United States Patent

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[54] **HEAT-SENSITIVE COPY SHEET**
10 Claims, No Drawings

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[51] **Int. Cl.** **B41m 5/18**
[50] **Field of Search** 117/36.8, 36.9

[56] **References Cited**
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ABSTRACT: The reaction temperature of a copy-sheet containing bis(triphenylphosphine)borohydridocopper(I) as heat-decomposable image-forming component is significantly reduced by incorporating certain nonfugitive nitrogen bases or heat-decomposable progenitors of nitrogen bases.

HEAT-SENSITIVE COPY SHEET

This invention relates in a major aspect 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, while not limited thereto, has particular reference to novel heat-sensitive copy sheet articles and methods of making. The heat-sensitive coatings or coated articles are also useful in thermal telltales or temperature indicator devices.

In U.S. application Ser. No. 687,126 filed Dec. 1, 1967 now U.S. Pat. No. 3,205,093, there is described a heat-sensitive copy sheet containing as the visibly heat-sensitive material the compound bis(triphenyl-phosphine)borohydridocopper(I). Localized heating of the copy sheet under maximum exposure in a thermographic copying machine causes decomposition of the compound, with formation of a stable dark-colored residue which provides a visible record of the thermographically applied heat pattern.

Many commercially available thermographic copying machines operate at optimum temperatures which are significantly lower than that required for the sheet materials just described, so that such copy sheets either fail to produce a fully developed image, or require that the machine be operated above its normal rating or at less than its recommended speed, with attendant overheating of machine components and with other difficulties. A particular difficulty is the formation of "fuzzy" or filled letters in the copy, caused by excessive lateral diffusion of the heat pattern under the high operating temperatures.

In accordance with the present invention it has now been found possible to cause permanent visible change in the bis(triphenylphosphine)borohydridocopper(I) coatings at significantly lower temperatures by incorporating small amounts of certain nonfugitive nitrogen bases or heat-decomposable precursors of nitrogen bases. Where heat-sensitive copy sheets are involved, overheating of machine and of printed original is avoided, lamp life is increased, wrinkling of copy is prevented, and sharply defined copies, with letters free of fuzziness or filling, are obtained.

As described in application Ser. No. 687,126, the copy sheet will normally comprise a heat-resistant carrier or backing having a coating of the visibly heat-sensitive material in a heat-resistant film-forming binder, although other constructions may also be used. Thin paper and transparent plastic film are typical carriers. Polyvinyl acetate is a preferred binder, but others, such for example as ethyl cellulose, vinyl acetate-vinyl chloride copolymer, and vinylidene chloride-acrylonitrile copolymer are also useful. The compositions are ordinarily applied from solution or suspension in a volatile organic liquid vehicle which is then removed by evaporation at a temperature below the reaction temperature. Pigments, fillers, opacifiers, stabilizers, and other additives may be included with the reactant materials, and additional subcoatings or protective surface coatings may be added if desired.

The amount of bis(triphenylphosphine)borohydrid ocopper(I) applied per unit area of coating is at least sufficient to provide a readily visible image when locally heated but for reasons of economy should not be greatly in excess of such amount. Good results are obtained at a concentration of about 1 to 1½ grams of the copper compound per square meter, i.e., at least about 0.0016 gram mol per sq. m. The amount of nitrogen base compound required to cause decomposition of this minimal amount of the copper compound at the lower temperature is about 0.2 mol of the former to 1 mol of the latter, or at least about 0.0003 gram mol per sq. m.; and this minimal amount should therefore be present regardless of the total amount of the copper compound present per unit area. Larger amounts of the nitrogen base or base-liberating material may be added, e.g., up to 2 moles per mol of copper compound, but are not generally desirable and the introduction of excessive amounts of these materials has in some instances resulted in fading of the image during storage of the imaged copy sheet.

Fugitive nitrogen base compounds which are readily volatile under normal room conditions are obviously not suitable for use in copy sheets which are required to be stable under storage and use conditions. A large number and variety of nonfugitive nitrogen base compounds have been found fully effective in the practice of the invention; but others of closely similar structure and properties have been found to be of no value. However it has been found possible to distinguish between the effective and the ineffective materials by means of a simple test procedure which will now be described.

A solution of 100 mg. of triphenylphosphine in 2½ ml. of acetonitrile is mixed with a solution of 10 mg. of cuprous chloride in 2½ ml. of acetonitrile, with formation of a white precipitate. A solution of 25 mg. of the nitrogen base compound in 2 ml. of acetonitrile is added. If no observable change occurs, the mixture is heated to boiling (about 80° C.) for a few moments. In the absence of any visible change, the compound under test may be classed as ineffective. Useful compounds will cause a readily observable change in color or volume of the precipitate, or a change in color of the solution, or both.

Phenyldimethylurea and dimethyldodecylamine oxide are examples of nitrogen base compounds which cause no visible change in the precipitate when tested as just described. When combined with the bis(triphenylphosphine)borohydrid ocopper(I) in a copy sheet coating these compounds fail to lower the reaction temperature of the sheet.

Compounds which exert an easily recognizable effect both under test conditions and in the copy sheet include: tetramethylguanidine; dibenzylformamide; N,N-di-n-butyl benzene sulfonamide; 5,5-dimethylhydantoin; N-formylmorpholine; isobutyramide; methane sulfonamide; N-methylol pyrrolidone; N-methyl pyrrolidone; nitrophenyl pyrrolidone; 2-oxazolidone; N-phenyl pyrrolidone; pyridine-N-oxide; tetrabutyl urea; tri-isopropanol-amineborate; tributylamine; bipyridine; triethylene diamine; urea; N-allyl octylsulfonamide; sulfamide; and bis(N-ethyl)surfonamide. Each of the above-named compounds is a nonfugitive nitrogen base and when tested as above described gives a positive test result at room temperature. Another useful group of compounds, which give a positive test result at the elevated temperature, includes the following heat-decomposable nitrogen base precursors: tetramethylammonium cyanoacetate; tetraethylammonium cyanoacetate; octadecyldimethylammonium cyanoacetate; tetramethyl guanidinium cyanoacetate; biphenyl guanidinium cyanoacetate; tetramethylammonium bicarbonate; guanidinium carbonate; octadecyl dimethyl phenyl ammonium trichloroacetate; amine adducts of organic acidic materials, such as: morpholine/bisphenol A; diethanolamine/tetrachlorobisph enol A; aniline/salicylic acid; and metal complexes such as those of: nickel (II) thiocyanate and hexamethylenetetramine; nickel chloride and methyl hydrazine; nickel chloride and phenyl hydrazine; cadmium chloride and hydrazine; zinc chloride and hydrazine; zinc chloride and dimethyl hydrazine; ferrous chloride and hydrazine; cobaltous chloride and methyl hydrazine; cobaltous chloride, nickel chloride, and hydrazine; and copper iodide and picoline. Of these several compounds, tetramethylguanidine, bipyridine, the alkylammonium cyanoacetates, and the nickel chloride-phenyl hydrazine complex have provided greatest reduction in copying-temperature requirements and are presently preferred.

The amine adducts and metal complexes are readily prepared by adding an excess of the amine to a solution of the coreactant in a nonaqueous solvent and recovering the precipitated pure reaction product by filtration, washing and drying.

EXAMPLE 1

A mixture is prepared of 20 parts by weight of bis(triphenylphosphine)borohydridocopper(I) and five parts of tetraethylammonium cyanoacetate in 1,000 parts of a 10 per-

cent solution of polyvinyl acetate in methylethyl ketone. The mixture is coated uniformly on a thin paper carrier, using a knife coater set at an orifice of three mils, and the coating is permitted to dry.

The coated sheet produces clear and sharp copies of typewritten correspondence and other originals by the thermographic copying process.

For comparison, a copy sheet is prepared which is identical in other respects but from which the tetraethylammonium cyanoacetate is omitted. Copies prepared on such sheet by the thermographic copying process require significantly higher copying temperature and are not sharp, the images having diffuse outlines and the block letters being filled.

Other sheets are prepared in which the amount of tetraethylammonium cyanoacetate is varied between three and 15 parts by weight, or from about ½ to about 2½ mols per mol of the copper compound. In each instance the sheet produces sharp well-defined copy, with open block letters, of printed originals; but maximum image density is obtained using about four to about seven parts by weight of the additive.

EXAMPLE 2

To five parts by weight of a 10 percent solution of polyvinyl acetate in methylene chloride is added 0.15 part of bis(triphenylphosphine)borohydridocopper(I) and various amounts of 1,1,3,3-tetramethylguanidine. The several mixtures are coated uniformly at three mils wet thickness on two mil transparent "Mylar" polyester film and the coatings are permitted to dry. Copies of printed originals are prepared on these films by the thermographic process, and sharp well-defined images are obtained. Maximum image density is obtained with a sample prepared with 0.006 part by weight of the nitrogen base. At more than about 0.05 part of the base, the images initially produced are low in density and exhibit a tendency to fade during subsequent storage of the imaged sheet.

What is claimed is as follows:

1. An article capable of being heated and having on a surface thereof a coating of a visibly heat-sensitive composition comprising the compound bis(triphenylphosphine)borohydridocopper (I) and a nonfugitive nitrogen base compound or heat-decomposable progenitor thereof, said nitrogen base or progenitor being present in an amount of at least about 0.0003 gram mol per square meter and being further characterized as causing a visible change when mixed with the reaction product of cuprous chloride and triphenylphosphine in acetonitrile at temperatures up to about 80° C.

2. The article of claim **1** wherein said coating includes a polymeric film-forming binder.

3. The article of claim **2** in the form of a heat-sensitive copy sheet comprising a thin flexible backing with said coating extending over one entire major surface.

4. The copy sheet of claim **3** wherein the copper compound is present in an amount of at least about 1 gram per square meter.

5. The copy sheet of claim **4** wherein the backing is paper.

6. The copy sheet of claim **4** wherein the backing is a transparent plastic film.

7. The copy sheet of claim **4** wherein the heat-sensitive layer contains an alkyl ammonium cyanoacetate.

8. The copy sheet of claim **7** wherein the heat-sensitive layer contains tetramethylguanidine.

9. The copy sheet of claim **7** wherein the heat-sensitive layer contains bipyridine.

10. The copy sheet of claim **7** wherein the heat-sensitive layer contains a nickel chloride-phenyl hydrazine complex.

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