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Yamamoto et al.

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[54] **7-PIPERIDINOFLUORAN**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **260/293.58,** 117/36.2

[51] **Int. Cl.** **C07d 29/12**

[58] **Field of Search** 260/293.58, 335, 336

[56] **References Cited**

UNITED STATES PATENTS

3,442,908 5/1969 Orita et al. 260/335

OTHER PUBLICATIONS

Viktorova et al., Chem. Abstracts 64:7546d.

Ramette et al., J. Am. Chem. Soc. 78, 4872–8 (1956).

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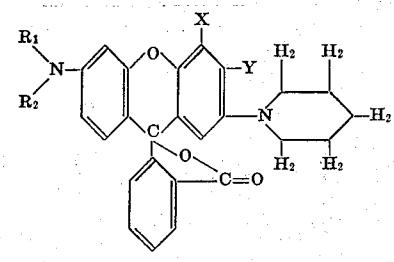
[57] **ABSTRACT**

Compounds and a pressure-sensitive copying sheet containing said compounds as a color-forming agent art provided said compounds have the following general formula:



wherein each of R_1 and R_2 is independently alkyl of up to 4 carbon atoms; and each of X and Y is independently hydrogen, halogen of alkyl of up to 4 carbon atoms.

7 Claims, No Drawings

7-PIPERIDINOFLUORAN

This invention relates to a pressure-sensitive copying sheet and more particularly to a pressure-sensitive copying sheet using a novel fluoran compound as a color forming agent.

As a copying sheet, the so-called "carbon paper" has been used for a long time. However, as is well known, such carbon paper has a serious drawback that it stains the hands, clothes, etc. of the user.

In order to overcome these drawbacks, there has been developed a pressure-sensitive copying sheet which comprises an upper sheet and a lower sheet. The back of the upper sheet is coated with a thin layer of micro-capsules which can be ruptured by a local pressure imparted, for example, by handwriting with pen, pencile, ball-point pen or the like or by typewriting and which contain an electron donating, adsorbable and color-developable colorless organic compound (hereinafter referred to as "color forming agent") dissolved in a non-volatile solvent or oil. The surface of the lower sheet is coated with a thin layer of fine particles of an electron acceptive solid adsorbent (e.g. acid clay, silton, attapulgite, zeolite, bentonite, phenolic resin, etc.) dispersed in a binder. In using such pressure-sensitive copying sheet, the upper sheet is placed upon the lower sheet in such a manner that the back face of the upper sheet would contact the surface of the lower sheet. When a local pressure is applied on the exposed surface of the upper sheet by handwriting or typewriting, the micro-capsules are ruptured and the color-forming colorless agent is transferred from the upper sheet to the surface layer on the lower sheet and is adsorbed by the electron acceptive adsorbent to develope color.

As for such color-forming colorless organic compounds there have been proposed various substances such as Crystal Violet Lactone, Malachite Green Lactone, Benzoyl Leucomethylene Blue, Michler's Hydrol, N-Phenyl Leucoaulamine, Leucotriphenyl Methane, Rhodamine Lactone, Diaminodiphenyl Methane, Spirodipyran, Benzodifurane, etc. However, in all the pressure-sensitive color-developing copying sheets now commercially available, there are used Crystal Violet Lactone (referred to as "CVL" hereinafter) and Benzoyl Leucomethylene Blue (referred to as "BLMB" hereinafter) together as their main color-forming agent.

As is known, CVL has an advantage that it is high in the color-forming reaction velocity but has a drawback that the resistance to light and water or moisture is poor. On the contrary, BLMB has a drawback that its color-forming reaction velocity is low but has an advantage that it, once color-developed, has a high resistance to light and water or moisture. Therefore, when these two agents are used together the respective drawbacks are mutually compensated.

However, such CVL + BLMB mixed system has another drawback that it can develope only a bluish color and not black.

The development of black color is desirable because a black image is more distinctively legible and because a black image can be reproduced or copyed in a more sharp, dense and legible image, than from a bluish image, by the presently available copying machines of various types such as Xerox, thermography, etc. utilizing ultraviolet rays or short wave visible rays.

Therefore there have been proposed various measures to resolve the above problems. Thus, the first one is to use a mixture of various color-forming agents to develope a color as close to black as possible. Most typical proposal in this respect is to add a red color-forming agent (such as Rhodamine-lactam) to the above mentioned CVL + BLMB system to develope violet color which is more close to black than blue of the CVL + BLMB system. Another measure which has been proposed is to incorporate an ultraviolet absorber into the color forming agent so that the developed image may be reproduced by copying machines. However, these methods have not been fully satisfactory.

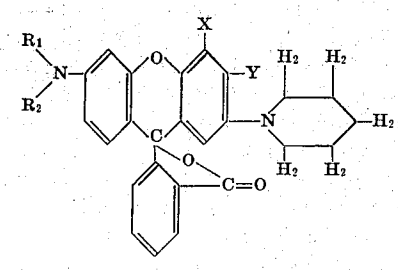
Therefore, a more endeavor has been directed to the development of a pressure-sensitive copying sheet which can form black color copy. The most simple way to attain the above object would, of course, be to prepare a color-forming colorless substance which alone can develope black color when adsorbed by an electron acceptive adsorbent on the lower copy sheet. However, as a result of various experiments and researches, it has been concluded that it is very difficult in the present chemical technology to synthesize a color-reactive colorless substance which alone can develope black color. Therefore, nowadays, researches are being concentrated mostly to the production of a pressure-sensitive copy sheet which makes use of a mixture of various different color-forming substances which can develope different colors such as red, blue, yellow, etc. and together or jointly form black color.

Therefore, it is a main object of this invention to provide novel compounds which are useful in developing black and suitable for use in pressure-sensitive copying sheet.

Another object of this invention is to provide a pressure-sensitive copying sheet by using the above mentioned novel compound.

Other objects of this invention will become apparent from the following description.

Briefly, this invention provides color-developable substantially colorless organic compounds having the following general formula:



(I)

wherein each of R_1 and R_2 is a lower alkyl radicals having 1 – 4 carbon atoms and each of X and Y a member selected from the group consisting of hydrogen, halogen atoms (e.g. chlorine, bromine, etc.) and lower alkyl radicals of 1 – 4 carbon atoms.

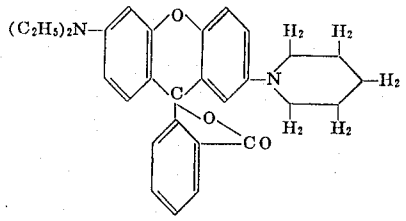
The piperidino radical-containing fluoran compounds represented by the above indicated general formula (I) are novel compounds which are substantially colorless but, upon adsorption on a phenolic resin (electron acceptive adsorbent) can develope black color. Upon adsorption on an inorganic electron acceptive adsorbent usually used in pressure-sensitive copy-

ing sheet, the said compounds may develope a color ranging from dark red to reddish violet. Therefore in latter cases (the use of an inorganic electron accepting solid adsorbent), black color can be developed by using the compound of the formula (I) together with a small amount of other color developing agent such as 3-diethylamino-7-benzylamino fluoran, etc. disclosed in U.S. Pat. No. 3,501,331 (Canadian Pat. No. 814,948).

Further, the piperidino group-containing fluoran compounds of this invention are compatible with conventional color-forming agent, soluble in various solvents or oils and the color developed therefrom is high in resistance or fastness to light. Therefore, the color-forming agents (piperidino group-containing fluoran compounds) of this invention are excellent for use in making pressure-sensitive copying sheet.

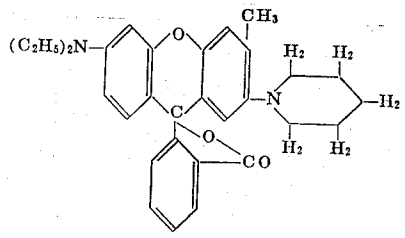
Typical compounds belonging to the above general formula (I) are indicated below together with their melting points and colors to be developed thereby upon adsorption on silton and phenolic resin.

A. 3-diethylamino-7-piperidinofluoran



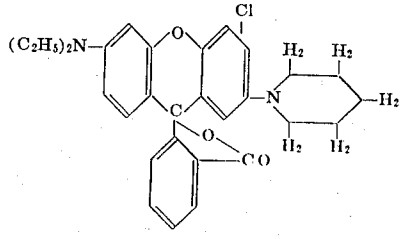
m.p. 182° – 185°C. Dark red on silton
Black on phenolic resin

B. 3-diethylamino-5-methyl-7-piperidinofluoran



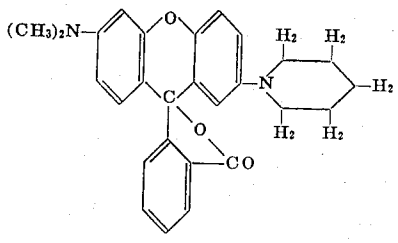
m.p. 152° – 153°C. Dark reddish violet on silton
Black on phenolic resin

C. 3-diethylamino-5-chloro-7-piperidinofluoran



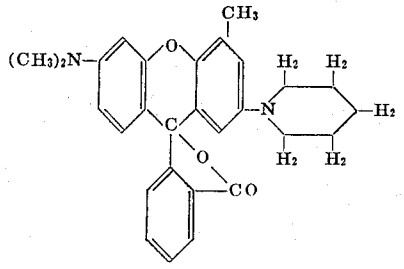
m.p. 125° – 130°C. Dark red on silton
Black on phenolic resin

D. 3-dimethylamino-7-piperidinofluoran



m.p. 193° – 195°C. Dark red on silton
Black on phenolic resin

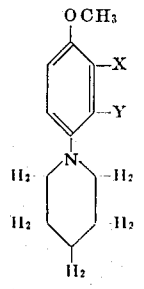
E. 3-dimethylamino-5-methyl-7-piperidinofluoran



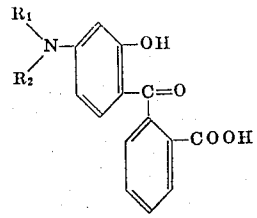
m.p. 235° – 236°C. Dark reddish violet on silton
Black on phenolic resin

The essential and novel feature of this invention is in the use of the novel piperidino group-containing fluoran compound of the general formula (I) as a color-forming agent for a pressure-sensitive copying sheet. In making a pressure-sensitive copying sheet any conventional manner which is well known in the art may be used and therefore no detailed explanation thereabout will be required. In this connection, reference may be made, for example, to U.S. Pat. Nos. 2,548,366, 2,800,457, 2,800,458 and 3,501,331. However, when a phenolic resin (e.g. novolac resin, p-phenylphenol-formaldehyde condensation product, p-chlorophenol-formaldehyde condensation product, etc.) is used as the electron accepting absorbent the fluoran compound of this invention can develope black color and therefore it is preferable to employ a phenolic resin as the electron accepting absorbent.

The piperidino-containing fluoran compounds of the general formula (I) may be prepared, for example, as follows. Thus, p-anisidine or its nucleus substitute is reacted with 1,5-dibromopentane to obtain p-peridinoanisol or its derivative of the formula:

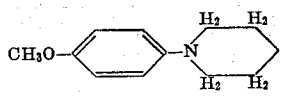


, which is then condensed with an o-(4-dialkylamino-2-hydroxy-benzoyl)-benzoic acid of the formula:



(wherein X. Y, R_1 and R_2 are as defined before) in the presence of a condensing agent such as sulfuric acid to obtain the desired piperidino-containing fluoran compound of the formula I.

As a more specific example, the production of 3-diethylamino-7-piperidinofluoran of the formula A is as follows. Thus, 27 g. of p-anisidine and 17.5 g. of 1,5-dibromopentane in 50 ml. of methanol were refluxed for 17 hours. To the reaction mixture was added 50 g. of 20 percent aqueous solution of sodium hydroxide, and the formed oily layer was separated and purified by vacuum distillation to recover the fraction of 114°–118 °C./4 mmHg., which is colorless p-piperidinoanisol. Yield 9.5 g. (65.6 percent of theory).



p-piperidinoanisol

Elementary analysis:

Calculated N 7.33 %

Found N 7.27 %

Then 5.73 g. of the above prepared p-piperidino anisol and 9.4 g. of o-(4-diethylamino-2-hydroxybenzoyl)benzoic acid were reacted together in 50 g. of 98 percent sulfuric acid for 60 hours at 35°–40°C. while stirring. Then the reaction mixture was poured into 200 ml. of water. The solution was rendered alkaline with the addition of 200 ml. of 25 percent solution of sodium hydroxide. The formed precipitate was recovered by filtration and dried to obtain 8.5 g. of violet brown powder, which was recrystallized from 300 ml. of benzene with the use of 2 g. active carbon. Thus, there were obtained 7.7 g. (yield 56.5 percent) of slightly reddish white crystals (m.p. 182°–185°C.) of 3-diethylamino-7-piperidinofluoran.

The invention will be further explained by referring to the following Examples which are given for illustra purpose only and not for limiting the scope of the invention.

EXAMPLE 1

In 500 ml. of water there were dissolved at 40°C. 600 g. of gelatin and 60 g. of gum arabic. On the other hand, 5 g. of 3-diethylamino-7-piperidinofluoran were dissolved in 150 g. of diphenylchloride. The latter solution was added to the former solution and the mixture was emulsified by a homogenizer. Then water at 50°C. was added thereto until the whole becomes 2000 ml. Then 90 ml. of 10 percent acetic acid were added and the mixture was stirred and further added with water at 50°C. until the whole becomes 4 kg. The stirring was continued for one hour and the mixture was cooled with ice water while continuing the stirring. When the mixture was cooled below 10°C., there was added a 10 percent aqueous solution of sodium hydroxide to increase the pH up to 9, whereupon the cooling is discontinued and the mixture is allowed to stand to return to the room temperature.

The coating composition thus prepared was applied on the lower surface of the upper sheet by roll-coating and dried. Apart from the above, an aqueous gelatine solution containing powder of phenolic resin (p-phenylphenol-formaldehyde condensation product) dispersed therein was applied on the upper face of a lower sheet and was dried.

The coated upper sheet was placed on the coated lower sheet in such a way that the respective coated layers contact intimately with each other. Upon writing with an inkfree steel point pen on the upper face of the upper sheet to exert pressure, black color was rapidly developed on the written area on the upper face of the lower sheet. This color did not fade even upon exposure to the sun light for a long time.

The same procedure as above was repeated except that there was used except silton powder was used in place of the phenolic resin powder. Upon writing there was developed dark red color, which is excellent in light-resistance.

EXAMPLE 2

The same procedure as in Example 1 was repeated except that 3-diethylamino-5-methyl-7-piperidinofluoran was used instead of 3-diethylamino-4-piperidinofluoran. Upon writing, black color was developed when phenolic resin used as the absorbent, while dark reddish violet was developed when silton was used as the adsorbent.

EXAMPLE 3

The procedure same as in Example 1 was repeated except that, instead of 5 g. of 3-diethylamino-7-piperidinofluoran, there were used a mixture of 4.5 g. of 3-diethylamino-7-piperidinofluoran and 0.5 g. of 3-diethylamino-7-benzylaminofluoran (U.S. Pat. No. 3,501,331), and silton was used as the adsorbent. Upon writing there was developed black color.

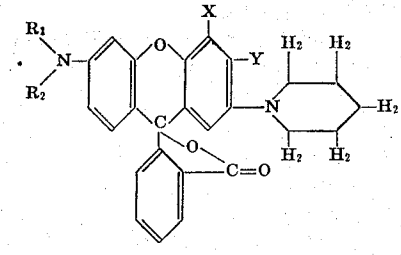
EXAMPLE 4

The same procedure as in Example 1 was repeated except that 3-diethylamino-5-chloro-7-piperidinofluoran (C), 3-dimethylamino-7-piperidinofluoran (D) or 3-dimethylamino-5-methyl-7-piperidinofluoran (E) was used in place of 3-diethylamino-7-piperidinofluoran. Upon writing the following colored copies were obtained.

Color forming agent	Phenolic resin	Silton
C	Black	Dark red
D	Black	Dark red
E	Black	Dark reddish violet

What we claim is:

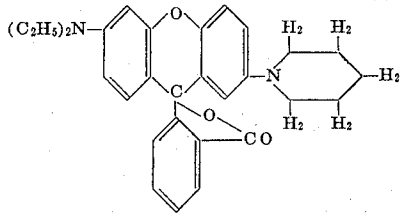
1. A compound of the formula



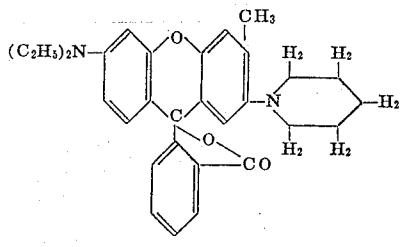
wherein each of R_1 and R_2 is independently alkyl of up to 4 carbon atoms; and each of X and Y is independently hydrogen, halogen or alkyl of up to 4 carbon atoms.

2. A compound of claim 1 wherein said halogen is chlorine or bromine.

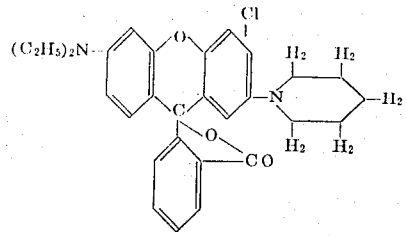
3. 3-diethylamino-7-piperidinofluoran



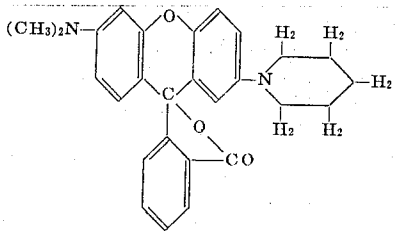
4. 3-diethylamino-5-methyl-7-piperidinofluoran



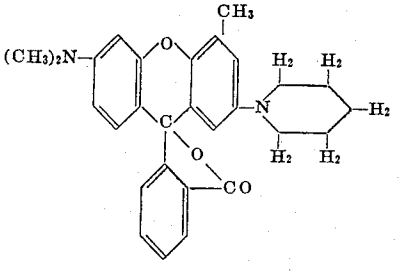
5. 3-diethylamino-5-chloro-7-piperidinofluoran



6. 3-dimethylamino-7-piperidinofluoran



7. 3-dimethylamino-5-methyl-7-piperidinofluoran



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