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PRESSURE SENSITIVE 3-SUBSTITUTED AMINO - 6 CHLOROFLUORAN CONTAINING COPYING PAPER

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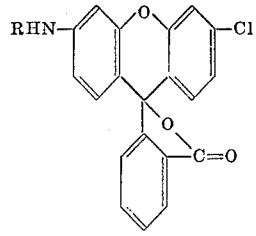
ABSTRACT OF THE DISCLOSURE

A color forming paper for use in pressure sensitive copying papers which comprises a support bearing a layer of microcapsules which contain at least one 3-substituted amino-6-chlorofluoran compound represented by the general formula:



wherein R represents a compound which is a hydrogen atom, a lower alkyl group, an aryl group, and an aralkyl group. Conventional color forming materials may also be present in the microcapsules.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to pressure-sensitive copying papers wherein a coloring reaction between a colorless "electron donor" organic compound (hereinafter referred to as the "color former") and an "electron acceptor" solid acid (hereinafter referred to as the "developer") is utilized.

Description of the prior art

In general, pressure sensitive copying papers are composed of a color former paper having a layer of the color former and a developer paper, or clay paper, having a layer of the developer, such as a clay. To prepare the color former paper, an oil solution of the color former is emulsified in water to form microscopically small oil drops. A rupturable capsule is formed around each oil drop to protect the oily material from air, so that the oily material can be preserved, and then the encapsulated oily materials are applied to a sheet of paper. The clay paper is prepared by applying the developer to a sheet of paper, with a proper binder.

The present invention is concerned with an improved color former paper having a layer of a specific color former that has never been used for such a purpose, either alone or in combination with known color formers.

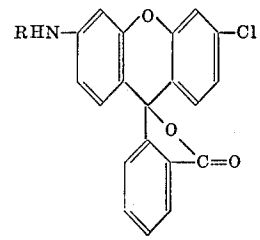
As the color formers for pressure-sensitive copying papers, there have generally been known and employed Crystal Violet Lactone, Malachite Green Lactone, Rhodamine Lactone, and Benzoyl Leuco Methylene Blue.

The above-mentioned color formers are used in pressure-sensitive copying papers which are blue colored.

The color formers used in the present invention are colored yellow, orange, red or purple.

SUMMARY OF THE INVENTION

It has been found that a color forming paper for use in pressure-sensitive copying papers comprising a support bearing thereon, a layer of microcapsules containing the improved color forming compound which comprises at least one 3-substituted amino-6-chlorofluoran compound represented by the general formula:



wherein R represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group, an aryl group, and an aralkyl group, may be formed. By utilizing the novel color forming chlorofluoran compound of the present invention, greatly improved results may be obtained.

Typically, the pressure-sensitive copying papers of the present invention utilize a coloring reaction between an electron donating organic compound and an electron accepting solid acid.

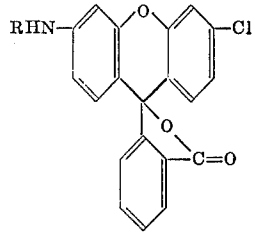
Conventional color forming materials may also be utilized in the microcapsules, and the microcapsules may be formed by common state of the art techniques.

An object of the present invention is to provide pressure-sensitive papers which are capable of being colored in black by using the color former of this invention together with a conventional blue color former.

Another object of the present invention is to provide pressure-sensitive copying papers capable of being colored in red, yellow, orange or purple, by employing the aforesaid color former alone, together with another red color former.

The color formers used in this invention can be colored very rapidly, and the material which is colored by the color former on the developer paper or clay paper has a very high light fastness.

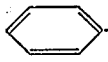
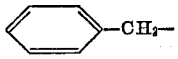
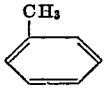
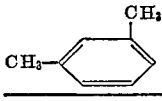
The color formers used in this invention have the structure of a silamine (3-substituted amino-6-chlorofluoran) having the following general formula:



wherein R represents a hydrogen atom, a lower alkyl group, an aryl group, or an aralkyl group.

By varying group R in the above formula, the color formed by the color formers can be varied within a wide range, from yellowish-orange to purple.

Typical examples of the color formers represented by the above general formula are as follows:

R	Chemical name	M.P., (° C.)	Color
H—	3-amino-6-chlorofluoran	215–223	Yellow-brown.
CH_3—	3-methylamino-6-chlorofluoran	198	Orange.
C_2H_5—	3-ethylamino-6-chlorofluoran	209	Do.
C_3H_7—	3-propylamino-6-chlorofluoran	179–180	Do.
	3-phenylamino-6-chlorofluoran	217	Orange-red.
	3-benzylamino-6-chlorofluoran	84–103	Orange.
	3-methatoluylamino-6-chlorofluoran.	184	Purple.
	3-methaxylylamino-6-chlorofluoran.	199	Do.

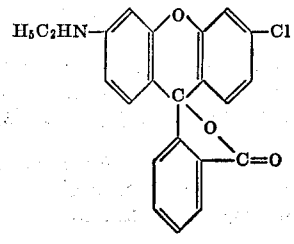
The color formers shown above have a fast rate of coloration and an excellent light fastness. Furthermore, when the aforesaid color formers are employed together with conventional color formers, such as Malachite Green Lactone, Crystal Violet Lactone, Michler's Hydrol, Rhodamine Lactone, and Leuco Methylene Blue, the coloring faculty of the color former of this invention is not reduced. The color formers of this invention illustrate no harmful effect on conventional color formers.

Moreover, the color formers used in this invention illustrate the properties required for pressure-sensitive copying papers, such as: coloring property, coloring rate, light fastness, preservability, oil-solubility, and water-insolubility.

The 3 - substituted - amino-6-chlorofluoran compound represented by the above general formula may generally be produced by reacting fluorescein with phosphorus pentachloride to form 3,6-dischlorofluoran, and condensing said 3,6-dichlorofluoran with an amine in the presence of zinc chloride as a condensing agent.

The production of the compounds of this invention will now be explained further with reference to the following examples.

PREPARATION 1



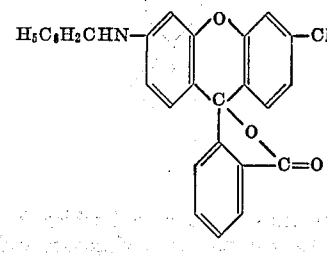
Preparation of 3-ethylamino-6-chlorofluoran.

A 300 cc. flask was charged with 60 g. of ethanol, 68 g. of zinc chloride and 10 g. of monoethylamine, and then 36.9 g. of 3,6-dichlorofluoran was added to the mixture.

The flask was heated in an oil bath. The mixture began to dissolve at 130–140° C., and the fluidity thereof was increased at 180° C. The reaction liquid was colored gradually with a yellow color. After three hours, the mixture was orange-red. The mixture was then cooled, solidified and crushed.

The solid thus obtained was mixed with water to dissolve a large amount of the zinc chloride present, which was removed by filtration. To the remaining solid, there was added toluene, and then a 3% aqueous solution of sodium hydroxide was added to adjust the solution to an alkaline pH whereby the product was extracted into the toluene. After separating the aqueous layer, the toluene layer was filtered by the addition of activated carbon, and the filtrate was concentrated under reduced pressure, and allowed to cool to provide 25 g. of a colorless or faint yellow crystal of the objective chlorofuran, which had a melting point of 209° C.

PREPARATION 2

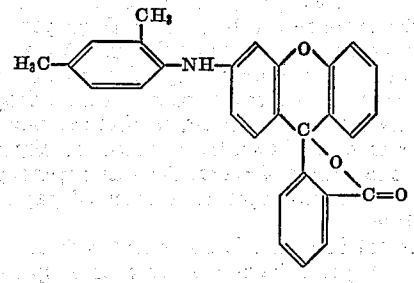


Preparation of 3-benzylamino-6-chlorofluoran:

Into a mixture of 90 g. of ethanol and 110 g. of zinc chloride there was added 39 g. of benzylamine to form a salt. After adding 60 g. of 3,6-dichlorofluoran to this mixture, the resultant mixture was reacted at 140° C. for four hours, the reaction mixture coloring from yellow to a red-brown color. The mixture was then allowed to cool, solidified, and crushed.

The solid thus obtained was mixed with water to dissolve a large amount of the zinc chloride present, which was removed by filtration. By treating the filtrate residue as in Example 1, 45 g. of the colorless or faintly orange crystal of the objective compound, having a melting point of 114° C. to 115° C., was obtained.

PREPARATION 3



Preparation of 3-m-xylylamino-6-chlorofluoran:

Into a mixture of 60 g. of ethanol and 68 g. of zinc chloride was added 25 g. of m-xylizine to form a salt. After adding thereto 36.9 g. of 3,6-dichlorofluoran, the resultant mixture was reacted at 150° C. for four hours. The mixture was allowed to cool, solidified, and crushed. The solid was mixed with water to dissolve a large amount

of the zinc chloride present, which was removed by filtration. By treating the filtration residue as in Example 1, 32 g. of the colorless or faintly purple crystal of the objective compound, having a melting point of 196° C. to 199° C., was obtained. The production of the color formers used in this invention has thus been illustrated by only a few examples, but it will be easily understood by one skilled in the art that the other color formers of the invention may be similarly prepared.

The invention will now be further illustrated by the following examples, in which all parts are by weight, unless otherwise indicated.

EXAMPLE 1

Into 100 parts of trichlorodiphenyl there was dissolved two parts of a color former, 3-amino-6-chlorofluoran. 20 parts of gum arabic and 20 parts of acid-treated gelatin were dissolved in 200 parts of water at 45° C., and the above color former oil was added to the resultant solution (with stirring to emulsify the solution). When the size of the oil drops in the emulsion was reduced to about 4–6 microns, 100 parts of water at 40° C. was added to the emulsion, and then acetic acid was added thereto (with stirring) to adjust the pH to 5. Thereafter, coacervation was caused to occur by the addition of 400 parts of water to form concentrated liquid films of gelatin and gum arabic around the oil drops. 3.8 parts of 37% formalin was then added to harden the aforesaid liquid films at a pH of 4.4. The system was then cooled to 10° C. to gelatinize the liquid films, and an aqueous sodium hydroxide solution was added to the system to adjust the pH to 9. The system was then allowed to stand for about 5–6 hours to complete the hardening of the capsules. The microcapsules were applied to a sheet of paper by a roll coating method or an air-knife coating method and dried. When the paper thus treated was closely contacted with a clay paper and the assembly was subjected to local pressure, by means of a pencil or typewriting, a deep yellow-orange color was immediately formed at the impressed areas of the clay paper. Almost no fading was observed when the colored clay paper was exposed to sunlight for a long period of time or was wet with water. Moreover, when the above-mentioned color forming paper was heated at 100° C. for 20 hours or exposed to sunlight for several hours, the reduction in color depth of the color forming paper was negligible.

EXAMPLE 2

By repeating the same procedure as in Example 1 using 2 parts of a color former, 3-methylamino-6-chlorofluoran, instead of the color former in the Example 1, a color former paper was prepared. When the color former paper was closely contacted with a clay paper and localized pressure was applied, an orange color was immediately formed on the clay paper. When the colored clay paper was exposed to sunlight for a long period of time, or was wet with water, almost no fading was observed. Furthermore, when the color former paper thus prepared was heated to 100° C. for 20 hours, or was exposed to sunlight for several hours, color reduction was negligible.

EXAMPLE 3

By repeating the procedure of Example 1 using 2 parts of a color former, 3-phenylamino-6-chlorofluoran, instead of the color former in Example 1, a color former paper was prepared. When the color former paper was closely contacted with a clay paper and localized pressure was applied, a deep orange-red color was immediately formed on the clay paper. The light fastness and the water resisting property of the coloring matter formed from the color former were excellent, and also the light fastness and heat resistance of the color former paper before coloring were high.

EXAMPLE 4

By repeating the procedure of Example 1 using as the color former 3-methatoluylamino-6-chlorofluoran, a color former paper was prepared. When the color former paper was closely contacted with a clay paper and localized pressure was applied thereto, a deep purple color was rapidly formed on the clay paper. The coloring material thus formed showed good light fastness and good water resistance and, the color former paper (before coloring) also showed good light fastness and heat resistance.

EXAMPLE 5

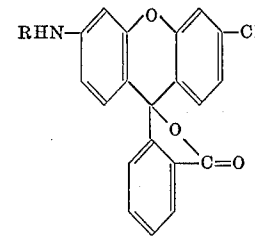
By repeating the procedure of Example 1 using 1 part of Crystal Violet Lactone, 0.5 parts of 3-phenylamino-6-chlorofluoran, 0.5 parts of 3-methaxylylamino-6-chlorofluorane, and 0.4 parts Benzoyl Leuco Methylene Blue instead of the color former in Example 1, a color former paper was prepared. When the color former paper was closely contacted with a clay paper and they were subjected to localized pressure, a deep blue-black color was immediately formed on the clay paper. The coloring matter thus formed showed good light fastness and the color former paper itself illustrated a sufficient light fastness and heat resistance.

EXAMPLE 66

By repeating the same procedure of Example 1 using as the color former 0.3 parts of Benzoyl Leuco Methylene Blue, 0.6 parts of Malachite Green Lactone, 0.6 parts of Crystal Violet Lactone, and 0.4 parts of 3-methatoluylamino-6-chlorofluoran, a color former paper was prepared. When the color former paper was closely contacted with a clay paper and then subjected to localized pressure, a deep black color was immediately formed on the clay paper. The coloring matter thus formed showed good light fastness, the color former paper also showed sufficient light fastness and heat resistance.

What is claimed is:

1. A pressure sensitive transferring sheet adapted to be used in conjunction with a receiving sheet having an electron accepting layer to form a pressure-sensitive copying assembly, said transferring sheet comprising a support and coated on said support, a layer containing pressure-rupturable microcapsules, said microcapsules containing oil and dissolved therein a coloring agent comprising at least one 3-substituted amino-6-chlorofluoran compound represented by the general formula



wherein R represents a member selected from the group consisting of a hydrogen atom, a lower alkyl group, an aryl group, and an aralkyl group.

2. The color former paper claimed in claim **1** wherein said color former is selected from the group consisting of 3-amino-6-chlorofluoran, 3-methylamino-6-chlorofluoran, 3-ethylamino - 6-chlorofluoran, 3-propylamino-6-chlorofluoran, 3-phenylamino - 6-chlorofluoran, 3-benzylamino-6-chlorofluoran, 3-methatoluylamino-6-chlorofluoran, and 3-methaxylylamino-6-chlorofluoran.

3. The color former paper as claimed in claim **1** wherein said microcapsules further contain at least one conventional blue color former.

4. The color former paper as claimed in claim **3** wherein said conventional blue color former is selected from

the group consisting of Crystal Violet Lactone, Benzoyl Leuco Methylene Blue, and Malachite Green Lactone.

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MURRAY KATZ, Primary Examiner

U.S. Cl. X.R.

117—36.8; 260—343.3