

1

3,146,348

HEAT-SENSITIVE COPY-SHEET

Wesley R. Workman, St. Paul, Minn., assignor to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware
 No Drawing. Filed Sept. 25, 1961, Ser. No. 140,237
 5 Claims. (Cl. 250—65)

This invention relates to the reproduction of graphic originals, such as printed matter or the like, by methods involving the application to a heat-sensitive copy-sheet of a heat-pattern conforming to said original. The invention has particular reference to novel heat-sensitive copy-sheet materials useful in such processes and which additionally are capable of providing fully stabilized permanent copies, and to methods of making and using the same.

One well-known and commercially important method for copying typewritten office correspondence and other differentially radiation-absorptive graphic originals is known as thermographic reproduction and involves brief irradiation of the original with high-intensity radiation, such as infra-red radiation, while the original is in heat-conductive pressure-contact with the heat-sensitive copy-sheet. Image areas of the copy-sheet corresponding to the radiation-absorptive inked areas of the original are visibly changed; background areas remain unchanged and still heat-sensitive. The present invention provides for the preparation, on initially heat-sensitive copy-sheets, of thermographic copies having visibly distinct image areas but in which the background areas are stabilized, i.e. rendered insensitive to heat. Stability is attained without chemical treatment, as with solutions or vapors, simply by subjecting the initially formed copy to additional radiation. The process may alternatively be applied in reverse, background areas being first insensitized and image-forming areas subsequently visibly changed; or the two steps may be accomplished simultaneously.

One form of heat-sensitive copy-sheet which has previously been found useful in thermographic copying comprises a visibly heat-sensitive layer containing dye-forming reactant materials which when heated together, as in the thermographic reproduction process just described, form an azo dye by a reaction involving oxidative coupling. Typically, a mixture of a heterocyclic hydrazone, an azo coupler, and, as an oxidizing agent, an organic amide having a positive halogen atom attached to a nitrogen atom, is deposited with a small amount of a suitable film-forming binder on a paper, film, or other thin flexible carrier web. The sheet is stable at room temperature, but localized heating of image areas, e.g. in the thermographic copying process or by brief contact with heated metal surfaces at temperatures of the order of 90–150° C., causes rapid reaction and color formation. The unheated background areas may subsequently be similarly visibly changed by heating.

A preferred form of the heat-sensitive copy-sheet of this invention is represented by the following symbolic diagram:

Coating containing heterocyclic hydrazone, azo coupler, N-chloro organic oxidizing agent, and photodecomposable progenitor of a reducing agent

paper-like backing

It has now been found that heat-sensitive copy-sheets as just described may be made capable of desensitization by actinic irradiation, by incorporating therein a photosensitive component which decomposes, when suitably irradiated, to yield in effect an inhibitor for the color-forming heat-reaction.

2

As noted hereinabove, an essential component of copy-sheets according to the present invention is a heterocyclic hydrazone. In order to provide stability and to avoid premature color formation in the heat-sensitive copy-sheet during storage prior to use, the hydrazone component is introduced in the form of a normally solid condensation composite of a heterocyclic hydrazone and an amine-reactive organic compound. Typical of such condensation products are the following:

- 3-methyl-2-benzothiazolinone tetradecanoylhydrazone;
- 3-methyl-x-sulfo-2-benzothiazoline acetylhydrazone (wherein the x signifies that the specific position of the sulfo group on the benzene ring is uncertain);
- 3-methyl-2-benzoselenazolinone acetylhydrazone;
- 3-ethyl-2-benzoxazolinone benzenesulfonylhydrazone;
- 1,3-dimethyl-5-methoxy-2-benzimidazolinone benzoylhydrazone;
- 3-methyl-4,5,6,7-tetrahydro-2-benzothiazolinone acetylhydrazone;
- 1-methylcarbostyryl phenoxyacetylhydrazone;
- 2-methylisocarbostyryl acetylhydrazone;
- 3,3-dimethyl-1-ethyloxindole octanoylhydrazone;
- 1-methylnaphtho(1,2-d)thiazolin-2-one acetylhydrazone;
- 3-methyl-2-benzothiazolinone methanesulfonylhydrazone;
- 3-methyl-2-benzothiazolinone acetylhydrazone;
- 3-methyl-2-benzothiazolinone semicarbazone;
- 3-methyl-2-benzothiazolinone p-toluenesulfonylhydrazone; and
- 3-methyl-2-benzothiazolinone carbethoxyhydrazone.

The hydrazones are capable of oxidation to intermediate diazonium compounds or residues which are reactive with azo coupling components to yield azo dyes. In the present invention, oxidation at elevated temperature is effected through the presence of a normally solid organic oxidizing agent having a positive chlorine or bromine atom attached to a nitrogen atom, typical representative examples of such compounds including:

- N-chlorosuccinimide;
- N-chlorophthalimide;
- Chloramine T;
- N,N',4,4'-tetrachlorooxanilide;
- N-chloro-N-methyl-m-nitrobenzenesulfonamide;
- N,N'-dichloro-N,N'-bis(m-nitrobenzenesulfonyl)-ethylenediamine;
- N,N'-dichloro-N,N'-bis(p-toluenesulfonyl)-ethylenediamine;
- N-chloro-N-ethyl-m-nitrobenzenesulfonamide;
- N,N'-dichloro-N,N'-bis(m-nitrobenzoyl)-ethylenediamine;
- N,N'-dichloro-N,N'-dibenzoyl-ethylenediamine;
- N,N'-dichloro-N,N'-diethylbiphenylenesulfone-4,4'-disulfonamide;
- N,N'-dichloro-N,N'-dimethylbiphenylenesulfone-4,4'-disulfonamide;
- N,N'-dichloro-N,N'-dimethylbiphenyl-4,4'-disulfonamide; and trichloromelamine. Chloranil is another chlorine-containing organic oxidizing agent which is fully equivalent for the purposes of this invention.

Reaction of the reactive diazonium residue with an azo coupler component produces a colored product which is responsible for the image color in the finished copy. Phenol, naphthol, aromatic amine, and alpha-keto methylene azo coupler components are all useful, although the naphthol-based "Naphtol AS" series of azo couplers are preferred. Representative examples of azo coupler com-

ponents useful in the practice of the invention include the following:

2-hydroxy-3-naphthanilide;
N-(2-naphthyl)-2-hydroxy-3-naphthamide;
N-(2-chloro-4-methylphenyl)-2-hydroxy-3-naphthamide;
N-(2,5-dimethoxyphenyl)benzoylacetylamide;
1-phenyl-3-methyl-5-pyrazolone;
1-phenyl-3-amino-5-pyrazolone;
S-acid;
H-acid;
N-phenyl-J-acid;
Salicylanilide;
Salicylamide;
N-(2-naphthyl)-1-hydroxy-2-naphthamide;
Ethyl 1-hydroxy-2-naphthoate;
Phenyl 1-hydroxy-2-naphthoate; and
4,4'-bi-o-acetoacetotoluidide.

Certain hydrazone-coupler composites which combine the functions of the oxidizable diazonium-forming hydrazone and the diazonium-reactive dye-forming azo coupler component may be used together with or in place of such coupler component or of the mixture of separate coupler and hydrazone, with the added advantage of generally darker-colored heat-reaction products than would normally be anticipated on the basis of reaction between the diazonium and coupler fragments forming such composites. One such composite is 3-methyl-2-benzothiazolinone-1'-hydroxy-2'-naphthoylhydrazone, melting at 194° C. and prepared by heating under vacuum, with elimination of phenol, a mixture of approximately equimolar quantities of 3-methyl-2-benzothiazolinone hydrazone and phenyl-1-hydroxy-2-naphthoate. Other composites, prepared by analogous condensation reactions and useful in the practice of the invention, include:

3-methyl-2-benzothiazolinone 2'-hydroxy-3'-naphthoylhydrazone;
3-methyl-2-benzothiazolinone 1'-phenyl-5'-pyrazolone-3'-carbonylhydrazone;
3-methyl-2-benzothiazolinone benzoylacetyldiazine;
3-methyl-2-benzothiazolinone 2'-naphthol-7'-sulfonylhydrazone;
3-methyl-2-benzothiazolinone salicylylhydrazone; and
3-methyl-4,5,6,7-tetrahydrobenzothiazolinone 1-hydroxy-2-naphthoylhydrazone.

In addition to the foregoing classes and combinations of reactants, the copy-sheets of the present invention include one or more photosensitive N-substituted p-amino-benzene diazonium salts. These compounds decompose when exposed to radiation in the near ultraviolet. The decomposition products, or at least certain of them, are highly reactive with the N-chloro oxidizing agent which is thereby consumed, thus rendering the sheet no longer visibly heat-sensitive. Representative exemplary compounds include the following:

N,N-diethyl-p-aminobenzene diazonium hexafluorophosphate;
N,N - diethyl-p-amino-o-methyl-benzenediazonium zinc chloride complex;
N - ethyl-N-betahydroxyethyl-p-aminobenzene diazonium hexafluorophosphate;
N-phenyl-p-aminobenzene diazonium acid sulfate;
N-phenyl-p-aminobenzene diazonium tetrafluoroborate;
N - phenyl-p-aminobenzene diazonium hexafluorophosphate; and
N - ethyl-N-betahydroxyethyl-p-aminobenzene diazonium zinc chloride complex.

Stoichiometric proportions of the several reactants may be determined and are effective but do not necessarily produce the best results. The color-forming components must be present in amounts sufficient to produce a readily visible change in the copy-sheet on heating, but may be considerably diluted with non-reactive components, e.g. resins, polymeric binder materials, pigments or fillers, or

various other additives. For example, addition to the heat-sensitive layer of significant amounts of titanium dioxide pigment provides a white background against which the heat-formed colored image areas show increased contrast.

Sufficient oxidizing agent must of course be present to cause adequate oxidation of hydrazone to reactive diazonium intermediate at heated image areas so that an effectively visible image is produced; but excess amounts provide no useful function and are to be avoided. The amount of photosensitive diazonium salt required is directly dependent on the amount of oxidizing agent; sufficient of the salt must be present so that all of the oxidizing agent may be rendered ineffective. Here again, excessive amounts are to be avoided, since any un-used portion adds to the cost of the sheet, imparts a yellow color to the sheet, and is destroyed only after excessive light-exposure. Preferably, the diazonium salt is added in an amount about 5-20% in excess of the amount required to produce, on complete photodecomposition, an amount of reactant sufficient to react with all of the oxidizing agent.

All of the reactants are preferably mixed together in a common binder composition and applied to a paper or film or other paper-like supporting web as a single layer. Alternatively, the several components may be applied separately or in various sub-combinations and with the same or different binders and volatile vehicles. The reactants may be distributed between two separate sheets which are then held in face-to-face contact to provide a unitary sensitive copy-sheet product.

Best results in terms of light-sensitivity are obtained with the photosensitive diazonium compounds applied from solution, although extremely fine dispersions are also useful. The remaining reactants may likewise be applied either as solutions or as dispersions, the latter procedure being preferred wherever there exists any likelihood of pre-reaction of the components while in solution form. The binder serves to retain the reactants in position in the heat-sensitive layer and on the paper or other carrier web; however it may, where employed in somewhat larger proportions, itself serve as the carrier or support layer, thereby making possible a heat-sensitive copy-sheet of extreme thinness. In some instances the binder component may be omitted.

The following examples will serve to illustrate but not to limit the invention.

Example 1

A binder solution is first prepared by dissolving ten parts by weight of cellulose acetate in 90 parts of acetone. In 15 parts of the solution is then dissolved, in the order listed, 0.1 part of N-betahydroxyethyl-N-ethyl-p-aminobenzene diazonium hexafluorophosphate, 0.1 part of 3-methyl-2-benzothiazolinone-2'-hydroxy-3'-naphthoylhydrazone, and 0.1 part of N,N'-dichloro-N,N'-bis-(p-toluenesulfonyl)ethylenediamine. The resulting solution is spread on map overlay tracing paper by means of a knife or bar coater at a coating orifice of 3 mils, and the coating is dried at room temperature. The faintly yellowish coating is converted to an intense dark purple on brief contact with metal type or a metal test bar at about 120° C.

The coated sheet is placed beneath a graphic original printed on thin paper and the composite is briefly intensely irradiated as for thermographic back-printing, producing a direct positive reproduction of the printed original.

The copy is next exposed to radiation from a 600-watt mercury vapor lamp ("UA-20B," made by G. E. Co.) at a distance of two inches and for a time of about 15 seconds. The image areas remain unchanged; the background areas, previously heat-sensitive, are rendered insensitive to normal copying temperatures. The resulting copy is permanent.

Another sample of the heat-sensitive copy-sheet is first exposed to a light-image from a source of ultraviolet light (a "BH-6" lamp, made by G. E. Co.) at a distance of 8 inches and about one minute exposure through a microfilm transparency. The sheet is then heated in an oven. The light-struck areas remain essentially colorless; the masked areas become strongly colored. The copy is stable against further exposure to light and heat.

Example 2

A copolymer of equal parts of butadiene and styrene (Parapol) is employed as the binder component and is supplied as a 10% solution in commercial heptane. Five parts by weight of N,N-diethyl-p-aminobenzene diazonium zinc chloride double salt and 100 parts of the binder solution are blended by prolonged milling on a ball mill. Separately, 2.18 parts of N,N'-dichloro-N,N'-bis(p-toluenesulfonyl)ethylene diamine and 3.49 parts of 3-methyl-2-benzothiazolinone-2'-hydroxy-3' - naphthoylhydrazone are similarly blended with 100-part portions of the binder solution. Equal weights of the three blends are then mixed together and coated at an orifice of 4 mils on glassine paper, and the coating is dried at room temperature.

The resulting heat-sensitive copy-sheet is useful in the reproduction of differentially radiation-absorptive graphic originals by thermographic methods involving either front-printing or back-printing. The heated areas appear as purple image areas on an essentially colorless or faintly colored background. Exposure of the copy to brief irradiation with ultraviolet light followed immediately by heating in an oven causes darkening of the background areas but the image areas remain readily visible. Storing the copy at room temperature for several days prior to heating in the oven reduces or eliminates the heat-darkening of the background areas.

The copy-sheet is also useful in the heat-printing of light-images as described under Example 1.

Example 3

A thin paper backing is first provided with a thin dried coating of the mixture of N,N'-dichloro-N,N'-bis(p-toluenesulfonyl)ethylene diamine and Parapol binder as described under Example 2. A further coating is provided using a mixture consisting of 0.3 part of 3-methyl-2-benzothiazolinone-2' - hydroxy - 3' - naphthoylhydrazone dispersed by ball milling in a solution of 0.3 part of N,N-diethyl-p-aminobenzene diazonium zinc chloride double salt in 15 parts of a 5% solution of polyvinyl butyral binder in methanol. The sheet is useful in producing light-stabilized thermographic copies and as a dry process "printing-out" paper for light-images, as described in the previous examples. It is somewhat slower than the sheet of Example 2.

Example 4

Paper is first coated with a 2-mil layer of a blend of 3.49 parts of 3-methyl-2-benzothiazolinone-2'-hydroxy-3'-naphthoylhydrazone in a 10% solution of Parapol in heptane, produced as described under Example 2, and is dried. A second coat is applied at the same thickness, consisting of 0.2 part of the zinc chloride double salt of Example 3 in 10 parts of a binder solution containing 5% of polyvinyl acetate and 5% of cellulose acetate dissolved in acetone. Similarly, a third 2-mil coating is applied and dried, the composition in this instance consisting of 2.18 parts of N,N'-dichloro-N,N'-bis(p-toluenesulfonyl)ethylene diamine in 100 parts of 10% Parapol polymer in heptane as described under Example 2. The resulting copy-sheet is useful in making heat-stable thermographic reproductions and in the dry process printing-out of light-images as hereinbefore described, and has improved storage stability under high humidity as compared to the copy-sheet of Example 2.

Example 5

Equal weights of 3-methyl-2-benzthiazolinone-1'-hydroxy-2'-naphthoylhydrazone and of p-diazo-N-betahydroxyethyl-N-ethylaniline hexafluorophosphate are dissolved in methanol and applied to white absorbent paper in amount sufficient to produce a distinct yellow color after drying.

Separately, trichloromelamine in powder form is rubbed into the surface of another piece of the white absorbent paper, and any excess is removed by shaking.

The yellow sheet is first exposed to a light-image applied from a mercury vapor lamp through a photographic negative for a time sufficient to decompose the diazo compound in the light-struck areas. The sheet is then placed with the exposed surface in close contact with the treated surface of the second sheet and the composite copy-sheet product is heated at 150° C. for about 10 seconds. Heating is conveniently accomplished between pre-heated flat glass or metal plates. On removal of the second sheet, the initially yellow first sheet is found to be converted to a blue-green color in a pattern corresponding to the opaque areas of the photographic negative. Subsequent exposure to light converts the colored areas to a reddish blue color, the remaining areas being faintly colored or substantially colorless.

Equally effective image formation is obtained using as the second sheet a paper support carrying a surface coating of N,N' - bis-(p-toluenesulfonyl)-N,N'dichloroethylenediamine.

It will be recognized that the copy-sheets of this invention are to be protected from undue exposure to actinic light during storage prior to their use in copying; and it is ordinarily found that storage in cardboard shipping containers is entirely adequate for preventing desensitization of the sheets over prolonged periods of time. The desensitizing action appears to be relatively slow, at least as compared to the color-forming reaction, so that the illumination incident to irradiation of the graphic original in the heat-copying process, and particularly with the radiation normally employed, does not in any way affect the formation of the visible copy. Such illumination in many instances will be found, however, to produce a slow reaction in the unchanged background areas, resulting in gradual desensitization thereof; and this effect is accelerated by applying additional ultraviolet radiation during or subsequent to the radiation with infrared.

What is claimed is as follows:

1. A heat-sensitive copy-sheet product useful in the thermographic reproduction of differentially radiation-absorptive graphic originals and capable of providing permanent reproductions stable against further heating, said copy-sheet product including a visibly heat-sensitive layer containing, in intimate association, a visibly heat-sensitive azo-dye-forming oxidative coupling composition including a heterocyclic hydrazone and a normally solid organic oxidizing agent for the hydrazone linkage having a positive chlorine atom attached to the nitrogen atom, and a photo-sensitive N-substituted p-aminobenzene diazonium salt decomposable on exposure to radiation in the near-ultraviolet with formation of a reducing agent for said oxidizing agent and in amount at least stoichiometrically equivalent to said oxidizing agent.

2. A heat-sensitive copy-sheet product useful in the thermographic reproduction of differentially radiation-absorptive graphic originals and capable of providing permanent reproductions stable against further heating, said copy-sheet product including a visibly heat-sensitive layer containing, in intimate association, reactant means for forming an azo dye by a heat-induced oxidative coupling reaction and comprising a normally solid condensation composite of a heterocyclic hydrazone and an amine-reactive organic compound, and a normally solid organic amide oxidizing agent for the hydrazone linkage having a positive chlorine atom attached to a nitrogen atom, and

including an azo coupler component; and said layer further including an N-substituted p-aminobenzene diazonium zinc chloride double salt decomposable on exposure to radiation in the near-ultraviolet with formation of a reducing agent for said oxidizing agent and in an amount at least stoichiometrically equivalent to said oxidizing agent.

3. A heat-sensitive copy-sheet product useful in the thermographic reproduction of differentially radiation-absorptive graphic originals and capable of providing permanent reproductions stable against further heating, said copy-sheet product including a visibly heat-sensitive layer containing, in intimate association, 3-methyl-2-benzothiazolinone - 1' - hydroxy - 2' - naphthoylhydrazonone; N,N' - dichloro - N,N' - bis (p - toluenesulfonyl)ethylenediamine; and the zinc chloride salt of diazotized N-ethyl-N-hydroxyethyl-p-aminoaniline.

4. In the manufacture of a heat-sensitive copy-sheet including a visibly heat-sensitive layer comprising components inter-reactive at elevated temperatures of about 90-150° C. to produce an azo dye by oxidative coupling and including a heterocyclic hydrazone and a normally solid organic oxidizing agent for the hydrazone linkage having a positive halogen atom, selected from the class consisting of chlorine and bromine, attached to a nitrogen atom, the step of rendering said copy-sheet photo-stabilizable by incorporating with said inter-reactive components in said heat-sensitive layer an amount of a photosensitive N-substituted p-aminobenzene diazonium salt about 5-20% in excess stoichiometrically of the amount of said oxidizing agent, said salt being decomposable on

exposure to radiation in the near-ultraviolet range with formation of a reducing agent for said oxidizing agent.

5. The method of making a heat-stable reproduction on a heat-sensitive copy-sheet of a heat-image of a graphic original, comprising: subjecting said copy-sheet to said heat-image to convert image areas of said sheet to a permanently visibly distinct appearance; and subjecting at least the background areas of said sheet to actinic radiation to stabilize said areas against visible change on subsequent application of heat; said copy-sheet comprising a visibly heat-sensitive layer comprising (a) components inter-reactive at elevated temperatures of about 90-150° C. to produce an azo dye by oxidative coupling and including a heterocyclic hydrazone and a normally solid organic oxidizing agent for the hydrazone linkage having a positive halogen atom, selected from the class consisting of chlorine and bromine atoms, attached to a nitrogen atom, and (b) a photosensitive N-substituted p-aminobenzene diazonium salt in amount sufficient, on decomposition under actinic irradiation, to reduce said oxidizing agent, said salt being decomposable on exposure to near-ultraviolet radiation with formation of a reducing agent for said oxidizing agent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,593,911	Neumann et al.	Apr. 22, 1952
2,807,544	Frederick	Sept. 24, 1957
2,967,784	Newman et al.	Jan. 10, 1961
2,995,465	Richey	Aug. 8, 1961
2,995,466	Sorensen	Aug. 8, 1961