United States Patent Office

3,703,398

Patented Nov. 21, 1972

3,703,398

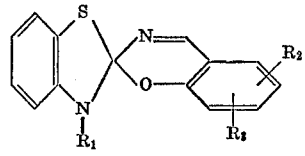
PRESSURE SENSITIVE COPYING PAPER

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No Drawing. Filed Oct. 8, 1970, Ser. No. 79,336
Claims priority, application Japan, Oct. 8, 1969, 44/80,537
Int. Cl. B41m 5/22
U.S. Cl. 117—36.2 6 Claims

ABSTRACT OF THE DISCLOSURE

Pressure-sensitive copying paper and process for preparing same comprising a support having coated thereon a layer of a color-forming compound having the formula



wherein R_1 is an alkyl group having 1 to 4 carbon atoms, R_2 and R_3 each is a member selected from the group consisting of a hydrogen atom, a halogen atom, a nitro group, an alkoxyl group of from 1 to 4 carbon atoms, an alkoxycarbonyl group of from 1 to 4 carbon atoms, and an aldehyde group, said compound reactive with an electron acceptive substance to produce a distinct color. The present invention also extends to the color-forming compounds employed and their process of preparation.

BACKGROUND OF THE INVENTION

The present invention relates to a pressure-sensitive copying paper.

In general, a pressure-sensitive copying paper is based on application of the principle that an electron-donative and color-reactive colorless organic substance is caused to react with an electron-acceptive substance in a medium of a non-polar oil solvent to produce a color. The electron-donative and color-reactive substantially colorless organic substance (hereinafter referred to as "color former"), includes such compounds as leuco methylene blue, crystal violet lactone, rhodamin B lactam, and acid rhodamin B sulfone, etc., while the electron-acceptive substance includes such substances as acid clay, active clay, attapulgite, aluminum sulfate, natural zeolite, kaolin, bentonite, silica gel, feldspar, pyrophylite, halloysite, magnesium trisilicate, zinc sulfate, zinc sulfide, calcium fluoride, lead sulfates, lead sulfide, and an organic acid or salt such as calcium citrate, tannic acid and benzoic acid.

In general, the pressure-sensitive copying paper comprises a combination of a sheet having microencapsulated thereon the above color-former dissolved in a non-polar solvent such as benzene, toluene, trichlorodiphenyl, coated on a paper, and a sheet having coated thereon the electron-acceptive substance together with a binder on a paper. In some cases, a sheet having coated thereon the microcapsule on one side and the electron-acceptive substance on the other side is placed between the above two

sheets or optionally, a sheet having coated thereon the microcapsule and the electron-acceptive substance simultaneously on the same surface of paper can be used. In either case, the microcapsule is ruptured by writing or printing pressure and the solution of color-former contained therein is contacted with the electron-acceptive substance to provide the colored copying image.

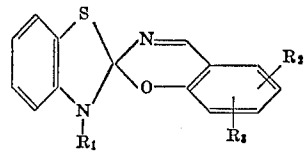
DESCRIPTION OF THE PRIOR ART

The principle form or preparation process which are described above have been known for a long time. (See U.S. Pat. Nos. 2,548,366, 2,711,375, 2,730,256, 2,812,507, 2,800,457 and 2,800,458.)

SUMMARY OF THE INVENTION

The primary object of the present invention is to provide a pressure-sensitive copying paper having encapsulated therein a novel compound as a color former.

The pressure-sensitive copying paper of the present invention is one incorporating as its color former a compound represented by the following formula:



wherein R_1 is an alkyl group of from 1 to 4 carbon atoms, R_2 and R_3 each is a hydrogen atom, a halogen, a nitro group, an alkoxy group of from 1 to 4 carbon atoms (wherein the alkyl group is an alkyl group having from 1 to 4 carbon atoms), an alkoxy carbonyl group of from 1 to 4 carbon atoms, or an aldehyde group.

DETAILED DESCRIPTION OF THE INVENTION

The above-mentioned compound is dissolved in a solvent such as benzene, toluene, dioctylphthalate, and chlorinated diphenyl, etc., microencapsulated and coated on the surface of paper.

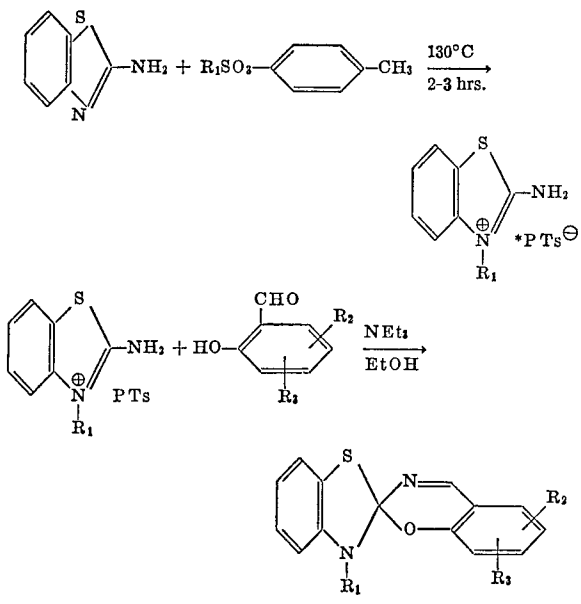
In use, it may be combined with a sheet having coated thereon the above-mentioned electron acceptive substances of the prior art.

Alternatively, the microcapsule containing a solution of the above-mentioned compound and the electron acceptive substance may be simultaneously coated on the surface of paper. The microcapsule containing a solution of color former can be prepared according to the specification of U.S. Pat. No. 2,800,457 and British Pat. Nos. 1,091,076, 1,091,077 and 1,091,078.

The compounds shown by the above-mentioned formula are generally prepared by the following process: The process is carried out at a temperature ranging from about 80° C. to about 150° C.

2-aminobenzothiazole and halogenated lower alkyl, dimethyl sulfate or diethyl sulfate p-toluene sulfonic acid alkyl ester are reacted in equimolar ratios. The quaternary salt so obtained and a salicyl aldehyde equimolar derivative can be refluxed in a lower alcohol (e.g., ethanol), acetonitrile, ethyl acetate or acetaldehyde, in the presence of an equimolar portion of triethylamine to obtain a compound shown by the above formula.

The above reaction is shown by the following equations:



*p-Toluene sulfonate.

The compound so obtained has sufficiently excellent properties as a compound for pressure-sensitive copying paper capable of forming red to red-violet when contacted with the electron-acceptive substance.

In case of preparing pressure-sensitive copying paper, the compound is microencapsulated together with a conventional color former such as crystal violet lactone or benzoyl leuco methylene blue, whereby various colors such as black are obtained when the mixture of color formers is contacted with the electron-acceptive substance.

A better understanding of the present invention will be further gathered from the following examples, which are merely illustrative and not limitative of the present invention. All parts are by weight unless otherwise stated.

Example 1

3.4 parts of 3-methyl-2-aminobenzothiazolium p-toluene sulfonate and 1.2 parts of salicyl aldehyde were dissolved in 25 parts (by volume) of ethanol and 1 part of triethyl amine was added thereto. After refluxing for about 3 hours, the mixture was allowed to stand and crystallize. This mixture was filtered and re-crystallized from ethanol to obtain 1.4 parts of a white crystal, 3-methyl spiro[benzothiazoline-2,2' - 2'H - (1,3)benzoxazine]. The melting point of this compound was 155 to 159° C.

Elemental analysis.—Calculated (percent): C, 67.38; H, 4.21; N, 9.93. Found (percent): C, 67.15; H, 4.51; N, 10.44.

A solution of this compound in benzene was microencapsulated and coated on the surface of paper which was then combined with clay paper, the surface of which was coated with acid white clay, and a binder. Upon being pressured with typewriter, the pressured part was immediately colored red.

Example 2

3.4 parts of 3-methyl-2-aminobenzothiazolium p-toluene sulfonate and 1.7 parts of 5-nitrosalicyl aldehyde were dissolved in 25 parts (by volume) of ethanol and part of triethylamine was added thereto. This mixture was refluxed for about 3 hours. After 2.5 hours from the beginning of reaction, a yellow crystal was crystallized out. After allowing the mixture to stand the crystal was filtered and recrystallized from benzene to obtain 2.3 g. of light yellow crystal, 3 - methyl - 6'-nitrospiro[benzothiazoline-2,2'-2'H-(1,3)benzoxazine]. The melting point of this compound was 195 to 198° C.

Elemental analysis.—Calculated (percent): C, 57.76; H, 3.85; N, 13.90. Found (percent): C, 57.51; H, 3.54; N, 13.42.

When this compound was pressured in the same manner as in Example 1, its pressured part was colored red violet.

Example 3

3.4 parts of 3-methyl-2-aminobenzothiazolium p-toluene sulfonate and 2 parts of 3-formyl-5-nitrosalicyl aldehyde were dissolved in 25 parts (by volume) of ethanol and 1 part of triethylamine was added thereto. This mixture was refluxed for about 3 hours. When the reaction liquid was concentrated to about ¼ and cooled, an orange crystal was crystallized out. The crystal was filtered and recrystallized from ethanol to obtain 2.1 parts of yellow crystal, 3-methyl-6'-nitro-8'-formyl spiro[benzothiazolium-2,2'-2'H-(1,3)benzoxazine] The melting point of this compound was 162 to 165° C.

Elemental analysis.—Calculated (percent): C, 55.92; H, 3.66; N, 12.90. Found (percent): C, 56.31; H, 3.25; N, 12.31.

When using this compound for writing was pressured in the same manner as in Example 1, the pressured part was colored red violet.

Example 4

3.4 parts of 3-methyl-2-aminobenzothiazolium p-toluene sulfonate and 2.8 parts of 3,5-dibromosalicyl aldehyde were dissolved in 25 parts (by volume) of ethanol and 1 part of triethylamine was added thereto. This mixture was refluxed for about 3 hours, and when the mixture was allowed to stand, a white crystal was crystallized out. It was filtered and recrystallized from a mixed solution of ethanol and benzene to obtain 3.3 parts of white crystal, 3-methyl-6',8'-dibromospiro[benzothiazoline-2,2'-2'H-(1,3)benzoxazine]. The melting point of this compound was 192 to 194° C.

When coating a solution of this compound dissolved in chlorinated diphenyl on the surface of paper, piling it on the surface of clay paper, and pressing them, the pressured part was immediately colored red.

Example 5

1.7 parts of 3-methyl-2-aminobenzothiazolium p-toluene sulfonate and 3-methoxy-5-nitrosalicyl aldehyde were dissolved in 20 parts (by weight) of ethanol and 0.5 parts of triethylamine was added thereto. This mixture was refluxed for about 2 hours. Then, after the reaction was complete and the mixture cooled, a yellow brown crystal was crystallized out. It was filtered and re-crystallized from ethanol to obtain 1.2 parts of light yellow crystal, 3-methyl-6'-nitro - 8' - methoxy spiro[benzothiazoline-2,2'-2'H-(1,3)benzoxazine]. The melting point of this compound was 195 to 198° C.

Elemental analysis.—Calculated (percent): C, 56.20; H, 4.08; N, 12.51. Found (percent): C, 55.98; H, 3.82; N, 12.24.

Example 6

10 parts of a solution of 1% of the compound obtained in Example 2 in chlorinated diphenyl was added to 100 parts of an aqueous solution of 10% of methyl cellulose and vigorously stirred to prepare an emulsion. Next, this emulsion was coated on the surface of paper and dried. The thickness of coating layer was 80μ.

When this color producing paper was piled on a clay paper and pressured by writing in the same manner as in Example 1, the pressured part was immediately colored red.

Example 7

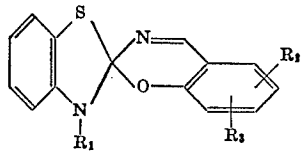
The paper coated with the compound obtained in Example 5 on its surface and dried in the same manner as in Example 6 was colored red when piling on a clay paper and pressuring.

Example 8

The compound obtained in Example 4 was encapsulated according to the method disclosed in the specification of Japanese Patent No. 493,064. This capsule solution was coated on the surface of paper and dried. When the color producing paper so obtained was piled on a clay paper and pressured, the pressured part was immediately colored red.

What is claimed is:

1. A pressure-sensitive copying paper comprising a support having coated thereon a layer of a color forming compound having the formula



wherein R_1 is an alkyl group having from 1 to 4 carbon atoms, R_2 and R_3 each is a member selected from the group consisting of a hydrogen atom, a halogen atom, a nitro group, an alkoxyl group of from 1 to 4 carbon atoms, an alkoxycarbonyl group of from 1 to 4 carbon atoms, and an aldehyde group, said compound being reactive with an electron-acceptive substance to produce a distinct color.

2. The pressure-sensitive copying paper of claim **1**, wherein said compound is

3-methyl-spiro[benzothiazoline-2,2'-2'H-(1,3) benzoxazine],

3-methyl-6'-nitrospiro[benzothiazoline-2,2'-2'H-(1,3)-benzoxazine],

3-methyl-6'-nitro-8'-formylspiro[benzothiazoline-2,2'-2'H-(1,3)-benzoxazine],

3-methyl-6',8'-dibutylspiro[benzothiazoline-2,2'-2'H-(1,3)-benzoxazine], or

3-methyl-6'-nitro-8'-methoxyspiro[benzothiazoline-2,2'-2'H-(1,3)-benzoxazine].

3. The pressure-sensitive copying paper of claim **1**, wherein said layer further comprises a conventional color former in addition to said compound.

4. The pressure-sensitive copying paper of claim **3**, wherein the conventional color former is a member selected from the group consisting of such compounds as leuco methylene blue, crystal violet lactone, rhodamin B lactam, and acid rhodamin B sulfone.

5. The pressure-sensitive copying paper of claim **1**, wherein the electron-acceptive substance is a member selected from the group consisting of such substances as acid clay, active clay, attapulgite, aluminum sulfate, natural zeolite, kaolin, bentonite, silica gel, feldspar, pyrophylite, halloysite, magnesium trisilicate, zinc sulfate, zinc sulfide, calcium fluoride, lead sulfates, lead sulfide, and an organic acid or salt such as calcium citrate, tannic acid and benzoic acid.

6. The pressure-sensitive copying paper of claim **1**, wherein the color-forming layer is microencapsulated.

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MURRAY KATZ, Primary Examiner

U.S. Cl. X.R.

117—36.8; 260—244 R