

United States Patent

[11] 3,619,239

[72] Inventors **Chiaki Osada;**
Hisatake Ono, both of Asaka-shi, Japan
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 [73] Assignee **Fuji Photo Film Co., Ltd.**
Kanagawa, Japan
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 [33] **Japan**
 [31] **43/90351**

3,293,060 12/1966 Harbort..... 117/36.2
 3,445,261 5/1969 Talvalkar 117/36.9
 3,451,338 6/1969 Baum 117/36.8

Primary Examiner—Murray Katz

Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

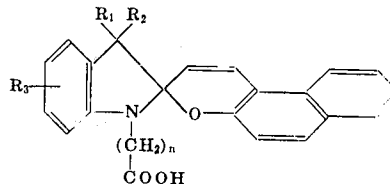
ABSTRACT: A novel color forming material used in a pressure sensitive copying paper comprises

[54] PRESSURE SENSITIVE COPYING PAPER 4 Claims, No Drawings

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 117/36.8, 260/326
 [51] Int. Cl..... B41m 5/22
 [50] Field of Search..... 117/36.2,
 36.8, 36.9; 260/326.11

[56] References Cited UNITED STATES PATENTS

3,231,584 1/1966 Berman et al..... 117/36.8
 3,239,366 3/1966 Miller et al. 117/36.2



wherein n is an integer of 1 to 4; R_1 and R_2 represent an alkyl group having 1 to 4 carbon atoms or a phenyl group; R_3 represents a hydrogen atom, an alkoxyl group wherein the alkyl group is an alkyl group having 1 to 4 carbon atoms, an alkoxycarbonyl group wherein the alkyl group is an alkyl group having 1 to 4 carbon atoms or a halogen atom.

PRESSURE SENSITIVE COPYING PAPER

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a pressure sensitive copying paper.

2. Description of the Prior Art

A pressure sensitive copying paper, as herein defined, is one wherein an electron donative, color reactive colorless organic substance (hereinafter referred to as a color former) reacts (usually) with an electron accepting substance in a nonpolar oily solvent medium to thereby assume a color.

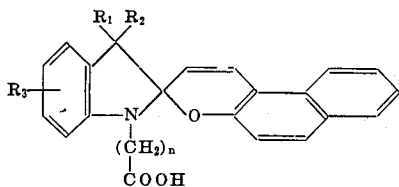
As a color former, there are leuco methylene blue, crystal violet lactone, Rhodamine B lactam, acid Rhodamine B sulfone, etc., as an electron accepting substance there are acid clay, active earth, attapulgite, aluminum sulfate, natural zeolite, kaolin, bentonite, silica gel, feldspar, pyrophyllite, halloysite, magnesium trisilicate, zinc sulfate, zinc sulfide calcium fluoride, and organic acids and salts thereof such as calcium citrate, tannic acid, benzoic acid, etc.

In general, a pressure sensitive copying paper comprises a combination of a sheet of paper the surface of which is coated with the above color former which is dissolved in a nonpolar solvent such as benzene, toluene, trichlorodiphenyl, etc. and then microencapsulated; and a sheet of paper the surface of which is coated with the electron acceptive substance together with a binder. In certain cases, a further sheet, one side of which is coated with the microcapsule and other side of which is coated with the electron accepting substance, may be used between the above two sheets. Also, a sheet coated with the microcapsules and the electron accepting substance on the same surface can occasionally be employed. In either case, the microcapsules are ruptured by writing or printing pressure and the color former solution contained therein is contacted with an electron accepting substance to give a colored copying image. The principles and preparation processes described above are well known. (Refer to the specifications of U.S. Pat. Nos. 2,548,366; 2,711,375; 2,730,256; 2,812,507; 2,800,457 and 2,800,458).

However, the above pressure sensitive copying papers must be preserved for long periods of time in some uses, and conventional color formers have not sufficiently satisfied the necessary requirements because the color formers have been poor in their weather-proofing qualities and limited in their color shade.

SUMMARY OF THE INVENTION

The present invention provides an improved pressure sensitive copying paper using a novel color-forming compound represented by the formula:



wherein n is an integer of 1 to 4; R_1 and R_2 represent an alkyl group having one to four carbon atoms or a phenyl group; R_3 represents a hydrogen atom, an alkoxyl group wherein the alkyl group is an alkyl group having one to four carbon atoms, an alkoxycarbonyl group wherein the alkyl group is an alkyl group having one to four carbon atoms or a halogen atom.

Typically used in combination with an electron acceptive material, the above color-forming compound yields a lasting color.

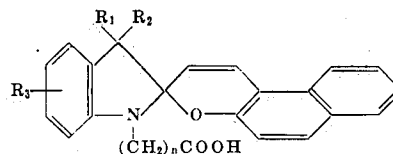
It is thus one object of this invention to provide an improved pressure sensitive copying paper.

It is a further object of the invention to provide an improved color-forming compound.

These and other objects will become clear upon a reading of the following material.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The 5, of the present invention is to provide a pressure sensitive copying paper using a compound represented by the formula:

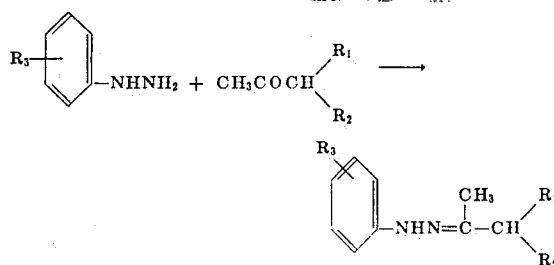
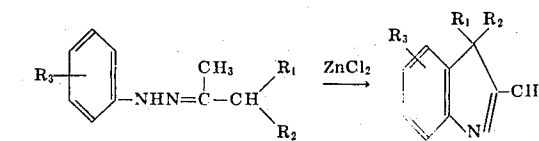
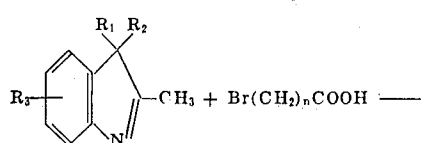
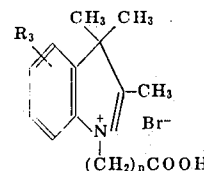


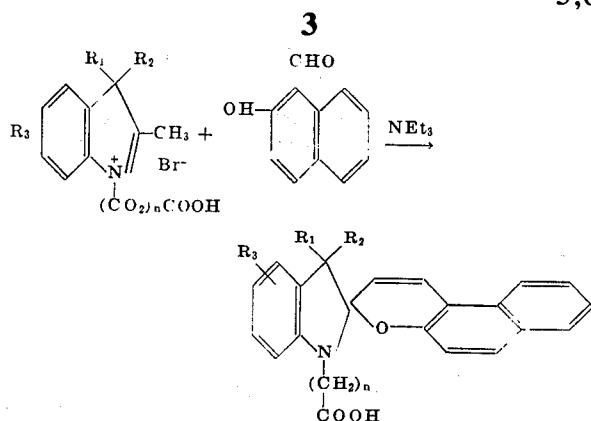
wherein n is an integer of 1 to 4, each of R_1 and R_2 is an alkyl group having one to four carbon atoms or a phenyl group, and R_3 is a hydrogen atom, an alkyl having one to four carbon atoms, an alkoxyl group, an alkoxycarbonyl group wherein the alkyl group is an alkyl group having one to four carbon atoms, or a halogen atom, as a color former.

It is sufficient if the above compounds are dissolved in a solvent such as benzene, toluene, diethylphthalate, chlorinated diphenyl, etc., and after being microencapsulated, coated on the surface of the paper. In use, this sheet may be combined with a sheet coated with the above-described electron acceptive substance. Further, microcapsules containing a solution of the above compound and the electron acceptive substance may be simultaneously coated on the surface of the same sheet of paper.

Microcapsules of a color former solution can be prepared according to the specifications of U.S. Pat. No. 2,800,457, or British Pat. Nos. 1,091,076; 1,091,077; or 1,091,078.

Compounds represented by the above formula can, in general, be synthesized by the following process: $R_3C_6H_4NH-NH_2$ and $R_1R_2CHCOCH_3$ are reacted in the absence of a solvent to synthesize a phenyl hydrazone derivative. Next, the above phenyl-hydrazone derivative is refluxed in the presence of $ZnCl_2$ in ethyl alcohol to synthesize the corresponding indolenine derivative. The indolenine derivative and $Br(CH_2)_nCOOH$ are then reacted either in the absence of solvent or using an appropriate solvent at 100° to 150° C. to thereby quaternarize. The quaternary salt thus obtained and α -formyl- β -naphthol can be refluxed together with triethylamine added in a calculated amount in absolute ethanol to obtain a compound represented by the above formula. These reactions are as shown in the following equations:





The pressure sensitive copying paper of the present invention is excellent in its preservability before and after use because the compound represented by the above formula has excellent solubility and stability, and, therefore, it is better in its weather-proofing qualities in comparison with conventional pressure sensitive copying papers. Further, the above compound yields an excellent color shade.

EXAMPLE 1

In 50 ml. of ethanol, 6.2 g. of 1-β-carboxyethyl-2,3,3-trimethyl-indolenium bromide and 3.4 g. of α-formyl-β-naphthol were dissolved and, after adding 2 g. of triethylamine, refluxed at 78° C. for 2 hours. After reaction, the ethanol was distilled out to obtain a white crystal which was then recrystallized from ethanol to obtain 3.6 g. of the white crystals of 1-β-carboxyethyl-3,3-dimethyl spiro-(indoline-2,2'-2'H-β-naphthopyrane). The melting point of this compound was 203 to 208° C. A piece of paper, the surface of which was coated with a solution of the present compound in ethanol and which was combined with a paper coated with acid clay and a binder was typed with a typewriter, whereby the place where pressure was applied immediately colored red. Encapsulation was by the procedure of U.S. Pat. No. 2,800,457.

EXAMPLE 2

To 100 g. of a 10 percent aqueous solution of methyl cellulose, 10 g. of a solution of 1 percent of compound obtained in example 1 in chlorinated diphenyl was added and vigorously stirred to form an emulsion. Next, the emulsion was coated on a paper surface and dried. The thickness of the coated layer was about 100 μ. When this color-forming paper was superposed on a clay-coated paper as in example 1 and subjected to local pressure, the area wherein pressure was applied immediately colored to red.

EXAMPLE 3

In the same manner as example 1, 3.3 g. of 1-β-carboxyethyl-2,3,3,5-tetramethylindolenium bromide and 1.7 g. of α-formyl-β-carboxyethyl-3,3,5-tetramethylindolenium bromide and 1.7 g. of α-formyl-β-naphthol were reacted to obtain 2.0 g. of the white crystals of 1-β-carboxyethyl-3,3,5-trimethyl spiro(indoline-2,2'-2'H-β-naphthopyrane). The melting point of this compound was 196° to 197° C. When pressure was locally applied, as by writing in example 2, the areas where pressure was applied colored red.

EXAMPLE 4

By the same procedure, as in example 1, 3.5 g. of 1-β-carboxyethyl-2,3,3-trimethyl-5-chloroindolenium bromide and 1.7 g. of α-formyl-β-naphthol were reacted to obtain 1.3 g. of

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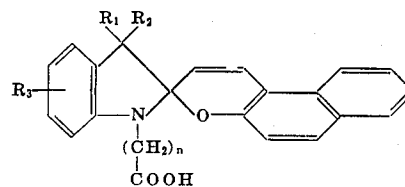
the white crystals of 1-β-carboxyethyl-3,3-dimethyl-5-chloro spiro (indoline-2,2'-2'H-β-naphthopyrane). The melting point of this compound was 206° to 208° C. A solution of this compound in chlorinated diphenyl was coated on a paper surface which was then superposed on the surface of clay-coated paper and subjected to the pressure. The area where pressure was applied immediately colored red.

EXAMPLE 5

The compound obtained in example 4 was microencapsulated according to the process described in the specification of Japanese Pat. No. 493,064. The microcapsules were coated on a paper and dried. The color-forming paper obtained was superposed on a clay-coated paper and subjected to local pressure, whereupon it immediately colored red.

What is claimed is:

1. A pressure sensitive copying paper having a coating layer of microcapsules containing a compound capable of causing a color-forming reaction with an electron acceptive material, said compound being represented by the general formula

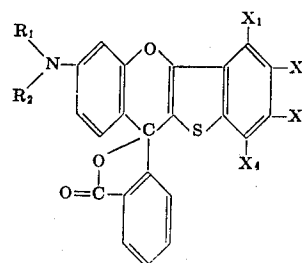


wherein n is an integer of 1 to 4; R_1 and R_2 represent an alkyl group having one to four carbon atoms or a phenyl group; R_3 represents a hydrogen atom, an alkoxy group wherein the alkyl group is an alkyl group having one to four carbon atoms, an alkoxy carbonyl group wherein the alkyl group is an alkyl group having one to four carbon atoms or a halogen atom.

2. The pressure sensitive copying paper as claimed in claim 1 wherein said compound is from the group consisting of 1-β-carboxyethyl-3,3-dimethyl-spiro(indoline-2,2'-2'H-β-naphthopyrane), 1-β-carboxyethyl-3,3,5-trimethyl-spiro(indoline-2,2'-2'H-β-naphthopyrane) or 1-β-carboxyethyl-3,3-dimethyl-5-chloro-spiro(indoline-2,2'-2'H-β-naphthopyrane).

3. The pressure sensitive copying paper as claimed in claim 1 wherein said electron acceptive material is from the group consisting of acid clay, active clay, attapulgite, zeolite, Roline, bentonite, silica gel, aluminum sulfate, feldspar, pyrophyllite, halloysite, magnesium trisilicate, zinc sulfate, zinc sulfide, calcium fluoride, calcium citrate, tannic acid or benzoic acid.

4. A coloring-forming compound represented by the formula:



wherein n is an integer of 1 to 4; R_1 and R_2 represent an alkyl group having one to four carbon atoms or a phenyl group; R_3 represents a hydrogen atom, an alkoxy group wherein the alkyl group is an alkyl group having one to four carbon atoms, an alkoxy carbonyl group wherein the alkyl group is an alkyl group having one to four carbon atoms, or a halogen atom.