United States Patent [19]

Hayashi et al.

[11] **3,900,217**

[45] **Aug. 19, 1975**

[54] **PRESSURE-SENSITIVE COPYING PAPER**

[75] Inventors: **Takao Hayashi; Hiroharu Matsukawa; Sadao Ishige,** all of Fujinomiya, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.,** Minami-Ashigara, Japan

[22] Filed: **July 11, 1973**

[21] Appl. No.: **378,105**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 152,831, June 14, 1971, abandoned.

[30] **Foreign Application Priority Data**

June 13, 1970 Japan 45-51116

[52] **U.S. Cl.** **282/27.5**

[51] **Int. Cl.** **B41c 1/06;** B41m 5/00

[58] **Field of Search** 117/36.2, 36.8, 36.9

[56] **References Cited**

UNITED STATES PATENTS

2,915,415	12/1959	Francis et al.	117/36.2
3,427,180	2/1969	Phillips	117/36.2
3,501,331	3/1970	Kimura et al.	117/36.2
3,540,909	11/1970	Lin	117/36.2
3,649,649	3/1972	Orita et al.	260/343.3
3,769,062	10/1973	Ishige et al.	117/36.8 X

Primary Examiner—Thomas J. Herbert, Jr.
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn and Macpeak

[57] **ABSTRACT**

Light-sensitivity and anti-fade of color-images formed by reaction of a color former and a solid acid substance can be improved by using a colorless phenothiazine compound such as 10-ethylphenothiazine-5-oxide or 3-methoxy-phenothiazine. The phenothiazine compound contained in microcapsules can be useful for pressure-sensitive copying paper.

3 Claims, 16 Drawing Figures

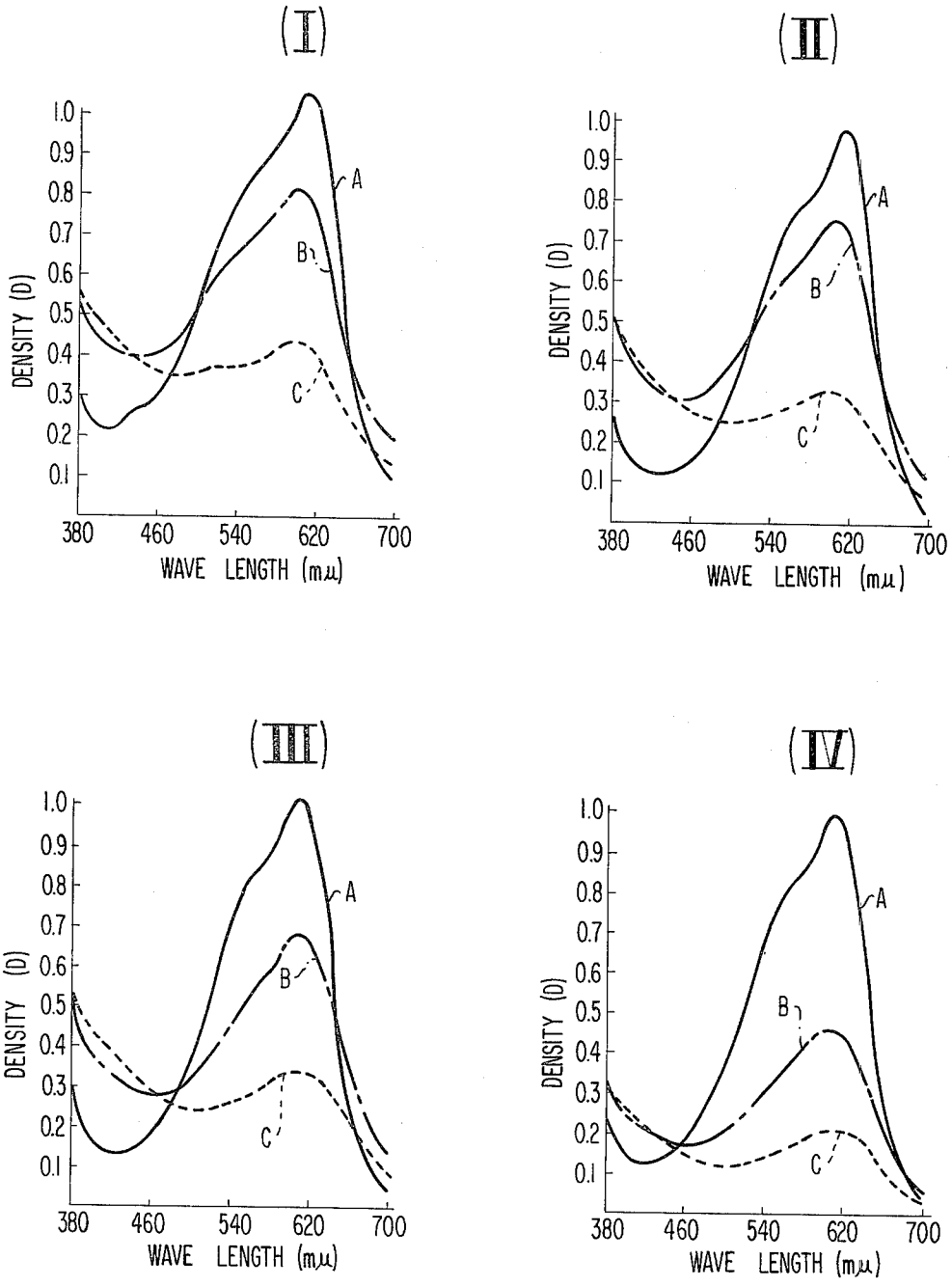


FIG. 1

INVENTORS
TAKAO HAYASHI
HIROHARU MATSUKAWA
SADAO ISHIGE

BY Sughrue, Rothwell, Mion, Zinn & Macpeak

ATTORNEYS

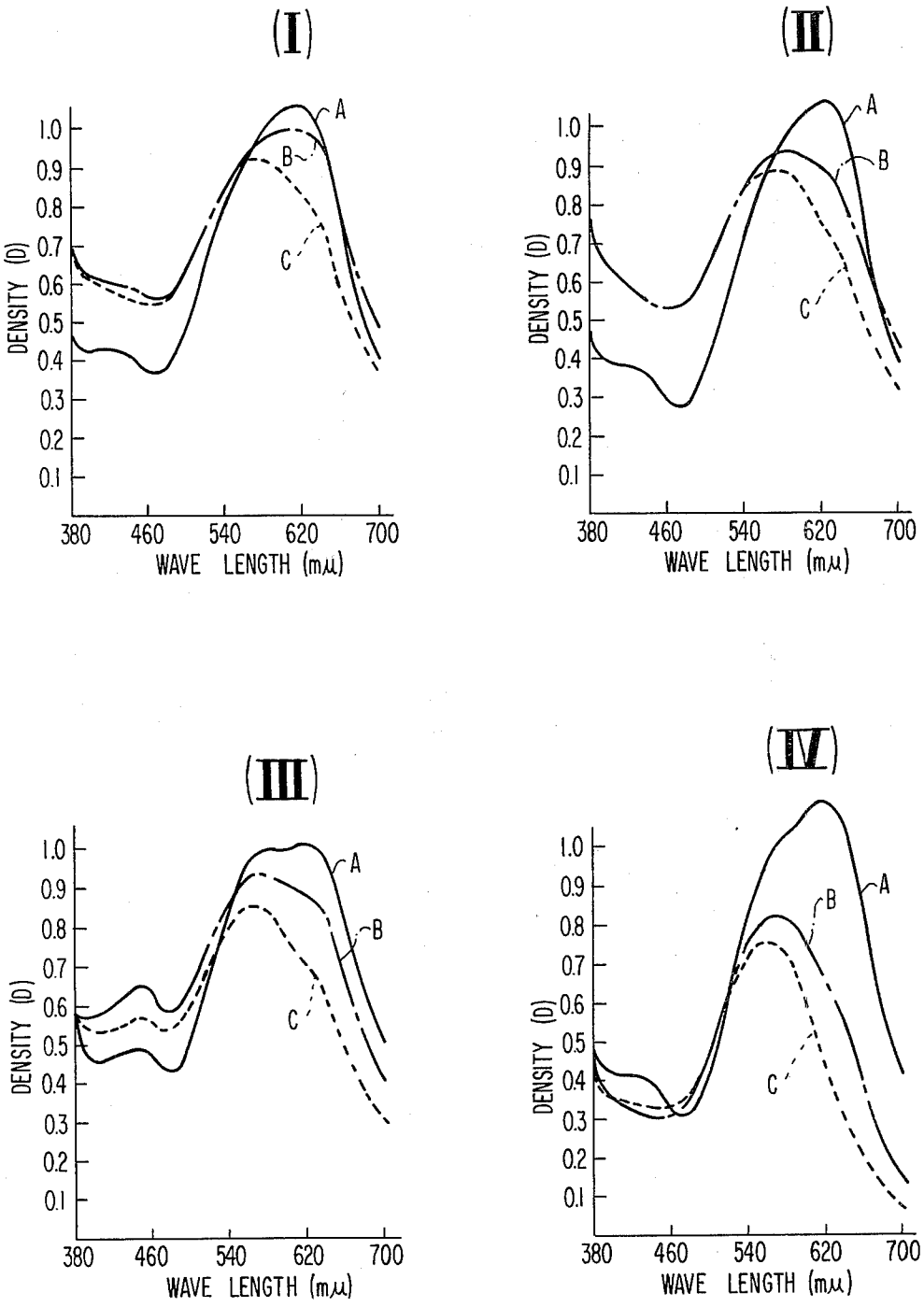

(I)
(II)
(III)
(IV)
DENSITY (D)
WAVE LENGTH (mμ)
A
B
C
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
380
460
540
620
700

FIG. 2

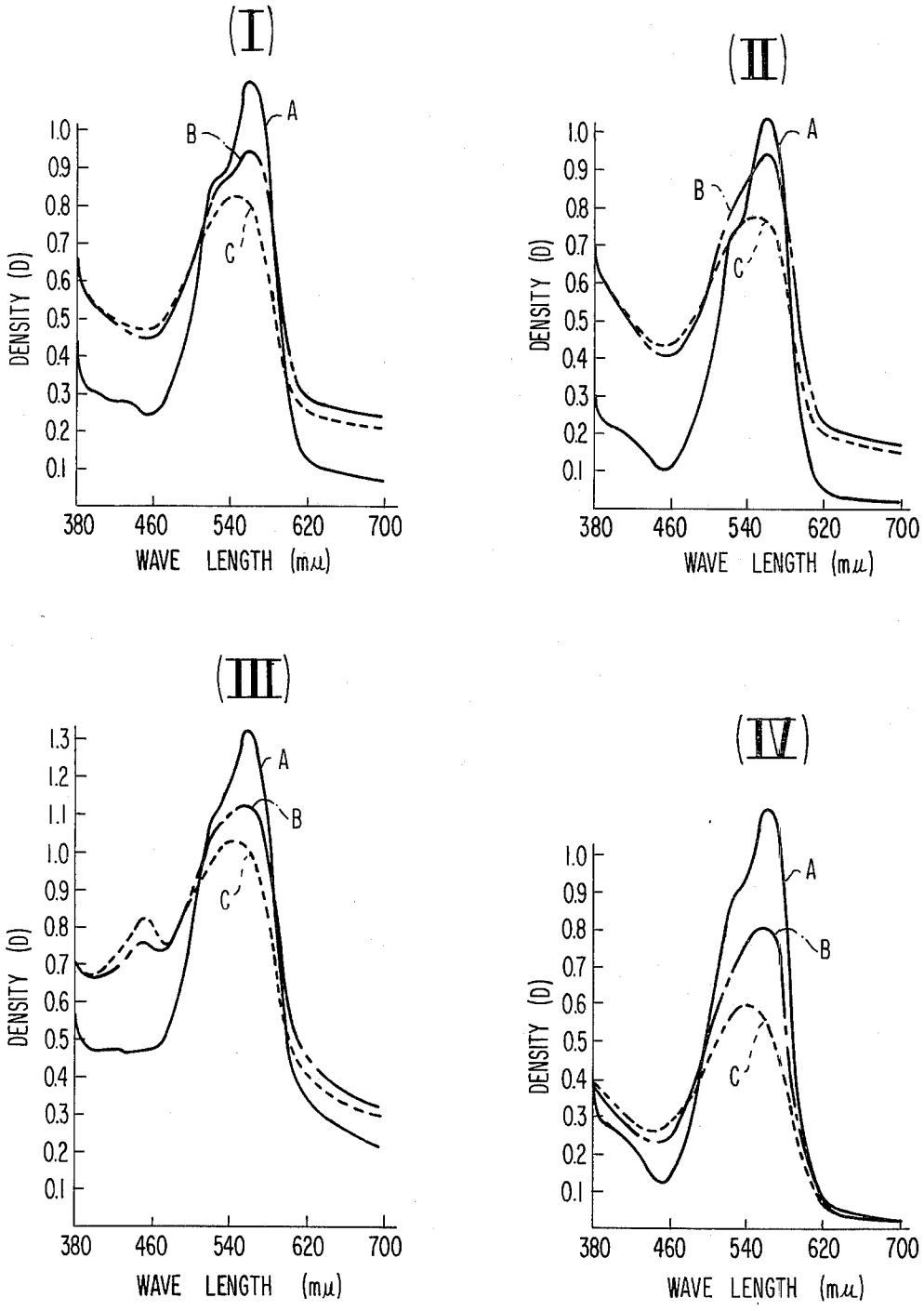


FIG. 3

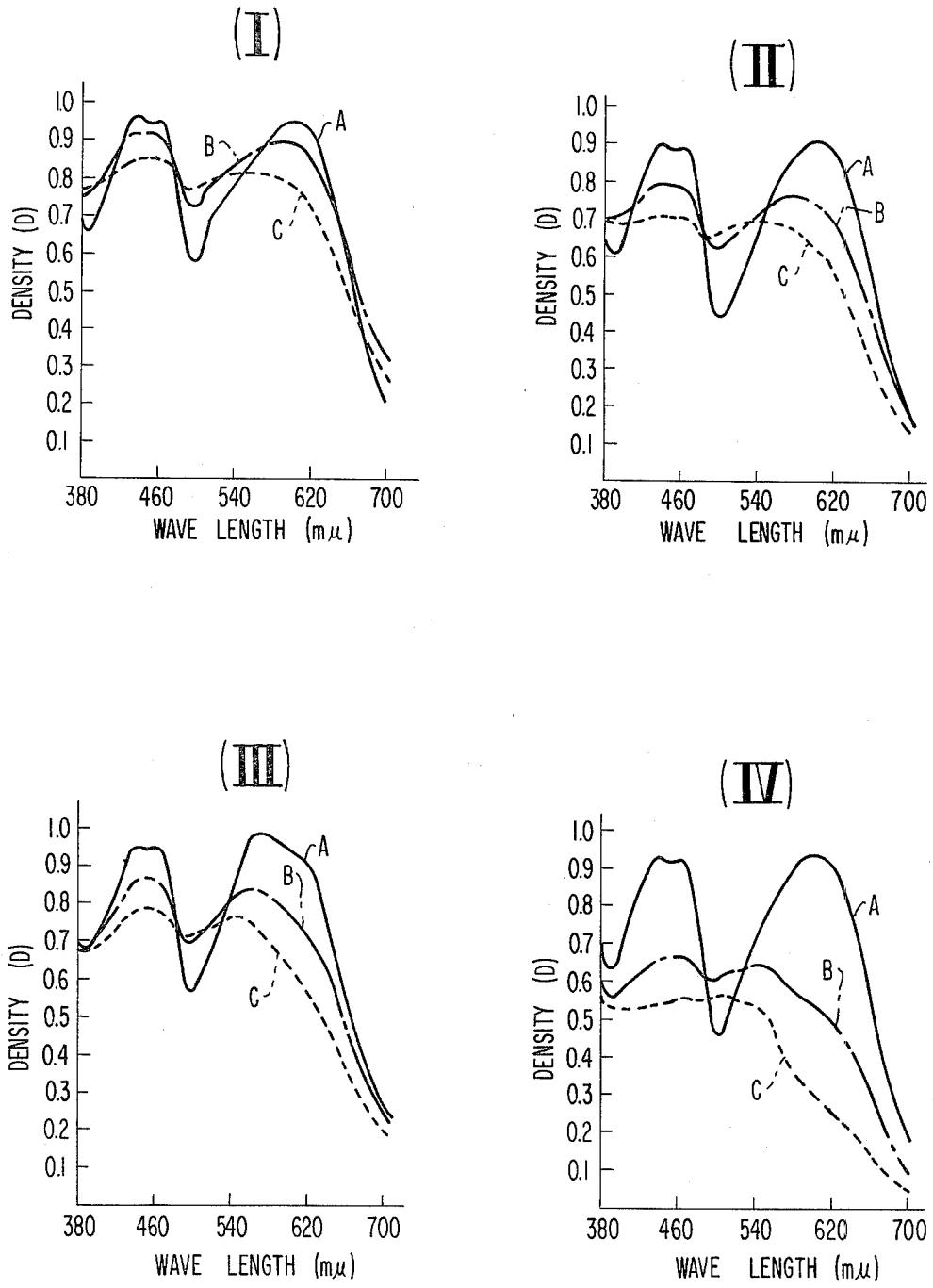

(I)
(II)
(III)
(IV)
DENSITY (D)
WAVE LENGTH (mμ)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
380
460
540
620
700
A
B
C

FIG. 4

PRESSURE-SENSITIVE COPYING PAPER

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part application of U.S. Ser. No. 152,831, filed on June 14, 1971 now abandoned, which claims priority from June 13, 1970, based on Japanese Patent Application Ser. No. 51116/70.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a pressure-sensitive copying paper. More particularly, this invention relates to a method for preventing discoloration and fading of a color formed by a pressure-sensitive copying paper utilizing color reaction of color former and a solid acid substance.

2. Description of the Prior Art

As has been known from U.S. Pat. Nos. 2,712,507; 2,730,465; 2,730,457; 3,418,250, etc., a pressure-sensitive copying paper is produced by utilizing microcapsules containing a solution of a substantially colorless organic compound (hereinafter, referred to as "color former") and a material hereinafter, referred to as "developer") which reacts in contact with the color-former to form a distinctive color.

In practice, both of these components are coated on the same support, or on different supports.

Examples of the developer include solid acid substances, for example, clay minerals such as acid clay, active clay, attapulgite, zeolite or bentonite; organic acids such as succinic acid, tannic acid, gallic acid or pentachlorophenol; phenol resins such as phenol-formaldehyde (novolac type); and mixture thereof. As the color-former, there can be used malachite green lactone which is 3,3-bis-(p-dimethylaminophenyl) phthalide, benzoyl leuco methylene blue, crystal violet lactone which 3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide, Rhodamine B lactam, 3-dialkylamino-7-dialkylamino fluoranes, 3-methyl-2,2'-spirobi (benzo [f] chromene), and mixtures thereof.

In the present invention, a color-former sheet is prepared by coating microcapsules containing a color-former on a support, and a developer sheet is prepared by coating a developer on a support. By the pressure-sensitive copying paper, used in the present invention, is meant not only a combination of the color-former sheet and the developer sheet, but also a combination of a color-former and a developer coated together on a surface of a support.

The light resistance of a color obtained by the color reaction between a color-former and a developer depends mainly on the structure of the color. But the light resistance is affected by the developer. Clays such as acid clay are the most widely used developers. The light resistance of a color formed by use of such developer varies according to the kind of coupler, but is generally weak except that of benzoyl leuco methylene blue. Accordingly, when allowed to stand indoors or exposed to sunlight, density of the color formed is reduced, and the color hue thereof readily changes. This phenomenon is very detrimental to the pressure-sensitive copying paper.

For example, microcapsule-coated paper (i.e. color-former sheet) produced in greatest quantities contains crystal violet lactone and benzoyl leuco methylene blue as couplers. Since crystal violet lactone has very poor resistance to light, the resulting color readily disappears on being allowed to stand indoors or on exposure to sunlight. Consequently, the color image formed becomes light blue formed from benzoyl leuco methylene blue, and reduces the commercial value of the copying paper produced. In black-forming copying paper and green-forming copying paper, 3-dibenzylamino-7-diethylamino fluorane is used as the coupler. It produces a green or black color in contact with acid clay as the developer, but turns red on being left to stand indoors or exposure to sunlight. Thus, the black or green color formed by black-forming or green-forming pressure-sensitive copying paper turns reddish on standing indoors or exposure to sunlight, and deteriorates its commercial value.

All conventional pressure-sensitive copying paper causes the above defects because a combination of two-type color formers has been used; one type is a rapid-color former and the other type is a slow-color former, and no color-former having good properties to all conditions has been found.

SUMMARY OF THE INVENTION

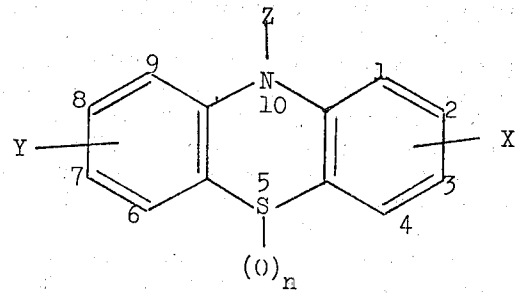
Therefore, an object of the invention is to provide a pressure-sensitive copying paper capable of forming color images of increased light-resistance and without discoloration and fade.

The inventors have found that the above objects can be attained by incorporating a phenothiazine compound soluble in or miscible with an organic solvent for the color former into microcapsules.

Phenothiazine compound of the invention must give useful effects to color former and dye thereof under varied atmosphere such as temperature, humidity, sunlight, etc., so it must not form distinct color when contacted with solid acid substance. If it forms distinct color when contacted with solid acid substance, finally obtained color is different from the color formed by only color former because it is a mixed color of both. Accordingly, the color-forming phenothiazine compound such as 3,7-dimethylamino phenothiazine or 3,-7-dimethylamino-10-benzoylphenothiazine can not improve the properties of color former or dye thereof.

From the point of the view, phenothiazine compound of the invention is defined as a substantially colorless compound incapable of forming a distinct color when contacted with a solid acid substance.

Preferred phenothiazine compound of the invention is represented by the formula,



wherein n is 0, 1 or 2; X, Y and Z each is a group having not smaller than −0.5 of Hammett constant (δ: sigma).

As well known in the art, an electron-attracting group has a positive value of the Hammett constant and an electron-donating group has a negative value of Hammett constant. In the invention, it is not preferred that the substituents, X, Y and Z have Hammett constant of smaller than −0.5 (that is, it is not preferred that the value is −0.6, −0.7, - - - - -, −1.0, - - -). Hammett constant is generally applied to meta or para- substituent, but the position thereof is not important in the invention, so long as the Hammett constant is satisfied with the critical value.

The preferred substituent, Z is a hydrogen atom; an alkyl group; an alkyl substituted with aryl, cyano, hydroxy, halogen, amino, alkoxy, alkoxycarbonyl or acyl group; an aryl group; an acyl group; an alkoxycarbonyl group and a formyl group.

The preferred substituents, X and Y each is a hydrogen atom, an alkyl group, a halogen atom, a nitro group, an acrylamino group, a hydroxyl group, an alkoxy group, an acyloxy group, an alkoxycarbonyl group, an alkylsulfonylamino group and an arylsulfonylamino group.

In the above definition of X, Y and Z, all alkyl groups including an alkoxy, acyl, etc. have 1 to 18 carbon atoms, preferably 1 to 5 carbon atoms, and all aryl groups includes phenyl and naphthyl groups.

The typical examples of the phenothiazine compounds of the invention are phenothiazine, 10-methylphenothiazine, 10-ethylphenothiazine, 10-octadecylphenothiazine, 10-allyl-phenothiazine, 10-benzylphenothiazine, 10-β-cyanoethyl-phenothiazine, 10-β-hydroxyethyl-phenothiazine, 10-β-chloroethylphenothiazine, 10-β-carboethoxy-phenothiazine, 10-acetyl-phenothiazine, 10-benzoyl-phenothiazine, 10-anisoyl-phenothiazine, 1-hydroxyphenothiazine, 1-methoxy-phenothiazine, 2-hydroxy-phenothiazine, 2-methoxy-phenothiazine, 3-hydroxy-phenothiazine, 3-methoxyphenothiazine, 4-methoxy-phenothiazine, 2-acetoxy-phenothiazine, 2,7-dimethoxyphenothiazine, 2-methoxy-7-chlorophenothiazine, 1-chlorophenothiazine, 2-chloro-10-β-cyanoethylphenothiazine, 3,10-dimethyl-phenothiazine, 10-methylphenothiazine-5-oxide, 3-nitrophenothiazine-5-oxide, 1,2-benzophenothiazine, 10-β-dimethylaminophenothiazine-5-oxide, 3-methoxy-10-acetyl phenothiazine, 3-acetaminophenothiazine, 2-carboethoxy-phenothiazine, 3-dodecyloxyphenothiazine, 2-trifluoromethyl-phenothiazine, 2,8-diacetylphenothiazine, 10-octadecyl-phenothiazine, 10-carboethoxyphenothiazine, 10-(p-nitrobenzenesulfonyl)-phenothiazine, 10-phenylacetyl-phenothiazine, 10-(p-tolyl)-phenothiazine, 10-(1-dimethylamino)-2-propyl-phenothiazine, 10-benzenesulfonyl-3,7-dinitrophenothiazine, 10-pyvaloyl-phenothiazine, 3-octyloxyphenothiazine, 10-phenoxyacetyl-phenothiazine, 3,7-dinitrophenothiazine-5-oxide, 10-formyl-1,3-dinitrophenothiazine, phenothiazine-5-dioxide, 10-benzylphenothiazine-5-dioxide, 10-(p-toluenesulfonyl)-5-dioxide, 10-cyclohexyloxycarbonylmethylphenothiazine and 3-(p-toluenesulfonylamino)-phenothiazine. These compounds are described in "Chemical Reviews" 54, Pages 797–833.

The phenothiazine compound can be incorporated into the solvent for the color former before or after the color former is dissolved in the solvent, and then the resulting solution is microencapsulated. The phenothiazine compound can be also dissolved in the solvent and microencapsulated. Thus obtained microcapsules are coated on a support such as a paper, a plastic sheet such as polypropylene or polyethylene terephthalate, or a resin-coated sheet such as polyethylene-laminated paper. Accordingly, a pressure-sensitive copying paper of the invention includes an embodiment of a support having coated thereon a microcapsule layer, of which microcapsules contains the phenothiazine compound and the color former, and an embodiment of a support having coated thereon a microcapsule layer including microcapsules which contains the phenothiazine compound and microcapsules which contains the color former. If necessary, the pressure-sensitive copying paper may include an embodiment of combination with the above two embodiment.

Such the microcapsules have about 1 to 500 microns and can be easily obtained by the well known methods disclosed in U.S. Pat. No. 2,800,457; 2,800,458; 3,429,827; 3,577,515; British Pat. No. 867,797; 989,264; 1,091,076, etc. In the microencapsulation methods, the phenothiazine compound and/or the color former can be advantageously dissolved in an organic solvent which is preferably immiscible with water. Such the solvent has preferably a boiling point of higher than 150°C. As the practical solvent, natural and synthetic oils can be used singly or in combination. There may be exemplified an vegetable oil such as cotton seed oil, bean oil or castor oil, and a synthetic oil such as chlorinated biphenyl, chlorinated terphenyl, alkylated biphenyl, alkylated terphenyl, chlorinated paraffin, chlorinated naphthalene, alkylated naphthalene, kerosene, paraffin or naphthene oil.

The color former is a colorless compound capable of forming a color dye when contacted with a solid acid substance. Therefore, the color former can be defined as a dye-precursor. The color formers of the invention can contain those used in the color formation systems based on a reaction between electron-donor and electron-acceptor. The kind of the color former to be used is not critical in this invention and all well-known color formers, for example, disclosed in U.S. Pat. Nos. 3,501,331; 3,514,310; 3,514,311; 3,540,911; 3,293,060 can be used. Examples of the color former usable in this invention are triarylmethane compounds such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide, i.e., Crystal Violet Lactone (which will be abbreviated as "CVL"), 3,3-bis(p-dimethyl-aminophenyl) phthalide, i.e., malachite green lactone, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl) phthalide, 3-(p-dimethylaminophenyl)-3-(2-phenylindol-3-yl) phthalide, 3,3-bis(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazol-3-yl)-5-dimethylaminophthalide, 3,3-bis(2-phenylindol-3-yl)-5-dimethylaminophthalide, and 3-p-dimethylaminophenyl-3-(1-methylpyrrol-2-yl)-6-dimethylamino-phthalide; diphenylmethane compounds such as 4,4′-bis-dimethyl-amino-benzhydrine benzyl ether, N-halophenylleuco-Auramine and N-2,4,5-trichlorophenyl-leuco-Auramine; xanthene compounds such as rhodamine-B-anilinolactam, rhodamine-(p-nitroanilino) lactam, rhodamine-B-(p-

chloroanilino) lactam, 7-dimethylamino-2-methoxyfluoran, 7-diethylamino-2-methoxyfluoran, 7-diethyl-amino-3-methyoxyfluoran, 7-diethylamino-3-chlorofluoran, 7-diethylamino-3-chloro-2-methylfluoran, 7-diethylamino-2,3-dimethylfluoran, 7-diethylamino-(3-acetylmethylamino) fluoran, 7-diethylamino-(3-methylamino) fluoran, 3,7-diethylaminofluoran, 7-diethylamino-3-(dibenzylamino) fluoran, 7-diethylamino-3-(methylbenzylamino) fluoran, 7-diethylamino-3-(chloroethyl-methylamino) fluoran and 7-diethylamino-3-(diethylamino) fluoran; thiazine compounds such as benzoyl leucomethylene blue, and p-nitrobenzyl leucomethylene blue; and spiropyran compounds such as 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3,3'-dichloro-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho-(3-methoxybenzo)-spiropyran and 3-propyl-spiro-dibenzopyran.

In the invention, an amount of color former is easily decided by one skilled in the art in relation to an amount of solid acid. Therefore, amounts of color former and solid acid substance are not important in the invention. But, an amount of phenothiazine compound is rather important.

The amount of the phenothiazine compound in the invention is about 10 to 200%, preferably 20 to 100% by weight based on the total amount of the color former coated on the support.

On the other hand, the solid acid substance can include those mentioned before and those disclosed in U.S. Pat. Nos. 2,777,780; 3,427,180; 3,455,721; 3,466,185; 3,516,845; 3,540,914; 3,634,121; 3,466,256; 3,672,935; 3,682,680; U.S. Ser. Nos. 184,608 and 192,593, etc. The solid acid substance is dissolved or dispersed and coated on such a support as mentioned above, if necessary, together with a well-known binder such as gum arabic, gelatin, ethyl cellulose, styrene-butadiene copolymer, styrene-butadiene latex, nitrocellulose, methyl-methacrylatebutadiene latex, etc.

The solution or dispersion can be coated on the afore-mentioned microcapsule layer provided on a support. Further, it is coated on a support and then the aforementioned microcapsules can be coated thereon.

The microcapsules and the solid acid substance can be coated by such the coating method as air knife coating method, a blade coating method, a roll coating method, and the like, and various printing methods.

The pressure-sensitive copying paper of the invention will be specifically illustrated by the following examples.

EXAMPLE 1

Ten parts by weight of acid-treated pigskin gelatin and 10 parts of gum arabic were dissolved in 400 parts by weight of water at 40°C. With the addition of 0.2 part by weight of Turkey red oil as an emulsifier, 40 parts by weight of a color-former oil was emulsified into the aqueous solution. The color-former oil had been prepared by dissolving in an oil consisting of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene, 2% by weight, based on the oil, of crystal violet lactone, and then dissolving 2% by weight, based on the oil, of phenothiazine. When the size of the oil droplet became about 5 microns on an average, the emulsification was stopped. Water at 40°C. was added to adjust the total amount to 900 parts by weight. At this time, care was taken not to lower the temperature of the liquid below 40°C. Then, a 10% aqueous acetic acid solution was added to adjust the pH of the liquid to 4.0 to cause coacervation (as disclosed in U.S. Pat. No. 2,800,457). With continued stirring, the mixture was cooled with ice water after a lapse of 20 minutes to gel the coacervate film deposited around the oil droplets. When the temperature of the liquid reached 20°C., 7 parts by weight of 37% formaldehyde was added. When the temperature became 10°C., a 15% aqueous solution of sodium hydroxide was poured to adjust the pH to 9. The addition of sodium hydroxide was performed with utmost care. Subsequently, the mixture was heated for 20 minutes with stirring to raise the temperature to 50°C. After lowering the temperature to 30°C., the resulting capsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

EXAMPLE 2

To 40 parts by weight of color-former oil consisting of 2% by weight of crystal violet lactone dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was added 2% by weight, based on the oil, of 10-ethylphenothiazine-5-oxide, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m², and allowed to dry to form a color-former sheet.

EXAMPLE 3

To 40 parts by weight of a color-former oil consisting of 2% by weight of crystal violet lactone dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was added 2% by weight, based on the oil, 3-methoxy-phenothiazine, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former.

COMPARATIVE EXAMPLE 1

A color-former oil consisting of 4 parts by weight of chlorodiphenyl and 1 part of kerosene and 2% by weight of crystal violet lactone was microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a based paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

COMPARATIVE TEST 1

Each of the color-former sheet obtained in Examples 1–3 and Comparative Example 1 was superposed on a test developer sheet, and a pressure of 600 Kg/cm² was applied thereto to form a color. The test developer sheet was prepared by the following procedure. Eight parts of 20% sodium hydroxide and a dispersing agent were added to 300 parts of water, and with stirring, 100 parts by weight of acid clay was gradually added. After thorough stirring, the stirring was slowed down, and 20 parts by weight, calculated as solids content, of a styrene-butadiene latex was added gradually. The result-

ing coating solution was applied to a base paper having a unit weight of 40 g/m² in an amount of 10 g/m² as solids content, and allowed to dry.

After allowing the color image to stand for one hour in a dark place, the absorption spectrum curve (fresh density designated by A) at a wavelength in the range of 700 to 380 mμ was measured. The absorption spectrum curve of the color-former was also measured after irradiation of sunlight for one hour (density designated by B) and three hours (density designated by C), respectively. The results obtained are shown in FIG. 1, I to IV, in which I refers to the coupler sheet of Example I, II refers to the sheet of Example 2, III refers to the sheet of Example 3, and IV refers to the sheet of Comparative Example 1. The measurement of the absorption spectrum curves was performed by a Beckman spectrophotometer, Type DB. The light resistance of crystal violet lactone was determined by the following formula, and the results are given in Table 1.

$$\text{Light resistance} = \frac{\text{Density at the absorption maximum after sunlight irradiation}}{\text{Fresh density at the absorption maximum}} \times 100$$

TABLE 1

Sheet	Light resistance value of crystal violet lactone at the absorption maximum. One-hour sunlight irradiation	Three-hour sunlight irradiation
Example 1	78.2%	50.2%
Example 2	77.3%	45.2%
Example 3	67.5%	41.0%
Comparative Ex. 1	46.4%	21.6%

These results demonstrate that the light resistance of crystal violet lactone increases by the addition of any of phenothiazine, 10-ethyl phenothiazine-5-oxide, or 3-methoxy phenothiazine.

EXAMPLE 4

In 40 parts by weight of a color-former oil, consisting of 2% by weight of 3-methyl-2,2'-spirobi(benzo [f] chromene) dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene, was dissolved 2% by weight, based on the oil, of phenothiazine, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color former sheet.

EXAMPLE 5

In 40 parts by weight of a coupler oil consisting of 2% by weight of 3-methyl-2,2'-spirobi(benzo [f] chromene) dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was dissolved 2% by weight of 10-ethylphenothiazine-5-oxide, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

EXAMPLE 6

In 40 parts by weight of a color-former oil consisting of 2% by weight of 3-methyl-2,2'-spirobi(benzo [f] chromene) dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was dissolved 2% by weight, based on the oil, of 3-methoxy phenothiazine, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

COMPARATIVE EXAMPLE 2

A coupler oil consisiting of 2% by weight of 3-methyl-2,2'-spirobi(benzo [f] chromene) dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was microencapsulated in the same manner as set forth in Example 1.

The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

COMPARATIVE TEST 2

Each of the color-former sheets obtained in Examples 4–6 and Comparative Example 2 was superposed on the test developer sheet described in Comparative Test 1, and a color was formed by applying a pressure of 600 Kg/cm². The absorption spectrum curve of the color-former at a wavelength in the range of 700 to 380 mμ (fresh density designated by A) was measured after allowing the color image to stand for one hour in a dark place. The absorption spectrum curve of the color-former was also measured after irradiation of sunlight for one hour (density designated by B) and three hours (density designated by C) respectively. The results obtained are shown in FIG. 2, I to IV, in which I, to III refer respectively to the sheets obtained in Examples 4–6, and IV, to Comparative Example 2. The light resistance of the color-former was determined in the same way as described in Comparative Test 1. The results are given in Table 2.

TABLE 2

Sheet	One-hour sunlight irradiation	Three-hours sunlight irradiation
Example 4	93.8%	86.8%
Example 5	87.5%	83.2%
Example 6	91.5%	83.3%
Comparative Ex. 2	73.5%	67.2%

It is seen from the foregoing results that the light resistance of 3-methyl-2,2'-spirobi(benzo [f] chromene) is improved and its color change considerably prevented, by the addition of phenothiazine and its derivatives.

EXAMPLE 7

In 40 parts by weight of a color-former oil consisting of 2% by weight of 3-diethylamino fluorance-p-nitroanilinolactam dissolved in an oil consisting of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was dissolved 2% by weight, based on the oil, of phenothiazine, and these were microencap-

sulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

EXAMPLE 8

In 40 parts by weight of a color-former oil consisting of 2% by weight of 3-diethylamino fluorance p-nitroanilide dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was dissolved 2% by weight, based on the oil, of 10-ethylphenothiazine-5-oxide, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

EXAMPLE 9

In 40 parts by weight of a color-former oil consisting of 2% by weight of 3-diethylamino fluorane p-nitroanilinolactam dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was dissolved 2% by weight, based on the oil, of 3-methoxy-phenothiazine, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

COMPARATIVE EXAMPLE 3

Forty parts by weight of a color-former oil consisting a 2% by weight of 3-diethylamino-fluorane p-nitroanilinolactam dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and alllowed to dry to form a color-former sheet.

COMPARATIVE TEST 3

Each of the color-former sheets obtained in Examples 7–9 and Comparative Example 3 was superposed on the test developer sheet described in Comparative Test 1, and a color was formed by applying a pressure of 600 Kg/cm². After allowing the color image to stand for one hour in a dark place, the absorption spectrum curve (fresh density designated by A) of the coupler at a wavelength in the range of 700 to 380 mμ was measured. The absorption spectrum curve of the coupler was also measured after subjecting it to irradiation of sunlight for one hour (density designated by B) and three hours (density designated by C), respectively. The results are shown in FIG. 3, I to IV, in which I to III refer to the sheets obtained in Examples 7–9 and IV, to the sheet of Comparative Example 3. The light resistance of the color-former was determined in the same way as described in Comparative Test 1. The results are given in Table 3.

TABLE 3

Sheet	Light resistance value of 3-diethylamino fluorane p-nitroanilinolactam at the absorption maximum	
	One-hour irradiation of sunlight	Three-hour irradiation of sunlight
Example 7	82.5%	70.9%
Example 8	90.1%	73.6%
Example 9	85.2%	76.3%
Comparative Ex. 3	70.6%	51.5%

s

It is understood from the results obtained that the light resistance of 3-diethylamino-fluorane-p-nitroanilinolactam is also improved by the addition of phenothiazine and its derivatives.

EXAMPLE 10

In 40 parts by weight of a color-former oil, consisting of 2% by weight of 3-dibenzylamino-7-diethylaminofluorane dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene, was dissolved 2% by weight, based on the oil, of phenothiazine, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsular solution was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

EXAMPLE 11

In 40 parts by weight of a color-former oil consisting of 2% by weight of 3-dibenzylamino-7-diethylaminofluorane dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was dissolved 2% by weight, based on the oil, of 10-ethylphenothiazine-5-oxide, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m², and allowed to dry to form a color-former sheet.

EXAMPLE 12

In 40 parts by weight of a color-former oil consisting of 5% by weight of 3-dibenzylamino-7-diethylaminofluorane dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was dissolved 2% by weight, based on the oil, of 7-methoxy-phenothiazine, and these were microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

COMPARATIVE EXAMPLE 4

Forty parts by weight of a color-former oil consisting of 2% by weight of 3-dibenzylamino-7-diethylaminofluorane dissolved in an oil composed of 4 parts by weight of chlorodiphenyl and 1 part by weight of kerosene was microencapsulated in the same manner as set forth in Example 1. The resulting microcapsule dispersion was coated on a base paper having a unit weight of 40 g/m² in an amount of 6 g/m² as solids content, and allowed to dry to form a color-former sheet.

COMPARATIVE TEST 4

Each of the color-former sheets obtained in Examples 10–12 and Comparative Example 4 was superposed on the test developer sheet described in Comparative Test 1, and a color was formed by applying a pressure of 600 Kg/cm². After allowing the color image to stand for one hour in a dark place, the absorption spectrum curve of the color image as a wavelength in the range of 700 to 380 mμ (fresh density designated by A) was measured. The absorption spectrum curve of the coupler was also measured after subjecting it to irradiation of sunlight for one hour (density designated by B) and three hours (density designated by C), respectively. The results are shown in FIG. 4, I to IV in which I to III refer to the coupler sheets obtained in Examples 10 to 12, and IV to the sheet obtained in Comparative Example 4. The light resistance of the coupler at the absorption maximum was determined in the same way as described in Comparative Test 1. The results are given in Table 4.

TABLE 4

Light resistance value of 3-dibenzylamino-7-diethylaminofluorane at the absorption maximum λ1

Sheet	One-hour irradiation of sunlight	Three-hours irradiation of sunlight
Example 10	94.8%	86.7%
Example 11	84.3%	76.0%
Example 12	85.0%	77.1%
Comparative Example 4	69.1%	59.9%

These results indicate that by use of phenothiazines, the light resistance of 3-dibenzylamino-7-diethylaminofluorane is markedly improved.

The transfer of the absorption maximum λ1 by sunlight irradiation is given in Table 5 on the basis of the absorption spectrum curves shown in FIG. 4.

TABLE 5

Transfer of the absorption maximum λ1 of 3-dibenzylamino-7-diethylaminofluorane by the irradiation of sunlight.

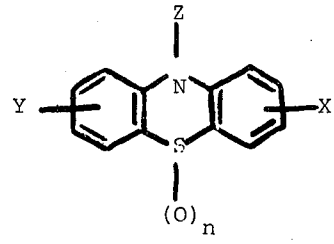
Sheet	Freshλ'	λ'After one-hour sunlight irradiation	λ'After three-hours sunlight irradiation
Example 10	610 mμ	590 mμ	550 mμ
Example 11	610 mμ	580 mμ	560 mμ
Example 12	610 mμ	560 mμ	545 mμ
Comparative Example 4	615 mμ	545 mμ	505 mμ

The results obtained demonstrate that when the phenothiazine is used, the transfer of the absorption maximum λ1 by sunlight irradiation is slight.

Similar results are obtainable with respect to other phenothiazines.

What is claimed is:

1. A pressure-sensitive copying paper comprising a support having coated thereon a layer of microcapsules containing a substantially colorless electron donor color-forming compound capable of forming a distinct color when contacted with an electron acceptor solid acid, said layer containing a colorless phenothiazene compound incapable of forming a distinct color when contacted with the electron acceptor solid acid, the amount of said phenothiazene compound being 10 to 200% by weight based on the color former, said phenothiazene compound being represented by the formula,



wherein *n* is 0, 1 or 2, X, Y and Z each is a hydrogen atom, an alkyl group, a halogen atom, a nitro group, an acylamino group, a hydroxyl group, an alkoxy group, an acyloxy group, an alkoxycarbonyl group, an alkylsulfonylamino group or an arylsulfonylamino group, said alkyl group and alkyls attached to the other substituents having 1 to 8 carbon atoms, and all aryl groups being phenyl or naphthyl groups.

2. The pressure-sensitive copying paper as claimed in claim **1** wherein said phenothiazine compound is contained in the microcapsules containing the color former.

3. The pressure-sensitive copying paper as claimed in claim **1** wherein said phenothiazine compound is contained in microcapsules other than the microcapsules containing the color former.

* * * * *