

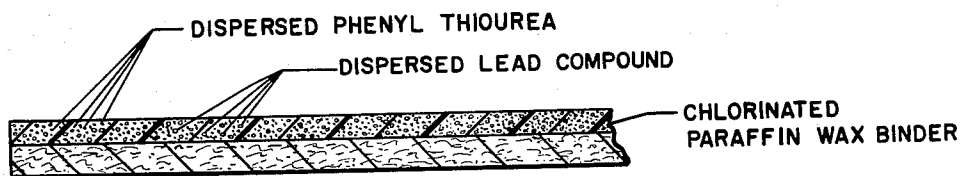
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HEAT-SENSITIVE SHEET FOR THERMOGRAPHIC COPYING

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2

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HEAT-SENSITIVE SHEET FOR THERMO-GRAPHIC COPYING

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14 Claims. (Cl. 117—36.9)

This invention relates to copy sheets and to a method of making copies therewith. More particularly the invention relates to copy sheets for use in making copies by a thermographic technique wherein the image on the copy sheet is the result of a chemical change produced by localized heating in the image area.

In recent years thermocopying of typed or printed originals has become increasingly popular. Thermographic copying involves placing the original in heat conductive relationship with a sheet of copy paper and then subjecting the original and copy sheet to intense irradiation of such character that the printed or type matter on the original absorbs that least a portion of the radiant energy thereby converting it into heat which causes the image of the original to be developed in the copy sheet. In such a process, it is apparent that the copy sheet must be constructed in such manner as to be capable of changing to a contrasting color when heated. The thermographic copying process machines for carrying out the process and certain types of heat-sensitive papers are described in numerous prior art patents, for instance, United States Patents 2,663,654-7; 2,710,263; 2,740,895-6.

The heat induced image may be formed either by a physical change in the copy sheet or by a chemical reaction induced by the heat. This invention is concerned with heat-sensitive sheets in which the image is formed as a result of a chemical reaction.

A typical thermographic copying paper in which image formation results from a chemical reaction is the copying paper described in U.S. Patent 2,663,657. This paper has a coating of two materials that are reactive with each other to produce a dark colored product which forms the image. The reactants are dispersed as discrete particles in a binder. At least one of the reactants is fusible within the range of 60 to 120° C. Thus, when the coating is heated to a temperature within said range, the fusible reactant particles melt and flow into contact with the particles of the other reactant with the resultant reaction. U.S. Patent 2,663,657 further states that the binder should be infusible within the 60° to 120° range in order to avoid undesirable sticking of the copying paper to contacting surfaces during copying.

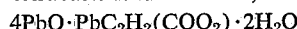
I have now discovered a novel thermographic copying paper of the chemically reactive type in which both of the reactants are infusible within the 60° to 120° C. range and which employs a binder which is fusible within the 60° to 120° C. range. Furthermore the use of the binder of this invention creates none of the problems of undesirable stickiness which eliminated the use of low melting binders in U.S. Patent No. 2,663,657.

The paper of this invention may be generally described as a heat-sensitive copying sheet comprising a base sheet, preferably of infrared transparent paper, carrying a coating comprising individual dispersions of two reactants which are capable of reacting to form colored sulfides of heavy metal. One of the reactants may be described as the heavy metal donor and the other reactant as the sulfide donor. The reactants are of very low water solubility and preferably are substantially insoluble in water. Both reactants have fusion points greater than 120° C. The reactants are dispersed in a binder which has a fusion point of from 60° to 120° C. Accordingly, the binder

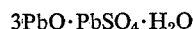
melts during the copying operation and carries the individual dispersed particles of the reactants into contact with each other where they may react.

While other heavy metal salts, notably mercury, silver, cadmium, nickel, cobalt and tin have been used with adequate results in this invention, the heavy metal donor is preferably a lead salt, having a fusion point greater than 120° C., lead hydroxide or a lead oxide compound. The lead salts may be the salt of any acid except strong acids such as sulfuric, hydrochloric or nitric acids. Suitable lead salts include lead maleate, lead carbonate, lead formate and lead phosphate. The term lead oxide is meant to include lead oxide containing compounds e.g., the commercially available compounds:

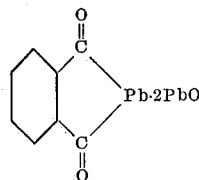
Lectro 78—tetrabasic lead fumarate,



Tribase—tribasic lead sulfate,



Dythal—dibasic or lead phthalate,



The sulfur donor is preferably a thiourea compound and most preferably a substituted thiourea having a fusion point above 120° C. and being substantially insoluble in water. Two such substituted thioureas which are very suitable for the practice of this invention are monophenyl thiourea and diphenyl thiourea.

The binder is preferably a chlorinated paraffin wax containing at least 50% chloride and having a fusion point between 60° and 120°. (It should be noted that in the present specification and claims, all proportions are by weight unless otherwise stated.) I have found such chlorinated paraffin wax binders display stability or aging characteristics far superior to other binders having the requisite 60° to 120° C. fusion point. Representative of the binders having the requisite melting points which were tried were ethyl cellulose polymer, chlorinated natural rubber having a 67% chlorine content and polyamides formed by the condensation polymerization of dilinolenic acid and ethylene diamine. These binders produced papers which had a lower stability and a lower resistance to aging as compared to the papers of this invention. I have further found that, in some instances, where the images on copy are lighter than desired, the darkness of the image may be enhanced by the addition to the binder of small amounts of a wax which has a lower viscosity than the chlorinated paraffin wax. Microcrystalline wax is an excellent additive for this purpose as is paraffin wax. When used, the wax additive preferably constitutes from 15% to 30% of the total binder weight.

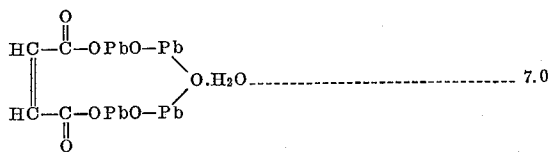
Preferably a sufficient amount of the lead donor is used to provide from 1 to 4 sulfur atoms for each lead atom. Preferably, from 0.2 to 2.0 parts of binder are used for each part of total reactants.

In preparing the paper, the reactants are applied to the substrate as dispersions in a volatile organic solvent solution of the binder. The coating may be applied in a single application. However, as the reactants display some tendency to react with each other while dispersed in these solutions, the preferable technique is to apply the coating layer in two steps. One of the reactants dispersed in the binder solution is first applied after which the second reactant in the same binder solution is applied. The use of this technique also permits the manufacture of a

	Parts by wt.
Chlorowax 70 (a resinous chlorinated paraffin wax having about a 70% chlorine content, a melting point of 95° to 110° C., Fisher-Johns method, an average molecular weight of 1060 and an average formula $C_{24}H_{29}Cl_{21}$) -----	7
Lead carbonate -----	8
Microcrystalline wax (M.P. about 90° C., Fisher-Johns method) -----	3
Toluene -----	15

	Parts by wt.
Chlorowax 70	6
Monophenyl thiourea	5
Microcrystalline wax (M.P. 90° C.)	1.5
Toluene	30

Batch A:	Parts by wt.
Chlorowax 70 -----	6.0
Tribasic lead maleate monohydrate having the formula—	



Batch B:	
Chlorowax 70	6.0
Monophenyl thiourea	5.0
Microcrystalline wax	1.5
Toluene	30.0

Example 7.—Example 5 is repeated using the same conditions, ingredients and proportions except that lead maleate is used in place of lead hydroxide. The results are the same as in Example 5.

5

Example 8.—Example 5 is repeated using the same conditions, ingredients and proportions except that lead oxide is used in place of lead hydroxide. The results are the same as in Example 5.

Example 9.—Example 3 is repeated using the same ingredients, proportions and conditions except that in place of the Chlorowax 70 binder in the compositions of both step 1 and step 2, there is used a combination of 4.0 parts of Chlorowax 70 and 2 parts of Chlorowax 50 in each step. (Chlorowax 50 is chlorinated paraffin having a chlorine content of 50% and a molecular weight of about 660.) The resulting paper had all of the desirable properties of the paper of Example 3 except that the paper of Example 3 had slightly better stability on accelerated aging.

Example 10.—Example 1 is repeated using the same ingredients, conditions and proportions except that, the second applied coating further includes 5 parts of mica. The resulting paper has all of the desirable properties of the paper of Example 1.

While there have been described what is at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is

1. A heat-sensitive copying sheet adapted, on being placed in heat-conductive relationship with a graphic original having graphic representations highly absorptive of infrared rays and on irradiation of said graphic original with infrared rays, to produce a copy of said graphic original, said copying sheet comprising a base sheet having thereon a coating comprising

(A) a dispersion of a lead compound having a melting point above 120° C. selected from the group consisting of lead salts of maleic acid, lead carbonate, lead phosphite, lead formate, lead hydroxide and lead oxide and

(B) a dispersion of phenyl substituted thiourea having a melting point above 120° C. in

(C) a binder comprising a major portion of chlorinated paraffin wax having a chloride content of at least 50% by weight and a melting point between 60° and 120° C.

2. The copying sheet of claim 1 wherein said lead compound is a lead salt of maleic acid.

6

3. The copy sheet of claim 2 wherein said lead salt is tribasic lead maleate monohydrate.

4. The copying sheet of claim 1 wherein said lead compound is lead carbonate.

5. The copying sheet of claim 1 wherein said lead compound is lead oxide.

6. The copying sheet of claim 1 wherein said lead compound is lead phosphite.

7. The copying sheet of claim 1 wherein said thiourea is monophenyl thiourea.

8. The copying sheet of claim 1 wherein said thiourea is diphenyl thiourea.

9. The copying sheet of claim 1 wherein the binder further comprises microcrystalline wax blended with the chlorinated paraffin wax.

10. The heat-sensitive copying sheet of claim 1 wherein the dispersion of the lead compound is situated predominantly in the lower half of the coating layer and the dispersion of the phenyl substituted thiourea is situated predominantly in the top half of the coating layer.

11. A copying sheet according to claim 1 comprising a dispersion of tribasic lead maleate monohydrate and of monophenyl thiourea in a binder comprising a chlorinated paraffin wax having a chlorine content of about 70% by weight.

12. A copying sheet according to claim 1 comprising a dispersion of tribasic lead maleate monohydrate and of monophenyl thiourea in a binder comprising a paraffin wax having a chlorine content of about 70% by weight and a microcrystalline wax.

13. The copying sheet of claim 1, further including a colorless filler having a melting point above 120° C.

14. The copying sheet of claim 13 wherein said filler is mica.

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