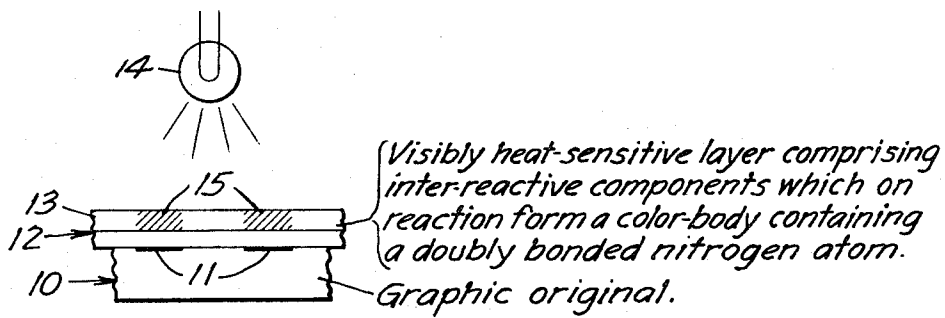
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HEAT-SENSITIVE COPY-SHEET

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HEAT-SENSITIVE 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 placing a heat-sensitive copy-sheet in heat-conductive pressure-contact with a differentially radiation-absorptive graphic original and subjecting the latter to brief intense irradiation, e.g. with radiation rich in infra-red. The heat-pattern produced in the original transfers to the copy-sheet; there results a corresponding visible change in the latter. A true reproduction of the original is produced directly, without the necessity of subsequent treatment with solutions or vapors to develop a latent image, or of other processing.

Stable heat-sensitive copy-sheets useful in preparing reproductions of graphic originals by thermographic procedures as thus defined have previously been described. One popular variety obtains the desired visible change by chemical reaction of components including salts or soaps of various heavy metals.

The present invention likewise provides normally stable heat-sensitive copy-sheets which are useful in the direct thermographic reproduction of graphic originals, solely through the action of radiant energy and without the addition of solutions or vapors or other analogous adjuvants, but which distinguish over the prior art in that the image-forming reaction is caused to occur between exclusively organic interreactant materials, with formation of an organic dye or color-body containing a doubly bonded nitrogen atom as an essential chromophore group.

The heat-sensitive copy-paper of this invention ordinarily includes a thin paper support web coated on one surface with a thin layer of a visibly heat-sensitive composition. Various binder materials may be employed where required for maintaining the heat-sensitive reactants in position. Such binders may be applied in monomeric or sub-polymeric form and then polymerized in situ, but are more conveniently handled as solutions of the polymeric material in volatile solvents which are subsequently removed. Additional coatings may be provided; for example a white opaque protective surface layer is frequently placed over a heat-sensitive layer on a transparent paper or film support web. Treated or impregnated paper, polymeric film, or other analogous fibrous or non-fibrous webs are useful as support or backing members. The heat-sensitive materials may be applied as a coating or incorporated within the body of the supporting web. These and other variations and modifications will become apparent on consideration of the following several illustrative but non-limiting working examples, in which all proportions are given in parts by weight unless otherwise specified.

Example 1

This example provides a normally stable heat-sensitive

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copy-sheet which converts from an off-white to a greenish black color at image areas under thermographic reproduction procedures through the controlled formation of an oxazine dye.

Three separate smooth mixtures are first prepared by ball-milling. Mixture A consists of 10 parts of gallic acid, 10 parts of polycarbonate resin ("Lexan" polycarbonate resin, and 80 parts of dioxan volatile liquid solvent. Mixture B is prepared from 5 parts of 3-methyl-4-nitrosophenol, 10 parts of polycarbonate resin, and 85 parts of dioxan. Mixture C contains 5 parts of p-N-methylacetylaminobenzene diazonium fluoborate, 10 parts of polystyrene resin, and 85 parts of acetone.

Mixture C is first applied as a thin uniform coating on flexible transparent polyester film (3-mil "Mylar" polyester film) by knife coating at an orifice of 2 mils, and dried. Equal weights of mixtures A and B are then blended together and the mixture applied by knife coating at an orifice of 3 mils over the dried first coating. The dried sheet is heat-sensitive and semi-transparent. A further thin coating of a mixture of 40 parts of titanium dioxide pigment, 10 parts of butadiene-styrene 3:1 copolymer ("Pliolite S-7"), and 50 parts of toluene, likewise prepared on the ball mill, is preferably next applied over the heat-sensitive coating and dried, to provide an opaque off-white background against which the dark-colored image areas produced in the thermographic copy-process are distinctly visible when viewed through the transparent polyester film. Color formation occurs substantially instantaneously in the dry copy-sheet on heating to or above the decomposition temperature of the diazonium fluoborate complex, i.e. to approximately 135° C. On again cooling the sheet, the dye-forming reaction immediately terminates, so that the initial sharp outline of the reproduced image areas is maintained and the background areas remain unaltered.

Other pairs of oxazine-dye-forming organic reactants which have likewise given good results in the preparation of heat-sensitive copy-sheets include: 2-hydroxy-3-methyl-5-nitrosobenzoic acid with gallic acid or resorcinol; nitrosothymol with gallic acid or 3-hydroxy-2-naphthoic acid or beta-naphthol; and para-nitrosobenzoic acid with gallic acid. In all cases these inter-reactant oxazine dye progenitors are colorless or weakly colored solids which react readily when mixed together in aqueous acetic acid at room temperature or with gentle warming.

Example 2

In this example the several components of the heat-sensitive layer are supplied from a single coating mixture, while still maintaining excellent stability even under high ambient humidity storage and use conditions.

Two mixtures are first separately prepared, e.g. by ball milling. One contains 10 parts of N-carbethoxy-p-nitrosodiphenylamine, 10 parts of methyl methacrylate resin ("Lucite 44" resin), and 80 parts of acetone. The second contains 9 parts of gallic acid, one part of (3-chloropropenyl) benzene, 10 grams of the methacrylate resin, and 80 parts of acetone. A blend of two parts of the first and three parts of the second is smoothly coated on 25 lb. map overlay tracing paper at an orifice of 3 mils, and dried at room temperature. The resulting light yellowish sheet forms deep blue heated image areas in the thermographic reproduction process herein described.

The color is due to the formation of an oxazine dye, as in Example 1.

Another dye-forming combination employing the same N-carbalkoxy nitroso compound and which has provided useful heat-sensitive copy-sheets in structures as here indicated contains N-carbethoxy-p-nitrosodiphenylamine and 3-hydroxy-2-naphthoic acid.

Example 3

The present example likewise provides heat-sensitive copy-sheets having excellent stability and light background color, and producing dark blue or blue-black heat-image areas.

Three parts of a first mixture of 6.8 parts of N-nitroso-diphenylamine, 8.2 parts of ethyl cellulose, and 85 parts of a 55:45 blend of acetone and heptane, are uniformly blended with two parts of a second mixture of 6.8 parts of protocatechuic acid, 1.0 part of alpha-naphthoylchloride, 8.2 parts of ethyl cellulose, and 84 parts of the acetone-heptane blend. The composition is coated on map overlay tracing paper using a coating orifice of 3 mils, and the sheet is dried at room temperature. The off-white sheet product converts to intense blue at heated image areas in the thermographic reproduction process.

Equally effective copy-sheets are produced on substitution of equivalent amounts of N-nitrosophenylbenzylamine for the N-nitrosodiphenylamine.

In each of the foregoing examples the principal color-body produced in the heated copy-sheet is an oxazine dye; and in each instance color formation proceeds by a mechanism involving conversion to reactive form of an initially non-reactive progenitor material in the presence of an acidic component. Thus in Example 3 the non-reactive N-nitroso compound first rearranges to a C-nitroso compound; in Example 2 the carbalkoxy group, which initially prevents coupling by steric hindrance, is decomposed and removed; and in each of Examples 1-3 the nitroso compound as thus formed or as initially present is converted to an intermediate reactive oxime which immediately couples with the aromatic hydroxy compound, producing an oxazine dye wherein a doubly bonded nitrogen atom is an essential chromophore.

A somewhat similar sequence occurs in each of the following examples, in which other classes of color-bodies form the image areas.

Example 4

Transparent polyester film is first coated with a two-mil layer of a smooth dispersion of 5 parts of para-aminoacetanilide benzenediazonium fluoborate in a solution of 10 parts of "Parapal" isobutylene-styrene resin in 85 parts of methylcyclohexane. Over the dried coating there is then applied a further 3-mil layer of a blend of equal parts of a first mixture of 10 parts of 3,3'-dimethoxy-4,4'-diphenylenebis(3-methyl-1-triazene), 10 parts of "Dow 700" polystyrene resin, and 80 parts of acetone, and a second mixture of 10 parts of "Naphtol AS-Supra" azo coupler, 10 parts of polystyrene resin, and 80 parts of acetone. The dried sheet is light yellow in color, stable under all normal office handling and filing, and convertible to deep blue at heat-image areas under thermographic reproduction conditions. The color-body produced is an azo dye, containing doubly bonded nitrogen as an essential chromophore.

The two layers may be reversed, the triazene-coupler layer being coated directly on the transparent film; or the components of the two layers may be mixed together and applied simultaneously. In the absence of the acid-liberating component, the triazene-coupler layer of this example does not form a visible image when subjected to thermographic reproduction processes in commercially available equipment. With the acid-progenitor present, cleavage of the normally stable triazene occurs under the thermographic heating, with formation of an intermediate diazo component which then immediately couples with the azo coupler component.

Since azo dyes of almost any color are available, the triazene-coupler combination provides for wide variety of image color; and the stability obtainable with triazene-coupler combinations permits the attaining of fully stable copy-sheets which retain their heat-sensitivity and show no discoloration or background darkening in normal storage and use.

Typical triazenes which have been used in producing these stable copy-sheets include 1,3-bis(2-carboxyphenyl) triazene, 1-(2-carboxyphenyl)-3-phenyl-3-ethyltriazene, 1-(2-methyl-4-chlorophenyl)-3-(p-N-methylacetamidophenyl) triazene, N-phenylazoisatoic anhydride, 3,3'-dimethoxy-4,4'-diphenylenebis(3-methyl-3-phenyl-1-triazene), 3-phenyl-4-oxo-3,4-dihydro-1,2,3-benzotriazine, and 4-hydroxy-1,2,3-naphthotriazene.

Other somewhat more reactive triazenes are known which in dry sheet form possess adequate stability and undergo a color-producing reaction with the azo coupler component at or near maximum commercially available thermographic copying conditions even in the absence of acid-progenitors. The incorporation of the diazonium fluoborate of Example 4 or analogous sources of Lewis acids in such sheets greatly increases the rate and decreases the temperature required for producing effective copy of graphic originals on copy-sheets employing such compounds, while having no deleterious effect on the stability of the sheet. Typical of such triazenes are 1-(2-carbomethoxyphenyl)-3-phenyltriazene and 1-(p-N-methylacetamidophenyl)-3-phenyltriazene. Compounds such as 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) are likewise useful and, while not strictly organic, on cleavage yield reactive organic diazo intermediates and are considered to be organic triazenes.

Although aromatic amine compounds and active methylene compounds known to be useful as azo coupling components are also applicable in the preparation of these copy-sheet materials in many instances, it is preferred to employ the more strongly reactive aromatic hydroxy azo couplers in copy-sheets prepared as in Example 4; and of these, the aryl amides of 3-hydroxy-2-naphthoic acid, known commercially as the "Naphtol AS" series of azo couplers, are found to be particularly desirable. Exemplary compounds are 3-hydroxy-2-naphthanilide and 3-hydroxy-N-2-naphthyl-2-naphthamide.

In addition to those illustrated in Examples 1 and 4, other diazonium fluoborates useful in these heat-sensitive copy-sheet formulations include para-acetylaminobenzenediazonium fluoborate, meta- and ortho-carboxybenzenediazonium fluoborate, orthophenylbenzenediazonium fluoborate, 3,5-dimethylbenzenediazonium fluoborate, para-(bisbenzenediazonium fluoborate), and ortho-carboxybenzenediazonium fluoborate. These compounds may effectively be replaced by analogous benzenediazonium hexafluorophosphates, exemplified by such compounds as para-anilinobenzenediazonium hexafluorophosphate, para-N-methylacetylaminobenzenediazonium hexafluorophosphate, para-acetylaminobenzenediazonium hexafluorophosphate, and para-chlorobenzenediazonium hexafluorophosphate. Each of these compounds is decomposable on heating under the time-temperature conditions of the thermographic reproduction process, with liberation of a Lewis acid which will be recognized from the above as including BF₃ and PF₃.

Example 5

Still a further specific illustration is provided by applying to a transparent thin carrier web a 3-mil coating of a mixture of 1 part of alpha-chlorophenylacetate, 5 parts of para-aminoacetanilide, 10 parts of polyvinyl formal ("Formvar") resin, and 84 parts of ethanol. Over the dried coating is next applied a thin opacifying layer of 40 parts of titanium dioxide, 10 parts of "Pliolite S-7" butadienestyrene copolymer, and 50 parts of toluene.

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The dry sheet is pure white and forms a brown heat-image. The reaction involves the formation in the dry heat-sensitive layer of a Schiff's base color-body by acid-induced liberation of aldehyde from the polyvinyl formal followed immediately by inter-reaction of the aldehyde and the p-aminoacetanilide. The color-body contains doubly bonded nitrogen as an essential chromophore. The polyvinyl formal resin serves both as a reactant progenitor and as a polymeric binder thus simplifying the preparation of the coating composition.

The same effect is attained with the same binder resin in conjunction with other reactive amino compounds including p-amino-N-methylacetanilide, dodecylamine, and p-phenylenediamine. Other acetal-type binders, e.g. polyvinyl butyral ("Butvar") resin, are equally as effective as the "Formvar" resin. Inert binders may be included if desired, although simplified formulations as described in the example are much preferred. Likewise, other equally reactive and otherwise suitable non-polymeric solid acetals may be incorporated together with suitable organic amines in a coating composition including an inert binder component, to provide useful but less desirable heat-sensitive copy-sheet materials.

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.

The invention is further illustrated in the drawing in which is schematically portrayed the thermographic reproduction of a graphic original 10, having radiation-absorptive inked image areas 11, on a copy-sheet 12 prepared in accordance with the invention and including a heat-sensitive layer 13 comprising inter-reactant components, which on reaction form a color-body containing a doubly bonded nitrogen atom, and an acid progenitor which liberates a Lewis acid on momentary heating. 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.

It will be understood that other equivalent specific structures employing the various reactant systems or equivalents thereof in other combinations are also to be considered as coming within the scope of the invention. For example, the opaque protective surface coating of Examples 1 and 5 may be omitted, or may be added to the copy-sheets of Examples 2-4 where the carrier web is transparent. The two coatings forming the heat-sensitive layer of Example 1 may be combined in a single coating, or separately applied in inverse order. Given a binder of sufficient strength and in sufficient amount, the heat-sensitive layer may be made in the form of a self-sustaining film; or the reactant materials may be supported within a fibrous web in the virtual absence of a film-forming binder.

Selection of the specific compound or class of compounds to be introduced as the acid-progenitor in any particular formulation will depend not only on the tem-

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perature at which the color-forming reaction is desired to occur but also on the other specific components of the formulation. Thus the fluoborate and fluophosphate compounds are preferably employed with binders soluble in hydrocarbon solvents, since their activity is reduced when combined in alcohol with binders soluble therein, presumably by some side-reaction. Again, formulations containing reactive amino components which are capable of forming color-bodies with diazonium radicals are preferably prepared with active-halogen-containing acid-progenitors rather than with the fluoborates or the like. On the other hand, since the acid-progenitors containing active halogens require the presence of amines, hydroxy compounds, or other sources of active hydrogen atoms for the effective liberation of a Lewis acid, other classes of acid-progenitors must be selected for formulations devoid of such compounds or sources.

The active-halogen-containing acid-progenitors of Examples 2, 3 and 5 and other useful compounds of the same general structure having one or more halogen atoms in activated positions on the skeletal carbon chain or ring, may be selected and characterized as being capable of precipitating the corresponding silver halide from an alcoholic aqueous solution of silver nitrate. As an illustration, the addition of a solution of one part of alpha-naphthoylechloride in ten parts of ethanol to a solution of one part of silver nitrate in ten parts of ethanol and ten parts of water produces an immediate copious precipitation of silver chloride.

What is claimed is as follows:

1. A heat-sensitive copy-sheet adapted for making a clear and sharp reproduction of a graphic original by a dry thermographic process involving brief application of a heat-pattern corresponding to said original, said copy-sheet being visibly stable under normal storage conditions and being rapidly permanently visibly changed on heating to a conversion temperature within the approximate range of 90-150° C., said copy-sheet including a visibly heat-sensitive layer containing, in intimate association, (1) weakly colored, normally solid, essentially non-hygroscopic and non-volatile, inter-reactant progenitors of intensely colored organic color-bodies containing doubly bonded nitrogen as an essential chromophore, one of said progenitors being acid-convertible to a modification which under acidic conditions is rapidly visibly irreversibly inter-reactive with another of said progenitors, and (2) acid-progenitor means, stable under said normal storage conditions and liberating a Lewis acid on being momentarily heated at said conversion temperature.

2. A heat-sensitive copy-sheet as defined in claim 1 in which the acid-progenitor means is a Lewis acid complex of a substituted-benzene diazonium radical.

3. A heat-sensitive copy-sheet as defined in claim 2 in which the acid-progenitor means is a fluoborate complex of a substituted-benzene diazonium radical.

4. A heat-sensitive copy-sheet as defined in claim 2 in which the acid-progenitor means is a hexafluorophosphate complex of a substituted-benzene diazonium radical.

5. A heat-sensitive copy-sheet as defined in claim 1 in which the acid-progenitor means includes a halogen-containing organic compound and a source of active hydrogen atoms, said compound being further characterized as being reactive with aqueous alcoholic silver nitrate solution, with formation of silver halide.

6. A heat-sensitive copy-sheet as defined in claim 5 in which the source of active hydrogen atoms is a non-tertiary amine.

7. A heat-sensitive copy-sheet as defined in claim 1 in which the inter-reactant progenitors are further characterized as being capable of forming an oxazine dye color-body when mixed together as dilute solutions under acidic conditions at moderately elevated temperatures.

8. A heat-sensitive copy-sheet as defined in claim 1 in which the inter-reactant progenitors are further characterized as being capable of forming an azo dye color-body when mixed together as dilute solutions under acidic conditions at moderately elevated temperatures.

9. A heat-sensitive copy-sheet as defined in claim 1 in which the inter-reactant progenitors are further characterized as being capable of forming a Schiff's base color-body when mixed together as dilute solutions under acidic conditions at moderately elevated temperatures.

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