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HEAT-SENSITIVE COPYING-PAPER

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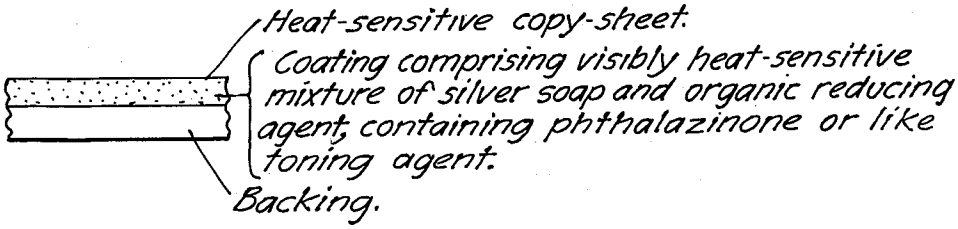

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HEAT-SENSITIVE COPYING-PAPER

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This invention is concerned with improvements in heat-sensitive copying-paper useful in preparing copies of differentially radiation-absorptive graphic originals, such as printed matter, by thermographic reproduction processes, for example as described in Miller Patent No. 2,740,896. More particularly, the invention concerns improved heat-sensitive copying-papers of the type described in Owen application Serial No. 594,540, filed June 28, 1956, now Patent No. 2,910,377, and in which the visible change obtained is a result of an oxidation-reduction reaction involving the liberation of a free metal.

A typical heat-sensitive copy-paper of the type just identified includes in the visibly heat-sensitive layer a water-insoluble silver salt, e.g. silver stearate, and an appropriate organic reducing agent, of which 4-methoxy-1-hydroxydihydronaphthalene is representative. Localized heating of the sheet in the thermographic reproduction process, or, for test purposes, by momentary contact with a metal test bar heated to a suitable conversion temperaure in the range of about 90–150° C., causes a visible change to occur in the heat-sensitive layer. The initially white or lightly colored layer is darkened to a brownish appearance at the heated area. The image areas thus formed are sharply outlined and distinctly visible, but normally differ considerably in color and general appearance from the corresponding areas of the printed or typewritten or other graphic original. In other instances the image areas may be yellowish, or greenish, or other less desirable color.

It has now been found that the color of the image areas obtained on heating these metal-liberating copy-sheets to conversion temperature may be desirably and effectively darkened, so that the resulting copy appears in the form of dense black or blue-black images on an essentially white background. Copies of typewritten correspondence, printed pages and the like having essentially the appearance of the original are thereby made possible.

The just-described improvement in image appearance is achieved, in accordance with the principles of my invention, by including with the metal-liberating heat-sensitive composition a significant small proportion of a heterocyclic organic toning agent containing at least two hetero atoms in the heterocyclic ring, of which at least one is a nitrogen atom.

The following examples and the appended drawing describe specific heat-sensitive copy-sheets illustrating the principles of the invention, which however is not to be construed as limited thereto.

Example 1

A mixture of equimolar proportions of auric behenate and behenic acid is first prepared by precipitation from a mixture of two mols of the water-soluble sodium salt of commercial behenic acid and one mol of auric chloride. Five grams of the washed and dried product is intimately dispersed, by prolonged grinding in a ball mill, in a solution of 2 grams of polystyrene resin binder in 93 grams of a mixture of equal parts of acetone and commercial heptane. Separately there is prepared a solution of 3.75 grams of hydroquinone in a solution of 14.5 grams of the styrene resin in 80 grams of the solvent mixture. The dispersion of metal salt and solution of reducing agent are mixed in the ratio of 2 parts of the former to one part of the latter, and a first portion of the mixture is applied in

a thin uniform layer to map overlay tracing paper and dried at room temperature. The resulting sheet is a pale yellow in color. It changes to a reddish purple when placed in momentary contact with a suitably heated metal test bar or when employed in the thermographic reproduction process.

To a second portion of the liquid mixture is added 0.1% of phthalazinone. This portion likewise is applied to paper and dried, providing a heat-sensitive copy-paper which converts from pale yellow to deep blue-black when heated as just described.

Example 2

Silver behenate is prepared by precipitation from an equimolar mixture of silver nitrate and sodium behenate. The water-insoluble salt is washed, dried, and dispersed in a solution of polystyrene in methyl ethyl ketone. Hydroquinone is separately dissolved in a solution of polystyrene in a 1:1 mixture of acetone and heptane. Equal quantities of the two products are mixed together to form a mixture having the formula

	Parts by weight
Silver behenate	10
Hydroquinone	4
Binder	12
Volatile liquid vehicle	174

One portion of the mixture is coated on a paper carrier web and dried. To other portions are first added small amounts of various nitrogen-containing heterocyclic toning compounds, the resulting compositions then being coated and dried in the same manner. The completed sheets are useful as heat-sensitive copy-sheets in thermographic reproduction processes and become colored on momentary contact with an appropriately heated metal test bar, the color in each case being indicated in the following tabulation.

Toning Agent	Gm./20 g. Mixture	Sheet Color	Image Color
(None)	(none)	White	Yellow-brown.
Barbituric acid	0.05	do	Black.
2-benzoxazolethiol	0.08	do	Do.
Saccharin	0.3	do	Dark brown-black.

Example 3

A mixture of 90% silver behenate and 10% behenic acid is first prepared, and 10 parts of the mixture then ball milled with a solution of 4 parts of ethyl cellulose in 86 parts of acetone. Three grams of spiroindane and 4 grams of ethyl cellulose are separately dissolved in 93 grams of acetone. Equal weights of dispersion and solution are mixed together, coated on a thin transparent carrier web at a thickness of two mils, and dried at room temperature. A further coating of a dispersion of 30 parts of zinc oxide and one part of silica gel in a solution of 3 parts of styrene-isobutylene copolymer in 66 parts of commercial heptane is applied at 1.5 mils thickness and dried to form a contrasting white opaque protective layer. The sheet yields yellow-brown image areas visible through the transparent carrier when heated in the thermographic process or on the test bar. Copy produced on such sheets is distinct and legible but lacks esthetic appeal when contrasted with the black-on-white typed or printed original.

Another copy-sheet is prepared in the same manner except that to the mixture of silver salt dispersion and reducing agent solution there is first added 2% of phthalazinone. Heat-image areas produced on this sheet are black, and the copy has substantially the appearance of the original.

Example 4

A copy-sheet prepared as in Example 3 except that gum guaiac is substituted in equal amount for the spiroindane produces heat-image areas which are yellowish green in color. The incorporation of two percent of phthalazinone (two parts in 100 parts of the coatable liquid mixture) results in the formation of deep blue-black heat-image areas and in much more attractive copies.

Similarly, the substitution of 1,5-dihydroxynaphthalene for the spiroindane of Example 3 results in a heat-sensitive copy-sheet which normally provides yellowish brown image areas, but with small amounts of phthalazinone provides black images.

Example 5

A mixture of equal molar amounts of silver behenate and behenic acid is dispersed in a solution of polystyrene resin in a 1:1 mixture of acetone and heptane. Tertiary-butyl catechol is separately dissolved in another portion of the same binder solution. The two compositions are mixed together, a small amount of phthalazinone is mixed in, and the mixture is coated on paper and dried. The proportions of "silver half soap," t-butyl catechol, and phthalazinone are approximately 50:50:1. The resulting copy-sheet provides black images. In the absence of the phthalazinone the image areas obtained are yellowish brown.

Phthalazinone is effective in small amounts, provides a particularly pleasing appearance to the heat-developed image areas without imparting any observable color to the unheated portions, and is a preferred toning agent in my heat-sensitive copy-sheets. Barbituric acid, 2-benzoxazolethiol, and 1-acetyl-2-thiohydantoin are fully as effective as phthalazinone. Saccharin is somewhat less effective, and much larger amounts of this material are ordinarily required, e.g. as indicated in connection with Example 2. Other examples of toning agents of about the same effectiveness as saccharin include: 5-nitrosaccharin; 2-hydroxybenzthiazole; imidazole; 2-amino-6-methylbenzothiazole; 2-amino-4-(4-biphenylyl)-thiazole; and N,N'-ethylenethiourea.

The effectiveness of the toning action obtained with these and other equivalent nitrogen-containing heterocyclic toning agents will vary with the particular toning agent and the amount thereof, and with the specific nature of the noble metal salt and the organic reducing agent, and with other factors. A test procedure is available, however, by means of which effective toning agents may be selected for any specified composition. In this test, the metal salt is suspended in a volatile vehicle such as methylethyl ketone, the reducing agent is dissolved in the slurry, the mixture is spread over a test sheet, a few small particles or crystals of the compound being tested are sprinkled over a portion of the coating and worked into the slurry with a stirring rod, the coating is permitted to dry, and the sheet is then placed into brief contact with a metal test bar at conversion temperature. For example, a solution of about one-half gram of hydroquinone in a slurry of one gram of silver behenate in 10 grams of methylethyl ketone is spread on a strip of white filter paper and powdered phthalazinone is dusted onto half of the coated area and mixed in. The coating dries rapidly. When placed on a metal rod heated to 120° C., the dusted portion becomes black, whereas the remaining portions turn yellowish brown. With compounds which have no toning action, no observable difference in color is obtained between the two areas of the test strip.

The image-forming reaction involves the reduction of a noble metal salt to free metal in an oxidation-reduction reaction. Silver behenate is a preferred salt, being colorless, visibly stable toward light, insoluble in the volatile liquid vehicle, and moisture-resistant. The presence of free behenic acid increases the moisture-resistant properties of the sheet. The salt, with or without the free acid, is produced in the desired physical form and chemical purity without difficulty and at reasonable cost. Silver stearate has been successfully substituted for silver behenate, and silver salts of many other organic acids have also been found useful in these heat-sensitive compositions and copying-papers. A partial list of such organic acids includes oleic, lauric, hydroxystearic, acetic, phthalic, terephthalic, butyric, m-nitrobenzoic, salicylic, phenylacetic, pyromellitic, p-phenylbenzoic, undecylenic, camphoric, furoic, acetamidobenzoic and o-aminobenzoic.

Reducing agents which have been found useful with such compounds in the formulation of heat-sensitive copy-sheets include: pyrogallol; 4-azeloyl-bis-pyrogallol; 4-stearoyl pyrogallol; galloacetophenone; di-tertiary-butyl pyrogallol; gallic acid anilide; methyl gallate, ethyl gallate; normal- and iso-propyl gallate; butyl gallate; dodecyl gallate; gallic acid; ammonium gallate; ethyl protocatechuate; cetyl protocatechuate; 2,5-dihydroxy benzoic acid, 1-hydroxy-2-naphthoic acid; 2-hydroxy, 3-naphthoic acid; phloroglucinol; catechol; 2,3-naphthalene diol; 4-lauroyl catechol; sodium gallate; protocatechualdehyde; 4-methyl esculetin; 3,4-dihydroxy benzoic acid; 2,3-dihydroxy benzoic acid; hydroquinone; 4,4'-dihydroxy biphenyl; 3,4-dihydroxyphenylacetic acid; 4(3',4'-dihydroxyphenylazo)benzoic acid; 2,2'-methylene bis-3,4,5-trihydroxybenzoic acid; ortho- and para-phenylene diamine; tetramethyl benzidine; 4,4',4''-diethylamino triphenylmethane; o-, m-, and p-aminobenzoic acids; alpha and beta naphthols; 4-methoxy, 1-hydroxy-dihydronaphthalene; and tetrahydroquinoline. These compounds are cyclic or aromatic compounds having an active hydrogen atom attached to an atom of carbon, oxygen or nitrogen which in turn is attached to an atom of the cyclic ring. They are capable of causing the reduction of silver ion and precipitation of metallic silver on being dissolved at moderate temperature in a solution of aqueous silver nitrate in an organic solvent.

The reactant materials are preferably applied to a thin flexible carrier or backing, such as paper or transparent film, in conjunction with a film-forming polymeric or resinous binder. In somewhat larger amounts the binder may itself serve the function of a carrier film; or the reactants may be supported in a fibrous web in the substantial absence of binder. Waxes, fibrous materials, pigments, fillers, dyes, fusible or infusible particulate materials, and various other additives may be included for special purposes. The metal salt and organic reducing agent are preferably intermixed prior to coating, but may be applied in separate but contiguous layers if desired, in which case the toning agent is present at least in the metal salt layer.

By means of the electron microscope it has been observed that the size of the metal particles appearing in the heated image areas of copy-sheets as hereinbefore described is significantly increased by the incorporation of the toning agent in the heat-sensitive layer. Again, the silver particles precipitated from silver nitrate solution by addition of an acetone solution of hydroquinone or the like are found to have a different shape and an increased apparent volume when precipitation occurs in the presence of a toning agent. Increase in apparent volume of precipitate may also be observed on addition of small amounts of a toning agent to the silver nitrate-hydroquinone mixture after initial precipitation. In possible explanation of these effects as well as of the toning effect generally, it is suggested that silver metal as normally precipitated carries with it adsorbed silver ions; that the toning agents are acidic, or contain labile hydrogen atoms, and permit anion formation; that fusion of one or more of the components of the heat-sensitive coupling permits in effect an ionization of the acidic toning agent along with oxidation-reduction reaction of the major reactants; that the resulting

anions then neutralize the adsorbed silver ions to permit the growth of particle size; and that the increased size of particles provides for increased internal reflection within the particles, resulting in a darker-appearing image. But regardless of theory, it has been shown that darker and more pleasing image-forming areas are obtainable by incorporation, in heat-sensitive copy-sheets employing metal-liberating oxidation-reduction reaction compositions, of heterocyclic organic toning agents containing at least two hetero atoms of which at least one is a nitrogen atom.

What I claim is as follows:

1. A heat-sensitive chemically reactive copy-sheet suitable for the preparation from differentially radiation-absorptive graphic originals of thermographic reproductions having dark-colored image areas of pleasing appearance, said copy-sheet comprising a thin flexible carrier web coated with a visibly heat-sensitive coating comprising (1) a film-forming binder, (2) a noble metal salt of an organic acid, and (3) a cyclic organic reducing agent for the noble metal ions, having an active hydrogen atom attached to an atom which is selected from the class of

oxygen, nitrogen and carbon atoms and is directly attached to an atom of the cyclic ring, and additionally including (4) a significant small proportion, sufficient to cause observable darkening of the thermographic image, of phthalazinone.

2. A heat-sensitive chemically reactive copy-sheet suitable for the preparation, from differentially radiation-absorptive graphic originals, of thermographic reproductions having dense black to blue-black image areas, said copy-sheet including a visibly heat-sensitive layer comprising a chemically reactive heat-sensitive mixture of a silver salt of an organic acid and an organic reducing agent for the silver ions, and phthalazinone in a small amount sufficient to cause observable darkening of the thermographic image.

References Cited in the file of this patent

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