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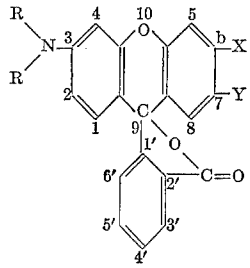
PRESSURE SENSITIVE FLUORAN DERIVATIVE COPYING PAPER

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ABSTRACT OF THE DISCLOSURE

A pressure-sensitive transferring sheet, adapted to be used in conjunction with another sheet having an electron accepting layer, comprising a support and, coated on said support, a layer containing pressure-rupturable microcapsules, said microcapsules containing as a color former, at least one fluoran derivative represented by the general formula:



wherein R represents a lower alkyl group,
when Y is a hydrogen atom, X is a radical selected from the group consisting of a lower alkyl group, a lower alkoxy group and a benzyloxy group,
when X is a hydrogen atom, Y is a radical selected from the group consisting of a chlorine atom, a lower alkyl group, a lower alkoxy group, a benzyloxy group, an acetoamino group, a N-acetyl-N-lower alkylamino group, and a N-acetyl-N-benzylamino group, and
when X is a methyl group, Y is a chlorine atom.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates generally to a pressure-sensitive copying paper and more particularly it relates to a pressure-sensitive copying paper containing a fluoran derivative as a color former.

Description of the prior art

Pressure-sensitive copying papers are usually composed of a transferring sheet, having thereon a layer of fine capsules containing therein a solution of an electron donating colorless organic compound (hereinafter the organic compound is called "color former") in an oil, and a receiving sheet, having thereon a layer of electron accepting solid and a suitable binder. When both sheets are put together such that the electron donating layer is brought into contact with the electron accepting layer, and the piled sheets are pressed partially by handwriting or typewriting, the capsules at the pressed areas are ruptured and the colorless color former contained in the capsules is adsorbed on the solid acid to form a color. There have also been employed pressure-sensitive copying paper systems consisting of the aforesaid transferring

sheet (hereinafter this sheet is called the "upper sheet") and a receiving sheet (hereinafter this sheet is called the "under sheet") and an intermediate sheet (hereinafter this sheet is called the "middle sheet") having coated on the opposite surfaces a layer of microcapsules containing the color former solution and a layer of the solid acid and a binder.

As the electron accepting solid acid, there are known acid clay, attapulgite, zeolite, bentonite, kaolin and the like.

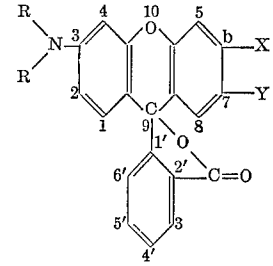
Also, as the electron donating color former, in particular, as a red color former, there are known Rhodamine Lactone, Rhodamine Anilinolactam and the like. However, the conventional red-color formers, for example, the lactonized products of Rhodamine B (Color Index (C.I.) No. 45,170, Rhodamine G (C.I. No. 45,150) and Rhodamine GCP (C.I. No. 45,160)) have the fault that when they are placed in a normal ambient atmosphere, they are soon colored owing to the instability thereof. Hence, the upper sheet, having a layer of microcapsules containing such a conventional red-color former, tends to be colored or fogged before use. Further, although the anilinolactamized products of the aforesaid rhodamines are stable when they are stored for a long period of time, it takes several minutes to finish completely the coloring at the partially pressed areas of a pressure-sensitive paper containing the color former. Also, since the color thus formed by the contact of the color former and a solid acid has a light absorption maximum near 550 mμ to 560 mμ, and has weak absorption in a range of from 560 mμ to 600 mμ, the color is purplish red, which gives a dark feeling.

An object of this invention is to provide a pressure-sensitive copying paper which is colored in red.

Another object of this invention is to provide pressure-sensitive copying papers which can be colored in various colors by using known yellow-, purple-, and blue-color formers together with a fluoran derivative shown by the general formula, as a red-color former.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a pressure-sensitive copying paper containing as a color-former, a fluoran derivative represented by the following general formula:



wherein R represents a lower alkyl group,
when Y is a hydrogen atom, X represents a group seselected from the group consisting of a lower alkyl group, a lower alkoxy group, and a benzyloxy group,
when X is a hydrogen atom Y represents a group selected from the class consisting of a chlorine atom, a lower alkyl group, a lower alkoxy group, a benzyloxy group, an acetoamino group, a N-acetyl-N-lower alkylamino group, and a N-acetyl-N-benzylamino group, and
when X is a lower alkyl group, Y represents a chlorine atom.

DETAILED DESCRIPTION OF THE INVENTION

Typical examples of the color formers used in this invention are shown in the following table.

Color former No.	General formula R	X	Y	Name of compound
1	C_2H_5	H	CH_3	3-diethylamino-7-methyl-fluoran.
2	C_2H_5	H	Cl	7-chloro-3-diethylamino-fluoran.
3	C_2H_5	CH_3	Cl	7-chloro-3-diethylamino-6-methyl-fluoran.
4	CH_3	H	CH_3	3-dimethylamino-7-methyl-fluoran.
5	CH_3	OCH_3	H	3-dimethylamino-6-methoxy-fluoran.
6	C_2H_5	OCH_3	H	3-diethylamino-6-methoxy-fluoran.
7	C_2H_5	OC_2H_5	H	3-diethylamino-6-ethoxy-fluoran.
8	C_2H_5	H	OCH_3	3-diethylamino-7-methoxy-fluoran.
9	C_2H_5	$OCH_2C_6H_5$	H	3-diethylamino-6-benzyloxy-fluoran.
10	C_2H_5	H	$OCH_2C_6H_5$	3-diethylamino-7-benzyloxy-fluoran.
11	C_2H_5	H	$NHCOCH_3$	7-acetamino-3-diethylamino-fluoran.
12	C_2H_5	H	$N(CH_3)COCH_3$	7-N-acetyl-N-methylamino-3-diethylamino-fluoran.
13	C_2H_5	H	$N(CH_2C_6H_5)COCH_3$	7-N-acetyl-N-benzylamino-3-diethylamino-fluoran.
14	CH_3	H	$NHCOCH_3$	7-acetamino-3-dimethylamino-fluoran.
15	CH_3	H	$N(C_2H_5)COCH_3$	7-N-acetyl-N-ethylamino-3-dimethylamino-fluoran.

Practical examples of preparing the above color formers are shown below, in which "Beilstein" refers to "Beilstein's Handbuch der Organischen Chemie."

PREPARATION 1

(Preparation of Color Former No. 1)

Into about 180 g. of concentrated sulfuric acid were dissolved 0.1 mol of 2'-carboxy-4-diethylamino - 2 - hydroxybenzophenone (cf., Beilstein; "Handbuch der Organischen Chemie"; vol. 14, page 675; ibid.; vol. 14, Supplement 1, p. 710; and "J. American Chemical Society"; vol. 38, p. 2102) and 0.1 mol of p-cresol, and the resulting solution was heated for 3 hours to 90–100° C. After cooling the reaction solution, it was poured into ice water to provide a precipitate, which was neutralized by aqueous ammonia or aqueous sodium carbonate solution and then extracted with chloroform. The extract was washed with water several times and concentrated under a reduced pressure to provide a crude crystal. By recrystallizing the crude crystal from a mixed solvent of benzene and petroleum ether, 27 g. of the white crystal of 3-diethylamino-7-methyl-fluoran having a melting point of 135° C., was obtained.

PREPARATION 2

(Preparation of Color Former No. 2)

By repeating the same procedure as in Preparation 1 while using p-chlorophenol instead of p-cresol, 33 g. of the white crystal of 7-chloro-3-diethylamino-fluoran having a melting point of 173–174° C., was obtained.

PREPARATION 3

(Preparation of Color Former No. 3)

By repeating the same procedure as in Preparation 1 while using 4-chloro-3-methyl-phenol instead of p-cresol, 31.9 g. of the white crystal of 7-chloro-3-diethylamino-6-methyl-fluoran having a melting point of 237–239° C., was obtained.

PREPARATION 4

(Preparation of Color Former No. 4)

By treating 0.1 mol of 2'-carboxy-4-dimethylamino-2-hydroxy-benzophenone (Beilstein; "Handbuch der Organischen Chemie"; vol. 14, p. 675 and ibid., Supplement 1, p. 710) and 0.1 mol of p-cresol in concentrated sulfuric acid as in Preparation 1, 25 g. of the white crystal of 3-dimethylamino-7-methyl-fluoran having a melting point 197° C., was obtained (cf., Beilstein; "Handbuch der Organischen Chemie"; vol. 19, p. 350).

PREPARATION 5

(Preparation of Color Former No. 5)

Into 30 ml. of concentrated sulfuric acid were dissolved 9.5 g. of 2'-carboxy-4-dimethylamino-2-hydroxybenzophenone and 5.5 g. (about 1.2 times of the theoretical amount) of resolcindimethyl ether, and the resulting solution was maintained for 48 hours at room temperature. Then, the solution was heated for one hour to 70–80° C., and after cooling, was poured into ice water. A precipitate thus formed was obtained by filtration, neutralized with aqueous ammonia and extracted with chloroform. The extract was washed with water several times and concentrated under a reduced pressure to provide a syruppy product. By recrystallizing the product from a benzene-ether mixed solution, 8.7 g. of the crystal of 3-dimethylamino-6-methoxy-fluoran having a melting point of 167–169° C., was obtained (Beilstein; vol. 19, p. 356).

PREPARATION 6

(Preparation of Color Former No. 6)

The above example was repeated while using 2'-carboxy-4-diethylamino-2 - hydroxybenzophenone (hereinafter, it is called intermediate A) and the crystal of 3-diethylamino-6-methoxy-fluoran having a melting point of 222° C., was obtained. Moreover, the same compound was obtained by methylating 3-diethylamino-6-hydroxy-fluoran (Beilstein; vol. 19, p. 356) with dimethyl sulfate and an alkali (Beilstein; vol. 19, p. 357).

PREPARATION 7

(Preparation of Color Former No. 7)

By repeating the same procedure as Preparation 5 while using intermediate A and resorcindiethyl ether, the crystal of 3-diethylamino-6-ethoxy-fluoran was obtained. Further, the same compound was obtained with diethyl sulfate as in Preparation 6.

PREPARATION 8

(Preparation of Color Former No. 8)

By condensing intermediate A and an equimole of hydroquinone dimethyl ether in sulfuric acid as in Preparation 5, the crystal of 3-diethylamino-7-methoxy-fluoran having a melting point of 129–130° C., was obtained.

PREPARATION 9

(Preparation of Color Former No. 9)

By treating intermediate A and an equimole of resorcindibenzyl ether in sulfuric acid in Preparation 5, the crystal of 3-dimethylamino-6-benzyloxy-fluoran was obtained. Further, the same compound was obtained by benzylating 3-diethylamino-6-hydroxy-fluoran with benzyl chloride under the presence of an alkali.

PREPARATION 10

(Preparation of Color Former No. 10)

By treating intermediate A and hydroquinone dibenzyl ether in sulfuric acid as in Preparation 5, the crystal of 3-dimethylamino-7-benzyloxy-fluoran was obtained. Further, the same compound was obtained by condensing intermediate A and hydroquinone in 50% sulfuric acid at 140° C. (Beilstein; vol. 19, p. 355).

PREPARATION 11

(Preparation of Color Former No. 11)

Into about 180 g. of concentrated sulfuric acid were dissolved 0.1 mol of intermediate A and 0.1 mol of 4-acetaminoanisole or 4-acetaminophenetole or 4-acetaminophenol, and the resulting solution was maintained for about 40 hours at 20–30° C. The solution was then poured into ice water to form a precipitate, and which was filtrated. The precipitate thus obtained was neutralized by aqueous ammonia or aqueous sodium carbonate solution and then extracted with chloroform. After washing with water several times, the extract was concentrated under a reduced pressure to provide a syrupy product which was dissolved into a mixed solvent of benzene and ether. This solution was allowed to cool to provide a white crystal of 7-acetamino-3-diethylamino-fluoran having a melting point of 142–143° C., with a yield of about 60%.

PREPARATION 12

(Preparation of Color Former No. 12)

The same procedure as in Preparation 11 was repeated using intermediate A and 4-N-acetyl-N-methylamino-anisole or -phenetole or -phenol and a white crystal of 7-N-acetyl-N-methylamino-3-diethylamino fluoran having a melting point of 132–133° C., was obtained.

PREPARATION 13

(Preparation of Color Former No. 13)

The same procedure as in Preparation 11 was repeated using intermediate A and 4-N-acetyl-N-benzylamino-anisole or -phenetole or -phenol and 7-N-acetyl-N-benzyl-amino-3-diethylamino-fluoran was obtained.

PREPARATION 14

(Preparation of Color Former No. 14)

The same procedure as in Preparation 11 was repeated using 2 - carboxy - 4 - dimethylamino - 2 - hydroxybenzophenone and 4-acetamino-anisole or -phenetole or -phenol and 7-acetamino-3-dimethylamino-fluoran was obtained.

PREPARATION 15

(Preparation of Color Former No. 15)

The same procedure as in Preparation 11 was repeated using 2 - carboxy - 4 - dimethylamino - 2 - hydroxybenzophenone and 4-N-acetyl-N-ethylamino-anisole or -phenetole or -phenol and 7-N-acetyl-N-ethylamino-3-dimethyl-amino-fluoran was obtained.

Each of the color formers No. 1 to No. 15, thus prepared, was dissolved in 95% acetic acid to cause red coloring and the absorption spectra of the red-colored solutions were measured. Their absorption maxima are shown in the following table.

Color former No.	Absorption maximum (mμ)	2nd absorption maximum (mμ)	3rd absorption maximum (mμ)
1	497	530	469
2	500	534	474
3	499	533	472
4	492	523	465
5	523	485	460
6	528	496	466
7	528	496	466
8	547	512	483
9	533	500	472
10	552	515	488
11	507	542	480
12	497	532	470
13	500	535	470
14	502	537	474
15	490	530	465

In order to prepare the pressure-sensitive copying paper of this invention using the color former mentioned above, there may be employed any known methods, for example, the methods disclosed in U.S. Pats. 2,548,366; 2,800,457 and 2,800,458 in which microcapsules containing color former are produced by utilizing a so-called composite coacervation.

The pressure-sensitive copying paper of this invention contains as a color former the compound represented by the aforesaid general former and the properties of the pressure-sensitive copying paper are not influenced by the manner employed for preparing it. Therefore, there are no limitations on the method of producing the pressure-sensitive copying papers of this invention.

The amount of the color former is usually 1–5% by weight based on the weight of the oily solvent.

The pressure-sensitive copying paper of this invention is colorless before use and is stable and forms no color fog when placed in atmosphere for a long period of time. When the pressure-sensitive copying paper is pressed partially by handwriting or typewriting, coloring occurs instantly. Moreover, since the color thus formed effectively absorbs light in the range of from about 470 mμ to about 550 mμ., the red color thus formed is brighter than that obtained by conventional pressure-sensitive copying papers, the color density is high, and the light resistance and water resistance thereof are excellent.

Furthermore, by using the aforesaid color former of this invention together with known yellow-color formers, purple-color formers, blue-color formers, bluish green-color formers, and the like, a pressure-sensitive copying paper capable of providing deep-black copying can be obtained without being accompanied by any bad influences, such as, desensitization.

The invention is further explained by the following examples:

EXAMPLE 1

Into 100 g. of diphenyl chloride was dissolved 3 g. of color former No. 1 and the solution was emulsified by mixing with a solution of 20 g. of gum arabic in 160 g. of water. Then, a solution of 29 g. of acid treated gelatin in 160 g. of water was added to the resulting emulsion, acetic acid was added to the mixture while stirring to reduce the pH thereof to 5, and 500 g. of water was added to the system to cause coacervation, whereby the oil drops containing the color former were covered by liquid films of a concentrated solution of gelatin and gum arabic. Thereafter, the pH of the system was further reduced up to 4.4 and then 4 g. of 37% formalin was added thereto for hardening. During the aforesaid procedure, the system was maintained at a temperature of 50° C. Thereafter, the temperature of the system was reduced to 10° C., to gel the films of the concentrated liquid and also the pH was increased to 9 for increasing the hardening effect of the films. The system was allowed to stand in these conditions for several hours to finish the capsulation. The coating composition containing the microcapsules thus prepared was applied to a paper by a conventional coating manner such as roller coating or air-knife coating and the like and dried to

provide an upper sheet. When the upper sheet thus prepared was placed on a clay paper or on the under sheet (having a clay-containing layer) and then the assembly was pressed partially by handwriting, a red copy was instantly formed on the clay paper. The thus formed red color did not fade when it was wet with water and directly exposed to sunlight for a long period of time. Also, when the upper sheet having the layer containing the color former was heated for 20 hours to 100° C., and also exposed to sunlight for a long period of time, the color forming property of the color former was not reduced. In other words, the pressure-sensitive copying paper of this invention had sufficient light resistance, water resistance and heat resistance both before and after color forming.

EXAMPLE 2

The same procedure as in Example 1 was repeated while using color formers No. 2 to No. 15 respectively instead of color former No. 1. In each case, red copy was formed rapidly on a clay paper. The properties of the color former of the pressure-sensitive papers thus prepared were almost the same as those in Example 1.

EXAMPLE 3

The absorption maxima of the red-colored color formers on a clay paper having an acid clay layer were measured. The results are shown in the following table.

Color former No.	Absorption maximum (mμ)	2nd absorption maximum (mμ)	3rd absorption maximum (mμ)
1	500	532	472
2	505	538	480
3	503	540	475
4	495	525	470
5	526	498	470
6	530	498	470
7	530	498	470
8	550	515	490
9	535	505	475
10	555	520	493
11	510	550	490
12	502	540	478
13	503	542	480
14	505	545	482
15	493	535	472

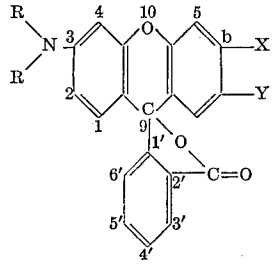
EXAMPLE 4

The same procedure as in Example 1 was repeated while using instead of color former No. 1 a mixed color former system of 0.9 g. of red-color former No. 1, 0.6 g. of benzoylleucomethylene blue, 0.7 g. of Malachite Green Lactone, 0.4 g. of N-phenylleuco Auramine (said three color formers are all blue-color formers), 0.8 g. of Crystal Violet Lactone (Bluish purple color former), and 1.2 g. of 3,6-diethoxyfluoran (yellow-color former). As a result, a black copy was instantly formed on the copy paper.

Further, almost the same results were obtained by using color formers No. 2 to No. 15, instead of color former No. 1, in the above example.

What is claimed is:

1. A pressure-sensitive transferring sheet, adapted to be used in conjunction with another sheet having an electron accepting layer, comprising a support and, coated on said support, a layer containing pressure-rupturable microcapsules, said microcapsules containing oil and dissolved therein a color former comprising at least one fluoran derivative represented by the general formula:



wherein R represents a lower alkyl group,

when Y is a hydrogen atom, X is a radical selected from the group consisting of a lower alkyl group, a lower alkoxy group and a benzyloxy group,

when X is a hydrogen atom, Y is a radical selected from the group consisting of a chlorine atom, a lower alkyl group, a lower alkoxy group, a benzyloxy group, an acetoamino group, a N-acetyl-N-lower alkylamino group, and a N-acetyl-N-benzylamino group, and

when X is a methyl group, Y is a chlorine atom.

2. The pressure-sensitive copying paper according to claim 1 wherein said color former is selected from the group consisting of 3-diethylamino-7-methyl-fluoran, 7-chloro-3-diethylamino-fluoran, 7-chloro-3-diethylamino-6-methyl-fluoran, 3 - dimethylamino-7-methyl-fluoran, 3-dimethylamino - 6 - methoxy-fluoran, 3 - diethylamino-6-methoxy-fluoran, 3-diethylamino-6 - ethoxy-fluoran, 3-diethylamino-7-methoxy-fluoran, 3-diethylamino - 6-benzyloxy-fluoran, 3-diethylamino-7-benzyloxy - fluoran, 7-acetamino-3-diethylamino-fluoran, 7 - N - acetyl-N-methylamino-3-diethylamino-fluoran, 7-N-acetyl-N-benzylamino-3-diethylamino-fluoran, 7-acetamino - 3 - dimethylamino-fluoran, and 7-N-acetyl-N-ethylamino-3 - dimethylamino-fluoran.

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