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HEAT-SENSITIVE COPY-SHEET

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This invention relates to heat-sensitive copy-sheets useful in the thermographic reproduction of differentially radiation-absorptive printed or other graphic originals.

Rubeanic acid, also known as dithiooxamide, has previously been suggested as a reactant component of chemically reactive heat-sensitive copy-sheets, for example in conjunction with salts or soaps of metals such as cobalt, copper and nickel. The resulting copy-sheet provides an effective blue image on a white background when subjected to a heat-pattern as in the thermographic copying process. It has been found, however, that the color-forming reaction proceeds slowly at normal room and storage temperatures, and particularly under conditions of high humidity, so that the sheet eventually becomes no longer visibly heat-reactive or, if previously heat-printed, the image becomes illegible due to increasing background color.

The present invention provides a highly stable but fully heat-sensitive copy-sheet by substituting for the rubeanic acid previously employed a polymeric N,N'-disubstituted rubeanic acid derivative.

A preferred reactant material is the polymeric reaction product of hexamethylene diamine and rubeanic acid in equimolar proportions, particularly when employed in conjunction with a water insoluble metal salt reactant such as nickel benzoate. The two reactants are intimately dispersed in a solution of a film forming resinous or polymeric binder and the mixture is formed into a heat-sensitive layer either as a self-sustaining film or as a coating on a paper-like carrier web; or the reactants may be incorporated within a fibrous web in the substantial absence of the polymeric binder. Any of the usual polymeric binders may be employed, particularly effective results having been obtained with a copolymer of isobutylene and styrene ("Parapol S-50") and with a copolymer of polyvinyl pyrollidone and vinyl acetate.

A typical heat-sensitive copy-sheet of the invention may be represented in cross-section as follows:

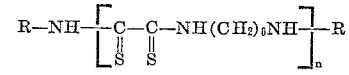
Heat-sensitive coating comprising inert binder, nickel benzoate, and long chain polymeric condensation product of rubeanic acid and hexamethylene diamine
Thin paper-like backing

The heat-sensitive layer may be a composite of two separately applied adjacent layers, the rubeanic acid derivative and the metal salt or equivalent being separately dispersed in appropriate binder solution and separately applied to a suitable carrier. Stability is still further improved, but heat-sensitivity is somewhat lessened in such sheet structures. In another variation, a further protective surface coating is applied over the visibly heat-reactive layer, in which case either the carrier web or the protective surface coating must be transparent. A preferred structure employs a pigmented surface coating and a transparent fibrous paper sheet or non-fibrous polymeric film carrier, the pigmented coating providing improved contrast for the colored image-forming areas of the copy.

The addition of rubeanic acid to an organic diamine

in equimolar proportions under reaction conditions produces a long chain polymeric product by a condensation reaction involving the evolution of ammonia. In the copy-sheet and under the influence of elevated temperature, the polymer reacts rapidly with the heavy metal ion, the reaction resulting in a visible change in the copy-sheet. However the reaction is effectively inhibited under normal storage and handling conditions, so that the copy-sheet remains highly stable under such conditions.

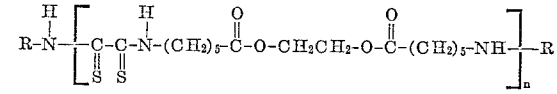
Analogous results are obtained with other polymeric derivatives of rubeanic acid in which adjacent rubeanic acid residues are joined together at secondary nitrogen atoms through intervening skeletal chains of carbon atoms or of carbon and oxygen or nitrogen atoms. Condensation of rubeanic acid with hexamethylene diamine results in a polymeric product which may be represented by the structural formula



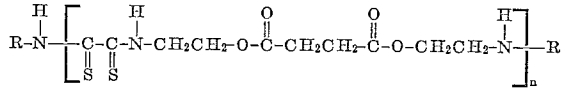
in which R represents a terminal radical and n is an integer. In this formula the skeletal chain connecting the rubeanic acid residues consists exclusively of carbon atoms.

An apparent exception is the condensation product of rubeanic acid with compounds having vicinal reactive amino groups, in which reaction there is formed a 5-membered ring structure which is non-reactive with nickel salts or the like. Vicinal amino groups are therefore to be excluded in calculating the number of amino groups in the aliphatic primary polyamines employed in the practice of this invention. Since any rubeanic acid reacting with these vicinal amino groups is rendered unavailable for the intended condensation, this quantity is likewise to be excluded in calculating the amount of reactant required.

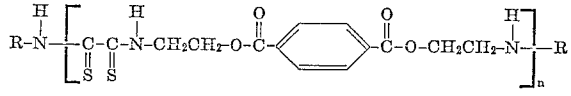
Condensation of rubeanic acid with an amino acid such as 6-aminohexanoic acid, $H_2N—(CH_2)_5—CO_2H$, followed by esterification with a glycol such as ethylene glycol, produces a structure which in the specific instance indicated may be represented as



and wherein the skeletal chain connecting the secondary nitrogen atoms of the rubeanic acid residues contains both carbon and oxygen atoms. The same is true of the polymeric derivative formed by condensation of rubeanic acid with an amino alcohol such as 2-aminoethanol, $H_2N—CH_2CH_2—OH$, followed by esterification with a dicarboxylic acid such as succinic or terephthalic acid. The structure produced with succinic acid may be represented as



Similarly, the structure of the terephthalic acid ester may be represented as



The dihydroxy intermediate may also be condensed with diisocyanates.

Compounds having more than two functional groups, for example aliphatic primary triamines such as 1,3,5-triaminopentane, trihydroxy alcohols such as glycerol, and tricarboxylic acids such as trimesic acid (1,3,5-benzenetri-

carboxylic acid) are similarly reactive to form polymeric derivatives of rubeanic acid or dicarboxy or dihydroxy intermediate derivatives thereof which are useful in the practice of the invention. It will be appreciated that the compounds listed are exemplary and that other polyamines, amino alcohols, amino acids, polycarboxy acids and polyalcohols having specifically different skeletal structures may equally well be substituted in place of those here named.

Nickel benzoate is a preferred example of a heavy metal salt which with the rubeanate polymers forms normally stable but rapidly visibly heat-sensitive copy-sheets. The salt is particularly effective in resisting discoloration under high humidity test conditions. When used in conjunction with the condensation product of rubeanic acid and hexamethylene diamine, nickel benzoate provides a substantially colorless copy-sheet which rapidly converts to a reddish color on heating to thermographic copying temperatures. Other heavy metal salts may be used with the same or other rubeanate polymers to provide other image colors, the water-insoluble salts being preferred. The following table indicates representative colors obtained with various metal salts in conjunction with the polymer of rubeanic acid and hexamethylene diamine.

Salt:	Image color
Silver behenate	Brown-black.
Gold chloride	Orange to black.
Lead naphthenate	Brown-black.
Lead octoate	Brown-black.
Mercuric oxalate	Brown-black.
Ceric sulfate	Brown-black.
Cerous behenate	Brown.
Manganese stearate	Brown.
Molybdenum oxalate	Blue.
Didymium behenate	Dark brown.
Cobalt behenate	Dark brown.
Cobalt octoate	Blue to brown.
Nickel stearate	Red-violet.
Cupric stearate	Green-black.

The following examples illustrate preferred materials and procedure in the practice of this invention, but the invention is not limited thereto, the scope of the invention being defined in the appended claims.

Example 1

A mixture of 11.6 parts by weight of hexamethylene diamine and 12.8 parts of rubeanic acid is moderately heated with gentle stirring for two hours and then permitted to remain overnight at room temperature. During the preliminary heating, ammonia is evolved, rapidly at first but at a decreasing rate during the two-hour heating period. The light yellow product is washed once with water and three times with warm ethyl alcohol and is air dried. The product melts at 85–90° C.

Five parts of the polymer thus formed is intimately dispersed in a solution of 10 parts of "Parapol S–50" isobutylene styrene copolymer in 85 parts of commercial heptane by prolonged milling in a ball mill. Separately, 20 parts of nickel benzoate is dispersed in 80 parts of heptane by ball milling. Equal parts of the two mixtures are then intimately mixed together and the resulting composition is coated on a thin paper carrier (30-pound map overlay tracing paper) by means of a coating bar set at an orifice of 2 mils. The coated sheet is dried at room temperature and provides a substantially colorless heat-sensitive copy-paper which when locally heated, as in the thermographic copying process or by momentary contact with a metal test bar heated to 120° C., provides a visibly distinct image area, in this case having a reddish color.

The copy-sheet prepared as above described remains visibly unchanged when heated for two hours at 60° C. under normal low-humidity conditions, and shows only a faint trace of color when heated for two hours at 53° C. and 90% relative humidity. In contrast, a copy-sheet

prepared identically except for the substitution of rubeanic acid for the polymeric derivatives becomes fully converted to the colored state under any of the test conditions described.

An equally effective polymer of somewhat higher molecular weight is prepared from the same reactants in the same proportions by refluxing in ethyl alcohol until a substantially completely insoluble product is obtained. The yellowish dried polymeric product melts at about 110–120° C.

Example 2

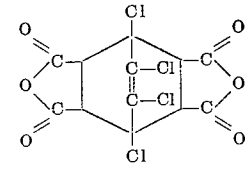
The following reactants are refluxed together for eight hours in a mixture of 150 ml. of dioxane and 5 ml. of pyridine.

	Grams
N,N'-bis-2-hydroxyethyl dithiooxamide	5.2
"TBO dianhydride"	9.5

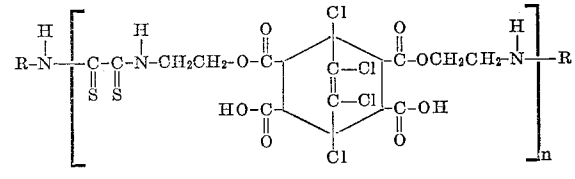
The mixture is allowed to stand at room temperature for 36 hours. It is then poured into 1,000 ml. of ice water. A light-colored precipitate forms which is recovered on a filter, washed with water and with ethanol, and dried. The light cream-colored powder melts at 163–170° C., is insoluble in heptane, soluble in acetone and in dioxane, very slightly soluble in ethanol. It reacts with nickel benzoate at 140–150° C. to give a red-brown color. Heat-sensitive copy-sheets made as in Example 1 but with the above polymer substituted for the rubeanic acid-hexamethylene diamine polymeric reaction product of that example are fully stable under normal storage and handling, and provide effective reproductions of graphic originals by thermographic copying procedures.

N,N'-bis-2-hydroxyethyl dithiooxamide is prepared by condensation of rubeanic acid and 2-aminoethanol, with elimination of ammonia.

"TBO dianhydride" is more specifically identified as the compound 1,4,7,8-tetrachlorobicyclo-[2,2,2]-7-octene-2,3,5,6-tetracarboxylic dianhydride, having the structure



The polymeric product therefore presumably has the structure



As in the polymer of Example 1, the secondary nitrogen atoms of the rubeanic acid residues are joined directly to termnial carbon atoms of the skeletal chains intermediate the rubeanic acid residues.

What is claimed is as follows:

1. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a salt of a heavy metal and a long chain polymeric N,N'-disubstituted rubeanic acid derivative.

2. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a salt of a heavy metal and a long chain polymeric N,N'-disubstituted rubeanic acid condensation derivative of an aliphatic primary diamine.

3. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a salt of a heavy metal and a long chain poly-

meric N,N'-disubstituted rubeanic acid condensation derivative wherein the rubeanic acid residues are joined at the secondary nitrogen atoms by a skeletal chain containing carbon and oxygen atoms.

4. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a nickel salt and a long chain polymeric N,N'-disubstituted rubeanic acid derivative.

5. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising nickel benzoate and a long chain polymeric N,N'-disubstituted condensation derivative of rubeanic acid and hexamethylene diamine.

6. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising nickel benzoate and a long chain polymeric N,N'-disubstituted rubeanic acid polyester condensation derivative wherein the rubeanic acid residues are joined at the secondary nitrogen atoms by a skeletal chain containing carbon and oxygen atoms.

7. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising nickel benzoate and a long chain polymeric N,N'-disubstituted polyester condensation derivative of N,N'-bis-2-hydroxyethyl dithiooxamide and a tetracarboxylic dianhydride.

8. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, comprising a paper-like carrier web coated with a visibly heat-sensitive layer including nickel benzoate, a long chain polymeric N,N'-disubstituted condensation product of rubeanic acid and hexamethylene diamine, and a minor proportion of a water-insoluble polymeric film-forming binder.

9. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer

comprising a salt of a heavy metal and a long chain polymeric N,N'-disubstituted rubeanic acid condensation derivative of an aliphatic primary polyamine.

10. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a salt of a heavy metal and a long chain polymeric N,N'-disubstituted polyester condensation derivative of an N,N'-bishydroxyalkyl dithiooxamide and a dianhydride of a tetracarboxylic acid.

11. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a salt of a heavy metal and a long chain polymeric N,N'-disubstituted polyester condensation derivative of an N,N'-bishydroxyalkyl dithiooxamide and a polycarboxylic acid.

12. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a salt of a heavy metal and a long chain polymeric N,N'-disubstituted condensation derivative of an N,N'-bishydroxyalkyl dithiooxamide and a diisocyanate.

13. A heat-sensitive copy-sheet useful in the thermographic reproduction of differentially radiation-absorptive graphic originals, including a visibly heat-sensitive layer comprising a salt of a heavy metal and a long chain polymeric N,N'-disubstituted polyester condensation derivative of an N,N'-biscarboxyalkyl dithiooxamide and a polyhydroxyalcohol.

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