

1

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**HEAT-SENSITIVE COPY-SHEET CONTAINING BIS(TRIPHENYLPHOSPHINE)BOROHYDRIDOCOPPER (I)**

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5 Claims

**ABSTRACT OF THE DISCLOSURE**

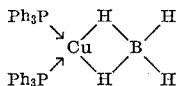
A heat-sensitive copy-sheet useful in thermographic copying contains bis(triphenylphosphine)borohydridocopper (I) as the visibly heat-sensitive component.

This invention relates to the copying of differentially radiation-absorptive graphic originals by thermographic methods involving brief exposure of the original to intense radiant energy while in heat-conductive contact with a heat-sensitive copy-sheet, and has particular reference to novel copy-sheet structures and compositions.

The copy-sheets of this invention may be white or colorless, or may be made in various pastel colors for purposes of identification or color coding. In most instances the sheet will comprise a carrier or backing having a coating of the visibly heat-sensitive material, although the latter material may if desired be incorporated directly in the backing. As an example the heat-sensitive material may be dispersed or dissolved in an appropriate heat-resistant film-forming binder in liquid form which is then applied to a thin flexible paper or film backing and solidified, e.g. by evaporation of solvent, at a temperature below the conversion temperature of the heat-sensitive material. Alternatively, the solution containing the heat-sensitive material may be deposited on a temporary support from which the dried residue is removed as a self-sustaining thin film. Or the heat-sensitive material may be applied directly to a suitably receptive paper or film surface, e.g. from solution in a volatile liquid vehicle, or incorporated in the paper sheet by adding the finely divided material to the paper-forming pulp in the beater or stuffing-box.

A particular advantage of the present invention is that but a single compound serves as the heat-sensitive material, thereby avoiding such problems as incorrect proportioning of reactants, separation of inter-reactive layers, pre-reaction during coating, etc. The compound is soluble in readily available and inexpensive volatile liquids without deterioration so that solutions may be prepared and stored as desired. It is stable under all normal storage and use conditions, and the copy-sheet remains heat-sensitive indefinitely even when stored under such normally adverse conditions as high relative humidity and direct sunlight. However when heated to a relatively high temperature, e.g. to about 165° C., the compound immediately undergoes an irreversible chemical change to form a dark-colored product which in the copy-sheet provides a visible record of the thermographically applied heat-pattern.

In accordance with the invention it has now been discovered that bis(triphenylphosphine)borohydridocopper (I) provides all of the advantages set forth above when employed as the heat-sensitive component in thermographic heat-sensitive copy-sheets. The compound may be represented by the structural formula



2

wherein Ph stands for phenyl. It is colorless, decomposes at about 165° C., and is soluble in acetone, benzene, chloroform, tetrahydrofuran, methylene chloride and butanone-2.

The phenyl radicals may be substituted, for example with halogen or alkyl, to provide compounds having equally useful freedom from color, solubility, and heat-sensitivity, and which are only slightly less resistant to deterioration on aging. The substitution of silver for copper produces a more expensive material which gives good images but is much less stable and in particular darkens during continued exposure to light. Compounds in which alkyl groups replace the phenyl (or substituted phenyl) radicals decompose to provide a visible change but with liberation of noxious and nauseating decomposition products. Accordingly the bis(triphenylphosphine) borohydridocopper (I) compounds are found to be particularly suitable and are at present greatly preferred.

The bis(triphenylphosphine)borohydridocopper (I) may be the sole component of the heat-sensitive stratum as hereinbefore indicated. More typically there will be included additional components, of which various film-forming binders, opacifying agents, coloring agents, etc., are exemplary. Other reactant materials may also be included for various purposes, in particular including image-stabilizing agents which are reactive with one or more of the heat decomposition products of the copper compound with formation of secondary image-forming compounds providing increased image density, contrasts, or permanence. An example is p-thiomethyl bromobenzene.

The following examples will serve to illustrate but not to limit the invention.

**Example 1**

To the blue-colored solution of 2 millimoles of copper sulfate pentahydrate in 25 ml. of anhydrous methanol is added 10 mM. of triphenylphosphine. The solution changes to a straw color, indicating coordination of the phosphine to the cupric ion. Powdered potassium borohydride (10 mM.) is added to the clear solution, with evolution of hydrogen and precipitation of potassium sulfate and bis(triphenylphosphine)borohydridocopper (I). The mixed precipitate is recovered by filtration and the colorless copper compound is removed by extraction with chloroform. The solution is clear and colorless.

A portion of the chloroform solution is uniformly applied over white bond paper, e.g. by brushing or with a cotton swab, and the solvent removed by evaporation at room temperature. The resulting sheet material serves as a heat-sensitive copy-sheet, producing a black image when heated at image areas in the thermographic copying process.

The solution is similarly applied to a transparent Mylar polyester film and after drying is subjected to the thermographic copying procedure to produce dark image areas on the transparent coated film.

The coated sheets remain visibly unchanged and fully heat-sensitive after prolonged storage at room temperature under all ranges of humidity.

**Example 2**

The bis(triphenylphosphine)borohydridocopper (I) is recovered from a separate portion of the saturated chloroform solution by precipitation with anhydrous ethanol, filtration, and air drying. The product is a white crystalline material which decomposes at about 165° C. and on analysis shows 10.2% Cu, 10.0% P, 2.6% B and 71.6% C, and is identified as  $((\text{C}_6\text{H}_5)_3\text{P})_2\text{CuBH}_4$ .

To a ten percent solution of "VYHH" vinyl resin (copolymer of 87 parts by weight of vinyl chloride and 13 parts vinyl acetate) in methylene chloride is added an amount of the crystalline compound equal to about 12%



by weight of the weight of binder, and the solution is uniformly lightly coated on transparent polyester film. The coating is dried. The film is placed in face-to-face contact with a printed original which is then exposed through the film in a thermographic copying machine and at maximum exposure. A clear copy of the printed image is produced which is right-reading when viewed through the film.

What is claimed is as follows:

1. A heat-sensitive copy-sheet adapted for use in the thermographic copying method and wherein the visibly heat-sensitive stratum comprises bis(triphenylphosphine)-borohydridocopper (I).

2. The copy-sheet of claim 1 wherein the bis(triphenylphosphine)borohydridocopper (I) is retained in a polymeric film-forming binder.

3. The copy-sheet of claim 1 wherein the visibly heat-sensitive stratum is carried by a thin flexible backing.

4. The copy-sheet of claim 3 wherein the backing is paper.

5. The copy-sheet of claim 3 wherein the backing is a transparent film.

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