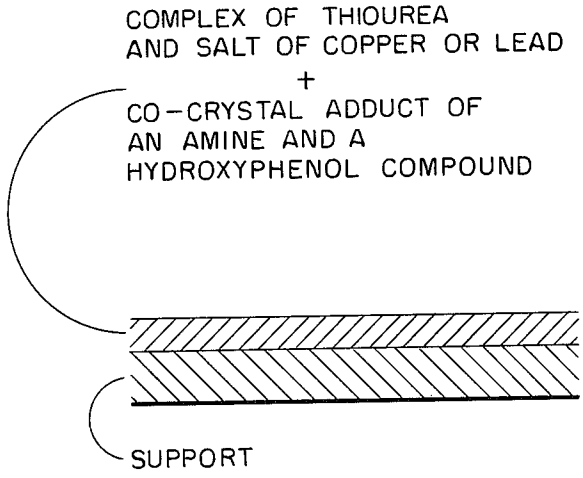
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HEAT RESPONSIVE MARKING SHEETS

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HEAT RESPONSIVE MARKING SHEETS

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This invention is concerned with heat marking sheets useful in copying and recording apparatus.

Sheets of this type carry heat-responsive coatings which form a mark of a contrasting color to the background wherever they are heated to temperatures in the range of 50 to 150° C. In thermographic copying such sheets placed next to a graphic original are exposed to infra-red radiation. The marks on the original convert the radiant energy to sensible heat. In this way, since the sheets are in contact, the copying sheet is subjected to selective, localized heating and wherever the copying sheet is heated. the contrasting mark appears. In recording apparatus, the sheet is heated directly by a hot stylus.

To avoid prolixity, we will use the words "Thermographic Process" to mean the making of a mark of a contrasting color by selectively heating the copying sheet either directly as by a hot stylus or by heat transfer from a graphic original. The words "Thermographic Conditions" will be used to mean those temperatures and times which are practicable and obtainable in office copying apparatus.

To be useful in the thermographic process however, sheets carrying heat-sensitive coatings must be stable during shelf-storage. They must be unaffected by atmospheric temperatures and they must remain indifferent to changes in atmospheric relative humidity. The coating, however, must produce a sharp color change at a well-defined temperature which is low enough to be non-destructive to the support and which is also obtainable on thermographic copying machinery. Compositions which may be coated on paper or other film support and which will produce colored images when exposed through a master copy to heat and which meet the above conditions have, in consequence, a high degree of usefulness.

For a long time it has been known that upon the heat decomposition of the reaction product of a thiourea with certain metals of the 4th and 8th periodic group, notably lead, cobalt and nickel, highly colored metal sulfides are formed. The conditions which bring this color forming reaction about do not fulfill the requirements for successful thermographic printing primarily because, if the thermographic exposure is to bring the sulfide reaction about in any reasonable time, the amount of heat required is excessive.

We have, however, found that a useful heat marking sheet may be formed from the thiourea complexes of copper and lead salts, by combining the complex with certain molecular compounds which contain an aimine and which are heat decomposible in the temperature range of 50° C. to 150° C. In particular the molecular compounds preferred in the practice of the invention are the co-crystal adducts containing an amine in combination with either a bisphenol or a hydroxyphenol substituted chroman. Preferably the amine is one of high basicity, as ones of lower basicity result in reduced sensitivity.

In accord with out present invention, we employ the above described classes of materials to prepare copy and recording sheets which are stable and do not discolor under normal conditions but which respond to the selective heating of the thermographic process to provide a correspondingly selective permanent contrasting coloration of the image or mark .

In accordance with out invention, heat marking sheets

are made by intimately dispersing the selected co-crystal adduct with a thiourea-metal salt complex in one or more coating compositions and then spreading the compositions on a flexible sheet support, typically paper or glassine. When the coatings are dry, the sheet becomes a normally stable, heat-responsive copy or marking sheet and is useful in thermographic processes.

Solid heat-dissociable co-crystal adducts containing bisphenols or hydroxyphenol substituted chromans and amines are well known. Many bisphenol adducts are described in U.S. Patent 2,829,175, and in the co-pending applications of William R. Lawton and Eugene F. Lopez, Serial No. 808,012, filed April 22, 1959, now Patent No. 3,076,707, and in the application of William R. Lawton (sole), Serial No. 206,186, filed June 29, 1962, both of which applications are assigned to assignee of this invention. The entire disclosure of both the Lawton et al. and Lawton (sole) applications is herein incorporated by reference. The hydroxyphenol substituted chroman adducts are described by Cramer, Einschlussverbindungen (Springer-Verlag, Berlin, 1954).

We prefer to use adducts which are light colored for thereby 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° C. to 150° C. when in a coated composition with the thiourea metal salt complex. By so doing, we provide a heat-marking sheet which is responsive to the practicable operating range of temperatures obtainable in the thermographic process. 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 this class of materials whenever lower temperatures are necessary or where higher speeds in the copying process are needed. Additionally, we find it preferable to make use of amines which normally are liquid since the released liquid amine provides a maximum degree of intimate admixing of the reactants after the heat dissociation of the adducts. Thus a complete color-forming reaction is secured.

The thiourea complexes with the selected metal salt are made by dissolving thiourea in water and then adding the thiourea solution to a previously prepared solution of the metal salt. If the resulting complex is water-insoluble, a fine white precipitate is obtained immediately. This is filtered, and the filter cake is washed and dried. After drying, coating compositions are made by grinding the complex, a resinous or adhesive binder, and a solvent for the binder together in a ball mill.

Ordinarily, any of the co-crystal adducts containing an amine and a hydroxyphenol substituted chroman, and adducts containing an amine and a bisphenol may be used interchangeably. The mark which is formed after the heating of either composiiton will exhibit a satisfactory color and density. However, as we have previously noted, some of the properties of the adducts vary, particularly in solubility. The chroman adducts generally are relatively water insensitive. The bisphenol adducts are frequently dissolved and dissociated by water or aqueous solutions.

These facts are advantageous because by a careful selection of one or the other of the bisphenol or the chroman adducts with an amine, a wide variety of manufacturing and operating conditions can be met. A chroman adduct, for example, may be preferred because of its water insensitivity, and whenever it is desired to apply the coating to the sheet in the form of a water dispersion. These adducts are also useful in sheets which may be subjected to high humidity conditions in storage.

PREPARATION OF THE THIOUREA COMPLEXES

Example 1

A complex of lead nitrate and thiourea is prepared in the following manner. 0.10 mole of lead nitrate (33.8 grams) is dissolved in 100 grams of water. 0.6 mole of thiourea (45.6 grams) is dissolved in 450 grams of water with slight heating. The solution of lead nitrate is slowly added to the solution of thiourea with agitation and white crystals are obtained which are collected on a filter paper, washed with water, and dried thoroughly. These crystals are the complex lead nitrate thiourea.

Example 2

A solution is prepared by dissolving 3 moles (456 grams) of 1-phenyl-2-thiourea in 1350 grams of methyl alcohol. A second solution is prepared by dissolving 1 mole (250 grams) of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 650 grams of water. The solution of copper sulfate is slowly added with agitation to the solution of phenyl thiourea and a yellow-gray precipitate is obtained. This precipitate is filtered, washed with water, and dried, and is the complex copper sulfate-phenyl thiourea.

PREPARATION OF BISPHENOL/AMINE ADDUCTS

Example 3

The solid molecular complex adduct of tetrachlorobisphenol A and diethanolamine is prepared in the following manner. 1 mole (366 grams) of tetrachlorobisphenol A is dissolved in 1098 grams of toluol with heat. To this solution is added 2 moles (210 grams) of diethanolamine with constant agitation. A fine crystalline precipitate is obtained and the crystals are collected by filtering and are washed three times with normal hexane and allowed to dry. The product is the adduct—tetrachlorobisphenol A/diethanolamine (TCBA/DEA).

Example 4

A solid molecular complex adduct is prepared of tetrachlorobisphenol A and ethylenediamine in the following manner. 1 mole (366 grams) of tetrachlorobisphenol A is dissolved in 1098 grams of toluol. To this solution 1 mole (60 grams) of ethylenediamine is slowly added with constant agitation and a precipitate is rapidly formed. This co-crystalline precipitate is filtered and washed three times with normal hexane and dried. The co-crystals are the adduct tetrachlorobisphenol A/ethylenediamine (TCBA/EDA).

PREPARATION OF THE COATING COMPOSITIONS

Separate dispersions are prepared of the thiourea-metal salt complexes and the bisphenol or chroman-amine adducts. These dispersions are ground in a ball mill to obtain fine-particle size.

Example 5

A first ball-mill dispersion is prepared by combining 10 grams of lead nitrate·thiourea complex (Ex. 1) in 90 grams of 2.5% polyvinylbutyral solution in trichloroethylene. A similar dispersion is prepared by combining 10 grams of the tetrachlorobisphenol A/diethanolamine adduct (TCBA/DEA, Ex. 3) with 90 grams of a 2.5% solution of polyvinylbutyral in trichloroethylene. The separate ball mill dispersions are ground for about 48 hours or until a suitable particle size is obtained. Thereafter the dispersions are combined in the following ratio: one part of the lead nitrate·thiourea dispersion and five parts of the TCBA/DEA dispersion. This combination of dispersions is mixed thoroughly and coated to a dry weight of about 3–4 lbs. per ream (24" x 36" x 500 sheets) on a thin paper web base stock having ream weight of about 22 lbs. per ream. Such a paper can be a glassine sheet or other thin paper base sheet. The dry coated sheet is satisfactory as a copy medium in dry thermographic copying processes.

Example 6

The procedure of Example 5 is followed except that the adduct of Example 4 (TCBA/EDA) is substituted for the TCBA/DEA of Example 3. In this case, the coating weight applied to the paper is about 4–5 lbs. per ream. The dry coated sheet is suitable as a copying medium in dry thermographic copying processes.

Example 7

(*a*) Ten parts of the adduct of Example 4 (TCBA/EDA) are added to 90 parts of a 2½% solution of polyvinylbutyral in trichlorethylene. The mixture is ground in a ball-mill from 12 to 18 hours.

(*b*) Ten parts of the copper sulfate·phenyl thiourea complex (Example 2) are added to 90 parts of a 2½% solution of polyvinylbutyral in trichlorethylene. This mixture is ground in a ball-mill for 12 to 18 hours. Following grinding, the separate, resulting, fine dispersions (*a*) and (*b*) are combined and thoroughly mixed.

The mixture is coated on a thin paper sheet, such as glassine, to a dry weight of about 6 to 8 pounds per ream (24" x 36" x 500 sheets).

The sheet may be used as a copy medium in dry thermographic copying processes.

PREPARATION OF THE CHROMAN ADDUCTS

Example 8

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 a m-cresol (440 grams) 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 a 10% hexane solution of the flavan ether complex with 7.5 parts of dicyclohexylamine, chilling the mixture overnight, and filtering the solid crystalline adduct product, M.P. 103–105° C.

PREPARATION OF THE CHROMAN-AMINE ADDUCT COATING COMPOSITION

A coating composition is prepared by dispersing 20 parts of the co-crystal adduct of Example 8 in 100 parts of a 2% solution of polyvinyl alcohol in water. The mixture is ball-milled to obtain a desired particle size and coated on a sheet of 25 lbs. per ream (24" x 36" x 500 sheets) glassine paper, to a dry weight of about 4 lbs. per ream. When dried, this layer is coated with about 4 dry lbs. per ream of one of the thiourea-metal salt complexes of Example 1 or 2. These substances are dispersed in the proportion of 10 grams of the complex in 90 grams of a 2.5% polyvinylbutyral solution in trichloroethylene. The resulting sheet is suitable for use in thermographic copying processes or heated stylus recording instruments.

In addition to the above material, numerous other hydroxyphenol substituted chromans may be used to prepare the adducts which are useful in connection with this invention.

Among the chromans which we have found to be useful 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.

Other amines are also used. Among these are diisopropanolamine, diethylamine, benzylamine, morpholine,

cyclohexylamine, diamylamine, di-n-butylamine, and the like.

For brevity, the word "thiourea" is used in this specification and the claims in a broad sense to include thiourea, substituted thioureas, and thiourea analogs, i.e. thiosemicarbazides, the complexes of several of which are illustrated in the foregoing examples.

Without in any way changing the nature of our invention, specific additives may be included in our coating compositions. Such materials may be fillers, substances to improve the "hand" of the resulting sheets, or to give the sheets anti-tack-properties. We may also add antistatic agents, anti-finger-print agents, etc.

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

We have set forth the preferred embodiments of our invention. Modifications will readily occur to those who are skilled in the art and familiar with this disclosure, and such modifications may be made without departing from the scope of this invention.

Having thus disclosed our invention, we claim and desire to secure by Letters Patent:

1. A heat-responsive copy sheet adapted to change visibly to a contrasting color wherever subjected to localized heating to temperature of about between 50 and 150° C. comprising, in combination,

(1) a supporting sheet carrying a coating comprising

(2) a normally stable thermally decomposible complex formed of a thiourea and a salt of a metal selected from the class consisting of copper and lead, and

(3) a solid, normally stable, co-crystalline adduct formed of an amine and an hydroxyphenol compound selected from the class consisting of bisphenols and hydroxyphenol substituted chromans, which is heat dissociable and reactive with said complex to produce a contrasting color in the temperature range of 50° C. to 150° C.,

(4) the complex and the adduct being in intimate contact and uniformly distributed on the surface of the supporting sheet.

2. A copy sheet according to claim 1 wherein the hydroxyphenol compound is a bisphenol.

3. A copy sheet according to claim 1 wherein the hydroxyphenol compound is a hydroxyphenol substituted chroman.

4. A heat-responsive copy sheet as claimed in claim 1 wherein the complex is the complex of copper sulfate and 1-phenyl-2-thiourea and the co-crystalline adduct is the adduct of tetrachlorobisphenol A and ethylenediamine and wherein the said complex and the adduct are in finely divided, intimate admixture and adhered to the support by a resinous binder.

5. A copy sheet according to claim 1 wherein the heat-responsive coating consists essentially of a chroman-amine adduct adhered to the sheet by a water-soluble binder, and in which a finely divided thiourea-metal salt complex is in intimate contact with the chroman adduct.

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