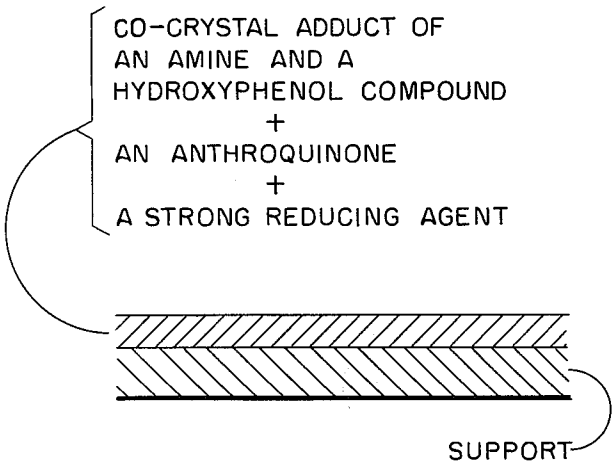
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HEAT RESPONSIVE MARKING SHEETS

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HEAT RESPONSIVE MARKING SHEETS

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This invention relates to thermographic copying sheets and is particularly concerned with a copy sheet which is characterized by its ability to form a colored image of a color contrasting to the background wherever the sheet is exposed to heat.

The exposure may be made through a master copy which is exposed to radiant energy. That energy is converted to sensible heat in the indicia appearing on the master sheet. Consequently the copy sheet is subjected to selective, localized heating under the indicia and a colored image of the original indicia appears. In recording apparatus, the sheet is heated directly by a hot stylus.

For brevity, both such modes of heating will be referred to as the "thermographic process."

The present invention is a continuation of work begun in the applications of William R. Lawton and Eugene F. Lopez, Serial No. 808,012, filed April 22, 1959, now Patent No. 3,076,707, and the application of William R. Lawton (sole), Serial No. 206,186, filed June 29, 1962, both of which are assigned to the assignee of this invention. The entire disclosure of both above identified applications is herein incorporated by reference.

The above applications disclosed that the co-crystal adducts of a bisphenol and an amine, or an hydroxyphenol substituted chroman and an amine can be coated on a copy sheet where they remain inert and no-reactive. When heated to between 50° and 150° C., however, these complex crystals dissociate, releasing the amine which thereupon can react with materials with which it is in intimate contact. In the two applications mentioned above, one such material is an azo compound which is "developed" or changed in color by the amine which has been released by the heat of the thermographic process.

As a class, the co-crystal adducts of bisphenols are well known. Many are described in U.S. Patent 2,829,175. The hydroxyphenol substituted chroman co-crystal adducts are described by Cramer, Einschlussverbindungen (published by Springer-Verlag, Berlin, 1954).

We have now discovered that if an anthraquinone, preferably a nitroanthraquinone is mixed with a strong reducing agent and this mixture in intimate contact with one of the above heat-decomposable amine-containing adducts is spread upon a supporting sheet, a strongly colored image will be formed wherever a sheet has been heated.

Although we do not wish to be bound by the following explanation, it is our present belief that the color results from a coordination compound formed between hydroquinone resulting from the reduction of the anthraquinone and the remaining anthaquinone. We believe, too, that the released amine not only provides the fluid medium but also the basicity which appears necessary to promote this reaction.

In one embodiment of the invention, thermographic copying sheets are produced by combining all ingredients in the single fine-grained dispersion in a solution of a resinous binder. The coating is spread by conventional coating machinery on a thin paper sheet. After the solvent is removed by drying, the sheet may be used to form copies or records in thermographic apparatus.

It is also possible to coat the sheet in successive coating operations. We find this latter procedure advantageous in those cases where it is desirable to adhere the adduct to the sheet with a water soluble binder.

Ordinarialy any of the co-crystal adducts containing an amine and a hydroxyphenol substituted chroman may be used interchangeably with adducts containing an amine and a bisphenol. The mark which is formed after heating either composition will exhibit a satisfactory color and density. However, some of the properties of the products vary, particularly the dissociation temperature and solubility. The chroman adducts generally are relatively water insensitive. The bisphenol adducts are frequently dissolved and dissociated by water or aqueous solution.

Of the two classes of adducts—bisphenols and hydroxyphenol substituted chromans—the chromans as a group possess the lower dissociation temperatures. Preferentially therefore, we employ the chromans whenever lower temperatures are necessary or where higher speeds in the copying process are needed. Also, a chroman adduct may be preferred because of its water insensitivity.

We prefer to use adducts which are light colored because in that case the background color is lighter and provides a maximum contrast for the colored marks. Additionally, we prefer to use adducts which dissociate in the temperature range of about 50–150° C. when in the coated composition. The variations in the properties of the specific adducts make it possible by a judicious selection of one or the other of the bisphenol or chroman adducts to meet a wide variety of manufacturing and operating conditions. For example, it is frequently desirable to coat the paper with a water suspension of the adduct in a water soluble binder. In consequence, in an alternative method of producing the copying sheets, we disperse the chroman adduct in an aqueous adhesive mixture, e.g., a 2% solution of polyvinylalcohol, and apply this dispersion on a coating machine as the first coat. Carboxymethylcellulose, hydroxyethylcellulose, natural gums, etc., are also effective adhesives. When the coating containing the chroman is dried, a coating containing the anthraquinone and the reducing agent is applied as a second coat. When the second coat is dry, the sheet is equally as effective as those made by the one-coat process.

We find it preferable to make use of amines which normally are liquid since we have found that the heat released liquid amines provide a medium in which a maximum reaction between the separate ingredients of the coating compositions can occur.

PREPARATION OF THE BISPHENOL ADDUCTS

Example 1

A co-crystal adduct is formed by combining:

	Parts
Tetrachlorobisphenol A (TCBA)	183
Ethylenediamine (EDA)	30
Toluene	364

by dissolving the tetrachlorobisphenol A in the toluene at about 150° F., adding the ethylenediamine, and stirring for about 30 minutes. Thereafter the mixture is chilled to about −30° F. and held at that temperature for about 14 hours (overnight). During this time a precipitate forms. The mass is filtered and the precipitate is washed thoroughly with N-hexane at about room temperature (70° F.) and dried. The solid crystal product is the co-crystal adduct of tetrachlorobisphenol A and ethylenediamine and has a M.P. 208–210° C. A dispersion of this co-crystal adduct is then made by ball milling 10 parts of the adduct with 90 parts of a 2.5% solution of polyvinyl butyral (Butvar B–76) in trichloroethylene.

In the foregoing example, the bisphenol used was tetrachlorobisphenol A (4,4'-isopropylidene-bis-(2,6-dichloro-

phenol). We have found that this material is effective in the formation of numerous of the co-crystal adducts which dissociate at temperatures within the range of about 50–150° C., but other bisphenols are available and are useful. These other bisphenol compounds may be employed in the preparation of solid heat-dissociable co-crystal adducts with amines. Compounds which are preferred include tetrabromobisphenol A; 4,4'-isopropylidenebisphenol; 2,2'-methylene-bis-(4-methyl-y-butylphenol); 4,4'-thio-bis-(6-tert. butyl-m-cresol); 4,4'-butylidene-bis-(6 tert. butyl-m-cresol); 2,2'-thio-bis-(4,6-dichlorophenol), 2,2' - methyl - 4,4-bis-(3,4,6-trichlorophenol), and 2,2'-thiobisnaphthol. Other bisphenol compounds which may be used in this manner are set forth in the previously mentioned patent, 2,829,175.

In addition to ethylenediamine other amines are useful, among which may be mentioned triethanolamine, ethanolamine, cyclohexylamine, tributylamine, di-n-propylamine, isopropylamine. Mixed amines are also useful.

PREPARATION OF THE CHROMAN ADDUCTS

Example 2

A hydroxyphenol substituted chroman, namely 2'-hydroxy-2,4,4,7,4'-pentamethylflavan is prepared according to a procedure described by Baker and Besley in J. Chem. Soc., 1951, 1102–6. A mixture of m-cresol (440 g.) and acetone is saturated with gaseous HCl without cooling and kept at 40° C. for two days with the exclusion of water. The dark product is added to an excess of 20% sodium hydroxide solution, a layer of ether is poured on the surface, and the mixture is vigorously stirred causing the ether addition product of the dimeride to crystallize. After standing overnight in an open vessel the solid is collected, washed thoroughly with water, dissolved in hexane, and dried with calcium chloride. The solution is filtered and a small amount of ether is added to the solution. The ether complex of the flavan compound separates in large, colorless, thick rhombic prisms having a melting point of 76–77° C. A flavan co-crystal adduct is prepared by mixing fifteen parts of the flavan-ether complex in a 10% hexane solution with 7.5 parts of diethanolamine, chilling the mixture overnight, and filtering the solid crystalline adduct product, M.P. 69–72° C.

While the above flavan is one which we have found to be effective in the formation of numerous co-crystal adducts which exhibit dissociation temperatures within the range of about 50–150° C. it is not the only available or useful hydroxyphenol substituted chroman. Numerous other hydroxyphenol substituted chromans may be used and among these which we prefer are 7,4'-diethyl-2'-hydroxy-2,4,4-trimethyl flavan; cyclohexanespiro-4-(2'-hydroxy-7,4'-dimethyl-2,3-tetramethylene) flavan; 2'-hydroxy-2,4,4,6,7,4',5'-heptamethyl flavan; 2'-hydroxy-2,4,4,6,5'-pentamethyl flavan; 4-p-hydroxyphenyl-2,2,4-trimethyl chroman. As in the case of the bisphenols, many amines are suitable, the most effective being the alcohol amines. The chroman adducts can normally be prepared by simple mixing of the selected chroman and amine in the manner shown above.

As a general procedure, separate dispersions of the various ingredients are formed by ball-milling the ingredients in a solution of the binder until a uniform small particle size dispersion is produced. Other known dispersing procedures may be followed, the requirement in this step of the process being the production of a uniform dispersion of small sized particles. When the desired size of each ingredient has been reached, the milling is stopped and the separate dispersions are combined and are thoroughly mixed. This mixture forms a coating composition which is spread on the supporting sheet to a final dry weight of about 5 lbs. per ream (24" x 36"–500 sheets). The coated sheet is thoroughly dried. Subsequently the sheet is cut to copy sheet size, and packaged.

Example 3

(A) 10 parts of dinitroanthraquinone is dispersed in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene by ball-milling until the desired particle size has been obtained.

(B) 10 parts of zinc hydrosulfite is dispersed in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene by ball-milling until the desired particle size has been obtained.

(C) 10 parts of the adduct of Example 1 is dispersed in 90 parts of a 2.5% solution of polyvinyl butyral (Butvar B–76) in trichloroethylene by ball-milling until the desired particle size has been obtained.

Thereafter, the separate dispersions are combined in the ratio of solid ingredients which follows: dispersion (A) 3 parts, dispersion (B) 2 parts, dispersion (C) 6 parts. The combined dispersion forms a coating composition which is spread on a thin paper sheet having a ream weight of about 22 lbs. per ream (24" x 36"–500 sheets) at the rate of about 5 lbs. (dry weight) per ream. The sheet is dried, cut to finished size, and packaged. When the sheet is exposed to heat in thermographic process apparatus, a deep red-brown image is produced.

Example 4

(A) 10 parts of dinitroanthraquinone is dispersed in a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene by ball-milling as described in Example 3.

(B) 10 parts of zinc sulfoxalate formaldehyde is dispersed in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene by ball-milling.

(C) 10 parts of the adduct of 2,2' thiobisnaphthol (TBN)/diethanolamine is dispersed in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene.

The separate dispersions are combined in the ratio of solid ingredients as follows:

	Parts
(A) Dinitroanthraquinone	3
(B) Zinc sulfoxalate formaldehyde	2
(C) Thiobisnaphthol (TBN)/diethanolamine	6

The resulting composition is coated to a dry weight of about 5 lbs. per ream (24" x 36"–500 sheets) on a thin paper sheet having ream weight of about 22 lbs. of sheets of the same dimensions and count. When exposed to heat in thermographic apparatus, a deep brown image results.

Example 5

(A) 10 parts of 1-nitro anthraquinone is dispersed in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene by ball-milling.

(B) 10 parts of zinc hydrosulfite is dispersed in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene by ball-milling.

(C) 10 parts of the adduct of tetrachlorobisphenol A and diethanolamine is dispersed in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene by ball-milling.

The dispersions are combined in the ratio of solid ingredients of (A) 3 parts, (B) 2 parts, (C) 6 parts, and spread as described in Example 3. The image formed by heating the sheet in thermographic apparatus is a deep red-brown.

Example 6

20 parts of the adduct of Example 2, namely 2'-hydroxy-2,4,4,7,4'-pentamethyl flavan/diethanolamine, is dispersed in 100 parts of a 2% aqueous solution of polyvinylalcohol.

This dispersion is coated on the base sheet to a dry weight of about 4 lbs. per ream (24" x 36"–500 sheets) and the coated sheet is dried.

A coating composition is prepared by combining fine-grained ball-milled dispersions of (A) 10 parts of dinitro-

anthraquinone in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) and (B) 10 parts of zinc sulfoxalate formaldehyde in 90 parts of a 2.5% solution of polyvinylbutyral (Butvar B–76) in trichloroethylene.

Equal parts (dry weight of solids) of these dispersions are combined and coated on the dried coating of flavan adduct to a dry coating weight of about 2 lbs. per ream. A deep color develops when the dried sheet is exposed in thermographic apparatus.

Example 7

The following adducts, whether used in the single or two-coat process in conjunction with dinitroanthraquinone and zinc sulfoxalate formaldehyde, gave substantially the same results.

(7.1) 7,4'-diethyl-2'-hydroxy-2,4,4,-trimethylflavan/cyclohexylamine
(7.2) 2'-hydroxy-2,4,4,7,4'-pentamethylflavan/diethylamine
(7.3) 2'-hydroxy-2,4,4,7,4'-pentamethylflavan/diisopropylamine
(7.4) 2'-hydroxy-2,4,4,7,4'-pentamethylflavan/benzylamine
(7.5) 2'-hydroxy-2,4,4,7,4'-pentamethylflavan/cyclohexylamine
(7.6) 2'-hydroxy-2,4,4,7,4'-pentamethylflavan/diethanolamine
(7.7) 2'-hydroxy-2,4,4,7,4'-pentamethylflavan/ethylenediamine
(7.8) 2'-hydroxy-2,4,4,7,4'-pentamethylflavan/dicyclohexylamine
(7.9) Cyclohexanespiro-4-(2'-hydroxy-7,4'-dimethyl-2,3-tetramethylene) flavan/benzylamine
(7.10) 2'-hydroxy-2,4,4,6,7,4',5'-heptamethylflavan/diethanolamine
(7.11) 2'-hydroxy-2,4,4,6,5'-pentamethylflavan/cyclohexylamine
(7.12) 2'-hydroxy-2,4,4,6,5'-pentamethylflavan/di-n-butylamine
(7.13) 2'-hydroxy-2,4,4,6,5'-pentamethylflavan/diisopropylamine
(7.14) 2'-hydroxy-2,4,4,6,5'-pentamethylflavan/diamylamine
(7.15) 2'-hydroxy-2,4,4,6,5'-pentamethylflavan/di-2-ethylhexylamine
(7.16) 2'-hydroxy-2,4,4,6,5'-pentamethylflavan/dicyclohexylamine

Useful results have been obtained by substitution for the dinitroanthraquinone in the previous example of 2-methyl anthraquinone, anthraquinone, 2-tert. butyl anthraquinone.

REDUCING AGENT

The reducing agent may be one of a number of strong reducing agents, the most active in these circumstances being (1) zinc hydro-sulfite (2) sodium sulfoxalate formaldehyde. Stability as well as activity is important and these substances, although they are most active, sublime when subjected to an increase in temperature. We prefer zinc sulfoxalate formaldehyde since it is effective and stable.

As a general procedure the respective amounts of the reacting materials should be such as to permit mutual reaction with a total amount sufficient to produce a clear, contrasting mark wherever the sheet is heated. The quantities and proportions may vary considerably but may be readily determined by a routine test.

The supporting sheet may be any of the numerous thin copy base materials, i.e., of rag stock, glassine, etc. When the thermographic apparatus is arranged to produce front printing, i.e., reflex printing where the copy sheet is interposed between the radiant heat source and the graphic original, the backing must be transparent to radiant heat. For direct reproduction or whenever the material is to be used with a heated stylus, any flexible material is suitable.

The accompanying drawing is a fragmentary viewing cross-section illustrating schematically the heat sensitive sheet of this invention.

What is claimed as the present invention is:

1. A heat-responsive sheet adapted to change visibly to a contrasting color wherever subjected to localized heating to a temperature of between 50° and 150° C. comprising in combination
   (*a*) a supporting sheet carrying on a surface thereof a coating comprising a uniformly distributed intimate association of finely divided particles of
   (*b*) a solid normally stable, co-crystal adduct comprising the reaction product of an amine and an hydroxyphenol compound selected from the class consisting of bisphenols and hydroxyphenol substituted chromans, and which is heat dissociable in the temperature range of 50° C.–150° C.,
   (*c*) a strong reducing agent selected from the group consisting of zinc hydrosulfite, sodium sulfoxalate formaldehyde and zinc sulfoxalate formaldehyde, and
   (*d*) an anthraquinone.

2. A heat-responsive copy sheet as claimed in claim 1 wherein the anthraquinone is dinitroanthraquinone, the reducing agent is zinc sulfoxalate formaldehyde and the co-crystal adduct is the reaction product of tetrachlorobisphenol A and diethanolamine.

3. A heat-responsive copy sheet as claimed in claim 1 wherein the anthraquinone is dinitroanthraquinone, the reducing agent is zinc sulfoxalate formaldehyde, and the co-crystal adduct is the reaction product of 2'-hydroxy-2,4,4,7,4'-pentamethyl flavan and diethanolamine.

4. A heat-responsive sheet as claimed in claim 1 wherein the coating comprises
   (*a*) a first layer comprising a finely divided co-crystal reaction product of an amine and a hydroxyphenol substituted chroman, and a water soluble adhesive binder, and
   (*b*) a second layer comprising a reducing agent and an anthraquinone.

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