⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 175 238**
A2

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **85111294.6**

㉒ Date of filing: **06.09.85**

(51) Int. Cl.^{4}: **G 03 C 1/72**

㉚ Priority: **07.09.84 JP 188684/84**
12.09.84 JP 191280/84
09.01.85 JP 1704/85
14.01.85 JP 4736/85
07.03.85 JP 45649/85
11.03.85 JP 48007/85
20.08.85 JP 181042/85
23.08.85 JP 185296/85
30.08.85 JP 191255/85

㊸ Date of publication of application: **26.03.86**
Bulletin 86/13

(84) Designated Contracting States: **DE FR GB IT SE**

(71) Applicant: **PILOT MAN-NEN-HITSU KABUSHIKI KAISHA,**
No. 5-18, Kyobashi 2-chome, Chuo-ku Tokyo (JP)

(72) Inventor: **Ishii, Hirokazu Pilot Man-Nen-Hitsu K.K.,**
Hiratsuka Factory No. 1-4-3, Nishiyahata, Hiratsuka-shi
Kanagawa (JP)
Inventor: **Igawa, Tatsuya Pilot Man-Nen-Hitsu K.K.,**
Hiratsuka Factory No. 1-4-3, Nishiyahata, Hiratsuka-shi
Kanagawa (JP)
Inventor: **Sato, Morio Pilot Man-Nen-Hitsu K.K.,**
Hiratsuka Factory No. 1-4-3, Nishiyahata, Hiratsuka-shi
Kanagawa (JP)
Inventor: **Anzai, Kazuo Pilot Man-Nen-Hitsu K.K.,**
Hiratsuka Factory No. 1-4-3, Nishiyahata, Hiratsuka-shi
Kanagawa (JP)

(74) Representative: **Patentanwälte Grünecker, Kinkeldey,**
Stockmair & Partner, Maximilianstrasse 58,
D-8000 München 22 (DE)

(54) Photosensitive composition.

(57) A photosensitive composition is described, comprising an electron donative chromatic organic compound, and a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and aromatic onium salt of elements belonging to Group Va in the periodic table, preferably further comprising at least one of a compound having oxyethylene groups and/or basic fine powder, and a compound having alcoholic hydroxy groups.

The photosensitive compositions have abundant kinds of color productions, and are superior in heat-proof, humidity-proof, and preservation properties.

PHOTOSENSITIVE COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a photosensitive composition in which color is developed by irradiation of light.

BACKGROUND OF THE INVENTION

Heretofore, various kinds of photosensitive compositions in which color is developed by light irradiation are known. One photosensitive composition is an irreversible photosensitive composition in which color developed by light irradiation does not change upon interruption of light irradiation, and another photosensitive composition is a reversible photosensitive composition in which color developed by light irradiation gradually disappears upon interruption of light irradiation.

As the former irreversible photosensitive composition, known is such a composition that is made up of a combination of an electron donative chromatic organic compound and a photoactivator. As the electron donative chromatic organic compound, known is the use of, for example, those compounds described in KAMIPAGIKYOHSHI, Vol. 30, p. 411 (1976), SHIKIZAI, Vol. 54, p. 355 (1981), KINOHSEISHIKISO NO KAGAKU (published by CMC Co. of Japan), pp. 189-210 (1981), and U.S. Patent 4,028,118, and as the photoactivator, known is the use of, for example, organic halides (described in U.S. Patents 3,042,515, 3,042,516, 3,042,517, 3,042,518 and 3,042,519 and Japanese Patent Publication No. 373/65), quinone diazides (described in Japanese Patent Publication No. 30885/70), and diazonium salts (described in Japanese Patent Publication No. 521/74).

As the latter reversible photosensitive composition, known are such an inorganic photosensitive composition that silver halides are dispersed into grass and an organic photosensitive composition such as azobenzene, N-salicylidene anilin, spiropyran, bis(triphenylimidazole), thionine, viologen, furgide, or the like.

However, both compositions have at least one of such disadvantages that gas bubbles may be often produced owing to the generation of gases at the time of light irradiation, an odious smell is strong, a variety of colors developed is poor, durability and long-term preservation property are poor due to lack of stability against heat and humidity, and so on. The reversible photosensitive composition has at least one of such disadvantages, in addition to the above-mentioned disadvantages, as poor color disappearing property at the time of interruption of light irradiation, poor durability in repeated use, difficulties in availability of materials, difficulties in work onto materials and so on. Accordingly, there has no photosensitive composition satisfactory for the multi-purpose use in industrial viewpoint yet.

That is, the photosensitive composition is required to have properties of color sensitivity in which color is rapidly developed by light irradiation, a variety of colors developed, high color density, no odious smell, no generation of gases at the time of light irradiation, high durability against heat and humidity, stability in long-term preservation, abundant variety of colors, easiness in availability of materials, easiness in work onto materials, and so on.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide novel photosensitive compositions by which the disadvantages in the conventional photosensitive compositions are improved and necessary performance is satisfied as well. Another object of the present invention is to provide novel photosensitive compositions by which color sensitivity can be improved at the time of light irradiation. Still another object of the present invention is to provide novel photosensitive compositions which are satisfactory for performance necessary for the reversible photosensitive composition.

The above-described objects of the present invention are attained with photosensitive compositions of the type as follows:

a photosensitive composition (1) comprising an electron donative chromatic organic compound, and a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table;

a photosensitive composition (2) comprising an electron donative chromatic organic compound, a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table, and a compound having alcoholic hydroxyl groups;

a photosensitive composition (3) comprising an electron donative chromatic organic compound, a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table, and at least one of a compound having oxyethylene groups and basic fine powder; and

a photosensitive composition (4) comprising an electron donative chromatic organic compound, a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table, at least one of a compound having oxyethylene groups and basic fine powder, and a compound having alcoholic hydroxyl groups.

DETAILED DESCRIPTION OF THE INVENTION

As the results of various investigations as to the improvement of the conventional photoactivators each having a defect in practical use, the inventors of this application have found that the desired objects can be attained in the case where a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table is used in combination with an electron donative chromatic organic compound.

That is, the inventors have found that in the case where a salt selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table is used in combination with an electron donative chromatic organic compound, the foregoing salt releases rapidly color forming components such as Brønstead acid, Lewis acid, and the like so as to immediately cause the electron donative chromatic organic compound to color without producing gas bubbles even if irradiated with light. The inventors have further found that the foregoing salt is an extremely superior photoactivator in that the foregoing salt per se has no odious smell and has high durability as well as a long-term preservation property are good due to stability against heat and humidity. Thus, the inventors have found that the compositions in which the foregoing photoactivator is combined with an electron donative chromatic organic compound are superior novel photosensitive compositions in which the disadvantages in the prior art are completely eliminated. This point is the most significant feature of the present invention.

Next, the photosensitive composition in which a compound having alcoholic hydroxyl groups coexists with the foregoing photosensitive composition (1), could have improvement in color sensitivity without deteriorating the performance of the photosensitive composition (1). This point is a significant feature of the invention.

Next, the photosensitive composition in which at least one of a compound having oxyethylene groups and basic fine powder coexists with the photosensitive composition (1), could have a property of color disappearance owing to interruption of light irradiation with respect to a coloring matter having color developed owing to light irradiation, that is, a so-called photochromic property, without deteriorating the performance of the photosensitive composition (1). Also this point is a significant feature of the invention.

Next, the photosensitive composition in which a compound having alcoholic hydroxyl groups coexists with the photosensitive composition (3), could have improvement in color sensitivity without deteriorating the performance of the photosensitive composition (3), and more, could have a property of color disappearance owing to interruption of light irradiation with respect to a coloring matter having color developed owing to light irradiation, that is, a so-called photochromic property. Also this point is a significant feature of the invention.

A combination of (1) an electron donative chromatic organic compound and a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table; (2) an electron donative chromatic organic compound, a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table, and a compound having alcoholic hydroxyl groups; (3) an electron donative chromatic organic compound, a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table, and at least one of a compound having oxyethylene groups and basic fine powder; or (4) an electron donative chromatic organic compound, a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table, at least one of a compound having oxyethylene groups and basic fine powder, and a compound having alcoholic hydroxyl groups is novel. Although the combination was found to have good properties as a photosensitive composition, the reason why such good properties could be shown would be thought vaguely as follows.

When light is irradiated onto the photosensitive composition, color forming components such as Brønstead acid, Lewis acid, and the like, to color sensitively the electron donative chromatic organic compound are released from the photoactivator and then the electron donative chromatic organic compound is colored by these color forming components.

It has been found that if a compound having alcoholic hydroxyl groups coexists the photosensitive composition exhibits superior properties in which the electron donative chromatic organic compound is colored in a moment of light irradiation. That is, it is to be supposed that the color forming components such as Brønstead acid, Lewis acid, and the like are rapidly produced by the interaction between the photoactivator and the compound having alcoholic hydroxyl groups, so that the electron donative chromatic organic compound donates electrons to the color forming components and color is developed in a moment.

In the photosensitive composition in which at least one of a compound having oxyethylene groups and basic fine powder coexists with the foregoing photosensitive composition (1) or (2), the electron donative chromatic organic compound is colored by the color forming components such as Brønstead acid, Lewis acid, and the like, released from the photoactivator owing to light irradiation. However, if the light irradiation is interrupted, the releasing of the color forming components such as Brønstead acid, Lewis acid, and the like, from the photoactivator is stopped and at the same time at least one of the compound having oxyethylene groups and basic fine powder begins to absorb the color forming components such as Brønstead acid, Lewis acid, and the like, so that the electron donative chromatic organic compound is decolored. That is, the electron donative chromatic organic compound which has been colored accepts electrons, and consequently, at least one of the compound having oxyethylene groups and basic fine powder absorbs all of the color forming components such as Brønstead acid, Lewis acid, and the like, which have been released from the photoactivator. In the photosensitive composition comprising at least one of the compound having oxyethylene groups and basic fine powder according to the present invention, it is to be supposed that the electron donative chromatic organic compound donates and accepts electrons corresponding to the presence of light, so that color is developed or disappears. That is, the photosensitive composition can be that having so-called photochromic property.

The electron donative chromatic organic compound used according to the present invention is generally colorless or light-colored, and has the property of color developed by the donation of electrons owing to the action of the color forming components such as Brønstead acid, Lewis acid, and the like. As the compound to be used, triphenylmethanephthalides, fluorans, phenothiazines, indolylphthalides, leucoauramines, rhodamine lactams, rhodamine lactones, indolines, triphonylmethanes, azaphthalides, chromenoindols, triazenes, etc., are preferable, and triphenylmethanephthalides, fluorans, indolylphthalides, leucoauramines, rhodamine lactams, triphenylmethanes, azaphthalides, etc., are more preferable. The compound may be used in the combination of two or more compounds which may be the same or different. The specific examples are as follows:

Crystal violet lactone, malachite green lactone, Michler's hydrol, 3-diethylamino-α-benzofluoran, 3-diethylamino-7-methylfluoran, 3-diethylamino-7-(o-chlorophenyl)-aminofluoran, 3-N-ethyl-N-p-tolylamino-7-methyl-N-phenylaminofluoran, 3-pyrrolidino-6-methyl-7-anilinofluoran, N-(2,3-dichlorophenyl)leucoauramine, N-2,4,5-trichlorophenylleucoauramine, N-benzoylauramine, N-phenylauramine, rhodamine B lactam, rhodamine B lactone, 2-(phenyliminoethanedilidene)-3,3'-dimethylindoline, p-nitrobenzylleucomethylene blue, benzoylleucomethylene blue, 3,7-bis(dimethylamino)-10-benzoylphenothiazine, 3,7-bisdimethylamino-10-(4'-aminobenzoyl) phenothiazine, 3,7-bisdimethylamino-10-(4'-pyridinobenzoyl) phenothiazine, 3,7-bisdimethylamino-10-[4'-bis-(4",4'"-dimethylaminophenyl) methylaminobenzoyl] phenothiazine, etc.

The photoactivator used according to the present invention, that is, the photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table is a compound being colorless or light-colored, and having the property of releasing the color forming components such as Brønstead acid, Lewis acid, and the like owing to light irradiation, so that the electron donative chromatic organic compound is colored.

The compound preferably used as the photoactivator is an aromatic halonium salt (a salt of an aromatic halonium and a halogen-containing complex ion of Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, B, P and As); a salt of an aromatic onium of element belonging to Group VIa in the periodic table (O, S, Se, and Te) and a halogen containing complex ion of Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, B, P and As; a salt of an aromatic onium of elements belonging to Group Va in the periodic table (N, P, As, Sb and Bi) and a halogen-containing complex ion of Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, B, P, and As; and a salt of an aromatic onium and a perchloric acid.

The more preferable compound is aromatic iodonium salt (a salt of an aromatic iodonium and a halogen-containing complex ion of Sb, B, P and As); a salt of an aromatic onium of element belonging to Group VIa in the periodic table (S) and a halogen-containing complex ion of Sb, B, P, and As; a salt of an aromatic onium of elements belonging to Group Va in the periodic table (N and P) and a halogen-containing complex ion of Sb, B, P, and As; and a salt of an aromatic onium and a perchloric acid.

The further preferable compound is a salt of an aromatic iodonium and BF_4^-; a salt of an aromatic iodonium and PF_6^-; a salt of an aromatic sulfonium and BF_4^-; and a salt of an aromatic sulfonium and PF_6^-.

The details of those compounds are described in the following literature:

<u>J. Org. Chem.</u>, Vol. 35 (8), p. 2532 (1970)

<u>Macromolecules</u>, Vol. 10 (6), p. 1307 (1977)

<u>J. Org. Chem.</u>, Vol. 43 (15), p. 3055 (1978)

<u>J. Radiat. Curing</u>, Vol. 5 (1), p. 2 (1978)

<u>J. Radiat. Curing</u>, Vol. 6, p. 22 (1979)

<u>J. Polym. Sci., Polym. chem. Ed.</u>, Vol. 17, pp. 977, 1047 (1979)

<u>J. Polym. Sci., Polym. chem. Ed.</u>, Vol. 18, pp. 2677, 2697 (1980)

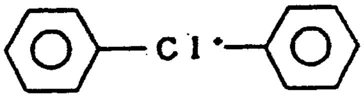
<u>J. Polym. Sci., Polym. chem. Ed.</u>, Vol. 22, p. 1789 (1984)

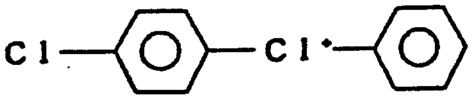
<u>Adv. Polymer. Sci.</u>, Vol. 62, p. 1 (1984)

<u>ZAIRYOH GIJUTSU</u>, Vol. 2 (10), p. 553 (1984)

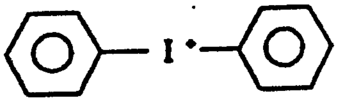
Next, specific examples of the photoactivator will be shown hereunder. However, the photoactivator according to the invention is not limited to the following compounds.

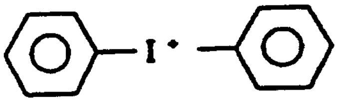
Aromatic halonium salts:

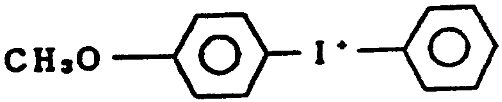

PF_6^-

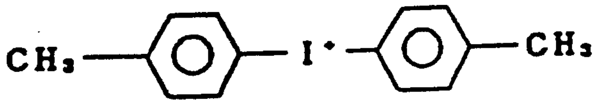

PF_6^-

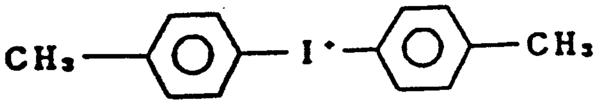

PF_6^-

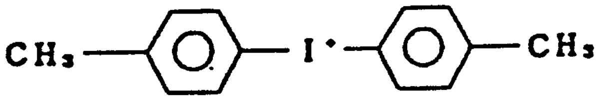

BF_4^-

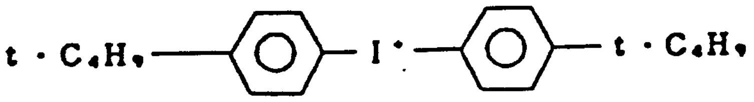

PF_6^-

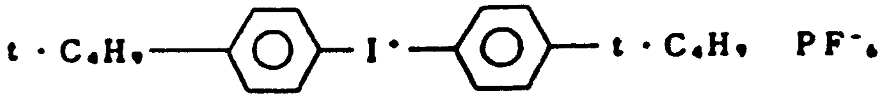

BF_4^-

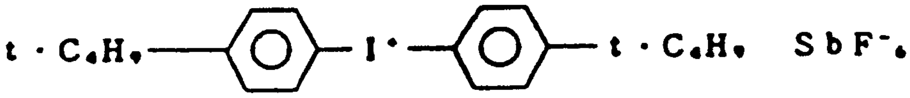

BF_4^-

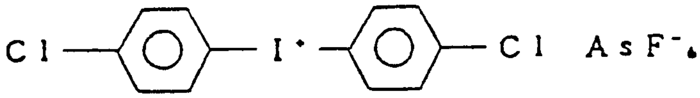

PF_6^-

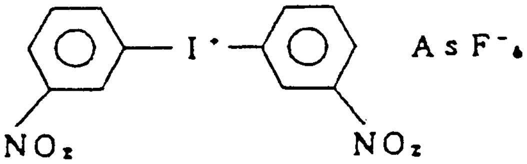

AsF_6^-

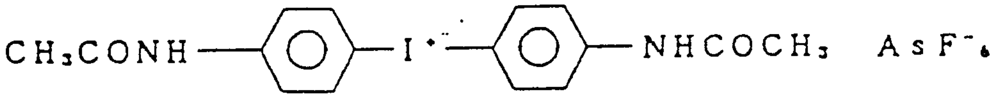

BF_4^-

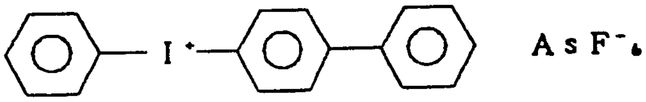

t · C₄H₉
I⁺
t · C₄H₉
PF⁻₆

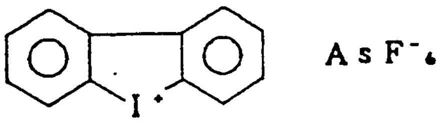

t · C₄H₉
I⁺
t · C₄H₉
SbF⁻₆

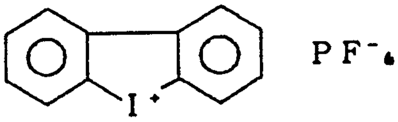

Cl
I⁺
Cl
AsF⁻₆

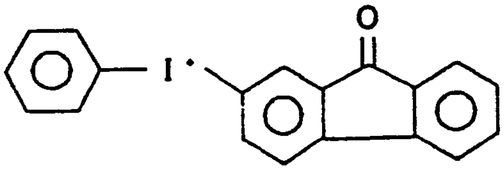

I⁺
AsF⁻₆
NO₂
NO₂


CH₃CONH
I⁺
NHCOCH₃
AsF⁻₆

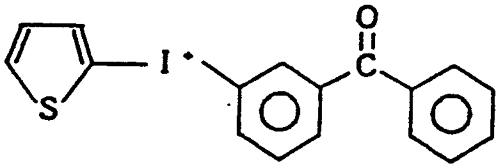

I⁺
AsF⁻₆


I⁺
AsF⁻₆

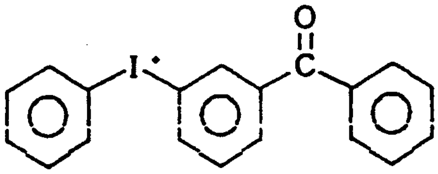

I⁺
PF⁻₆



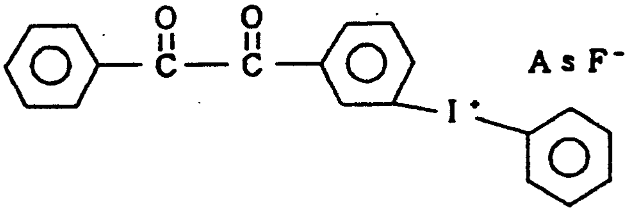
AsF_6^-



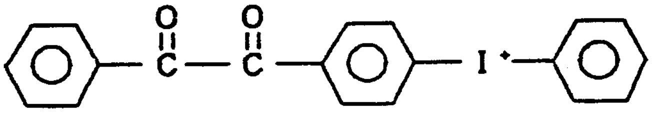
SbF_6^-



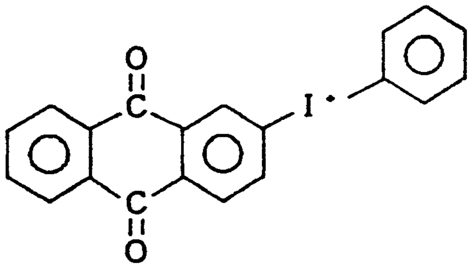
AsF_6^-



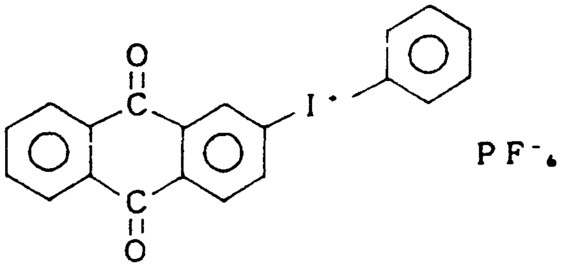
AsF_6^-

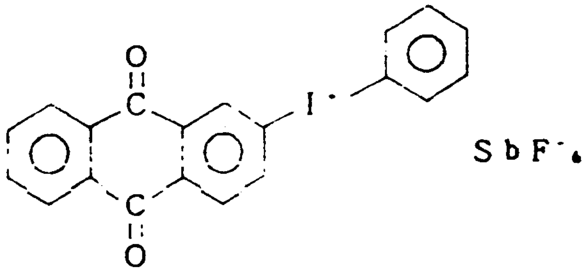


BF_4^-

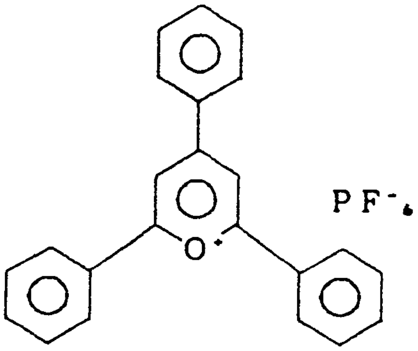


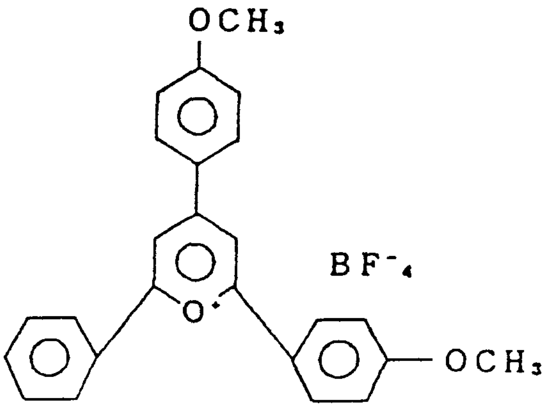
AsF_6^-

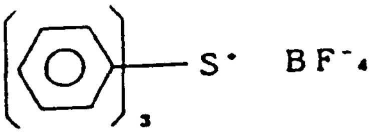


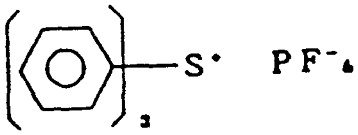


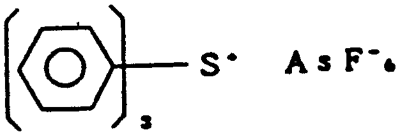
Aromatic onium salts of elements belonging to Group VIa in the periodic table:

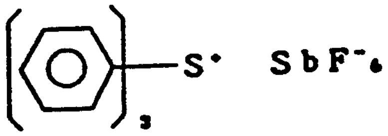


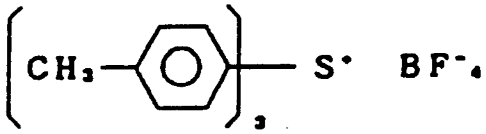


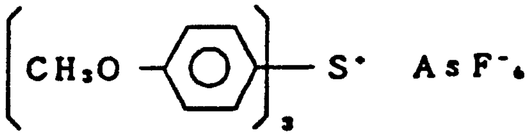


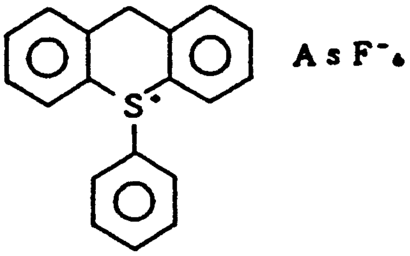


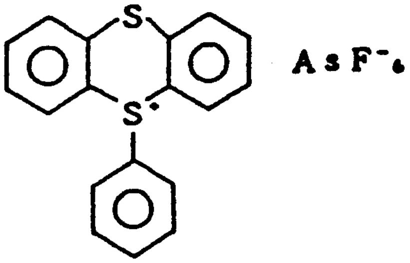

S⁺
AsF⁻₆
3

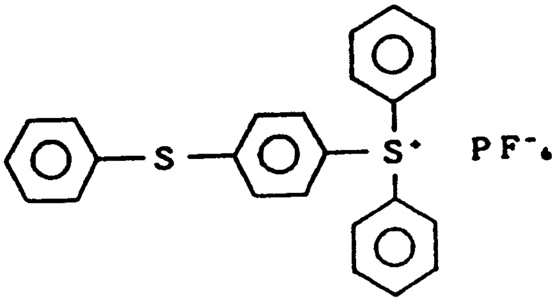

S⁺
SbF⁻₆
3

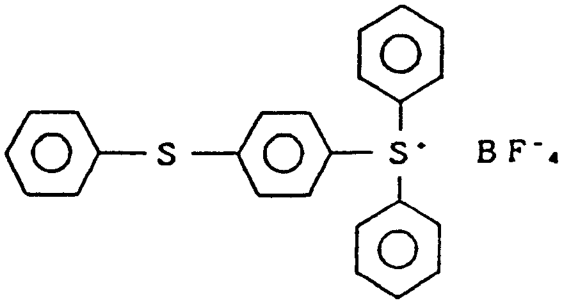

CH₃
S⁺
BF⁻₄
3

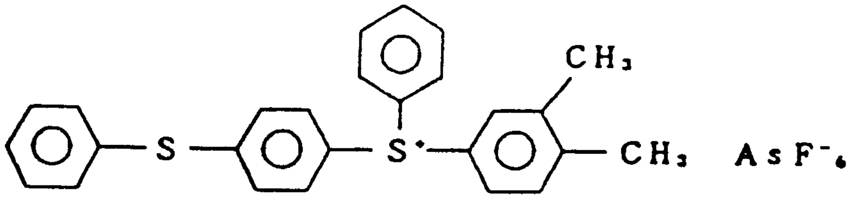

CH₃O
S⁺
AsF⁻₆
3

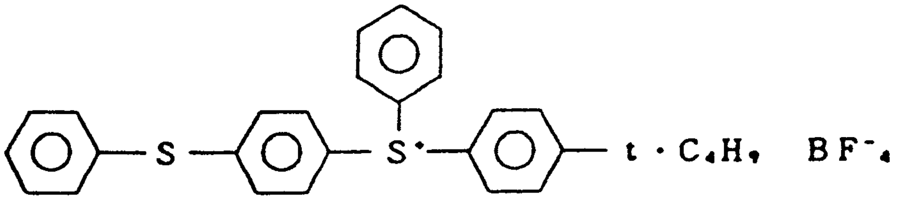

S⁺
AsF⁻₆

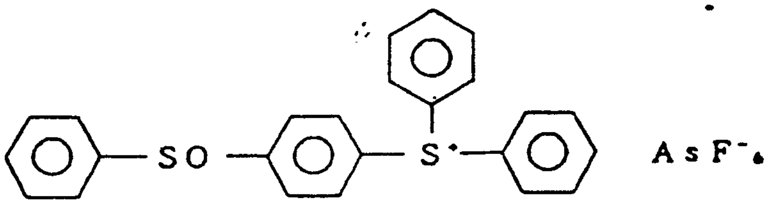

S
S⁺
AsF⁻₆

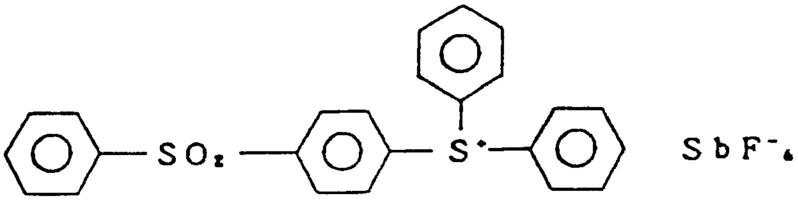

S
S⁺
PF⁻₆

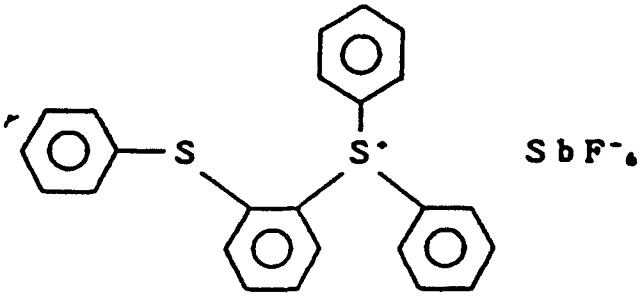

S
S⁺
BF⁻₄

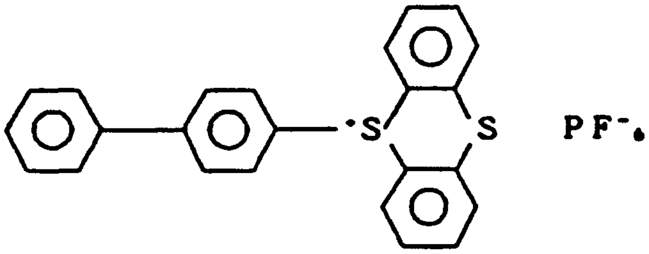

CH₃
S
S⁺
CH₃
AsF⁻₆

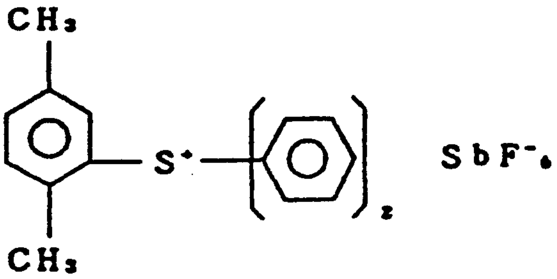

S
S⁺
t·C₄H₉
BF⁻₄

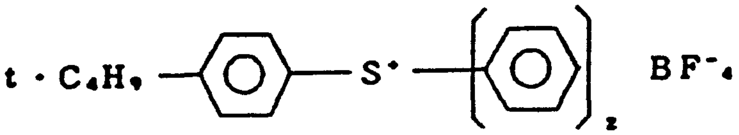

SO
S⁺
AsF⁻₆

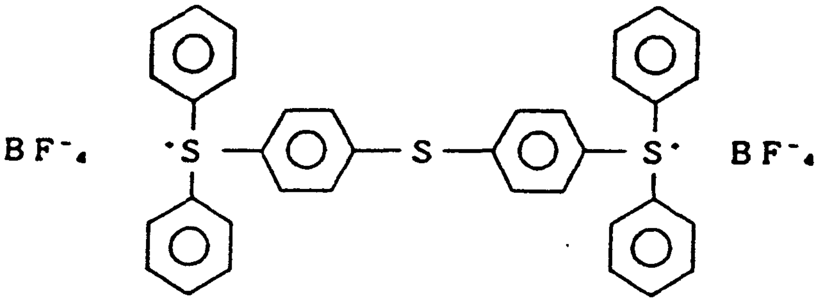

SO₂
S⁺
SbF⁻₆

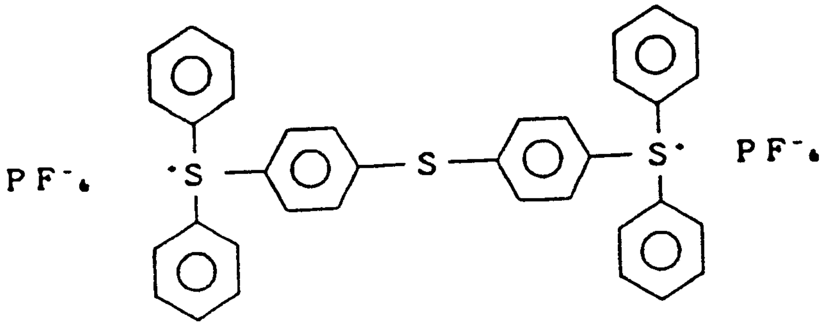

S
S+
SbF-6

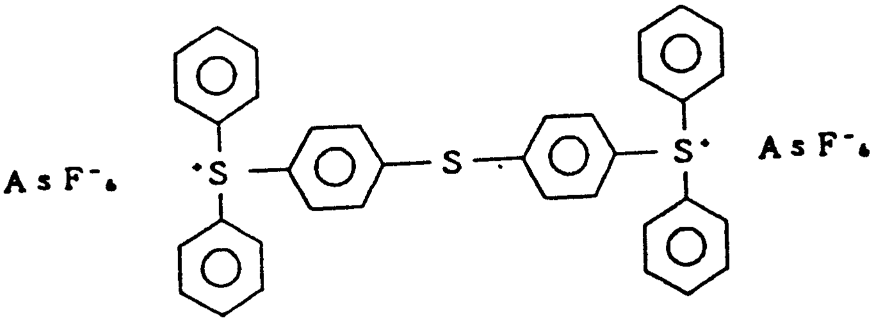

+S
S
PF-6

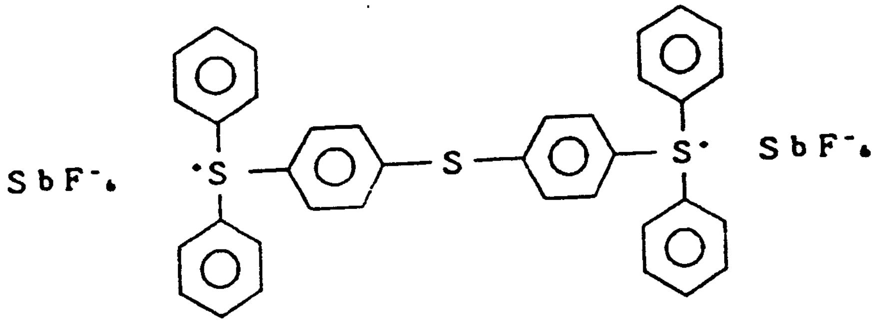

CH3
S+
2
SbF-6
CH3

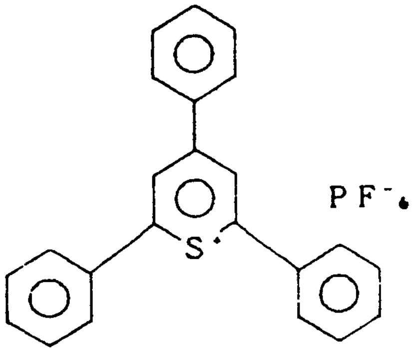

t · C4H9
S+
2
BF-4

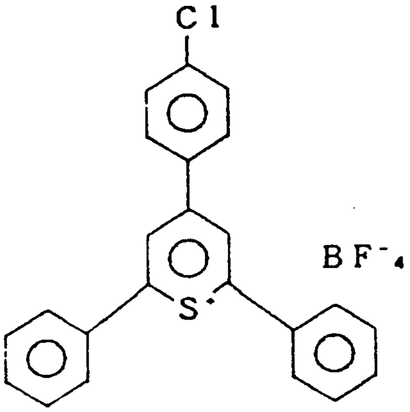

BF-4
+S
S
S+
BF-4

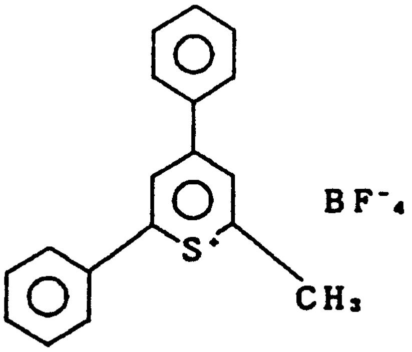

PF⁻₆
S
S
S
PF⁻₆

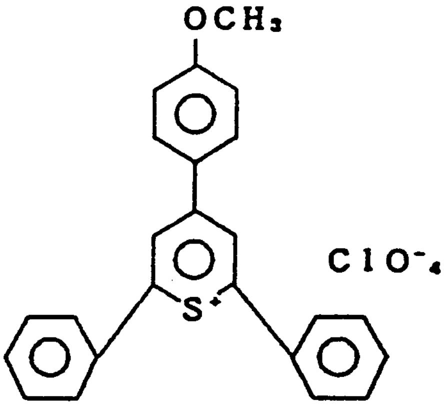

AsF⁻₆
S
S
S
AsF⁻₆

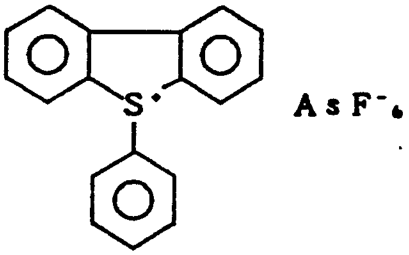

SbF⁻₆
S
S
S
SbF⁻₆

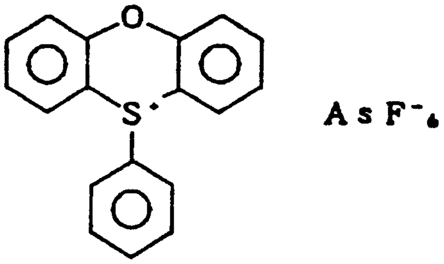

S
PF⁻₆

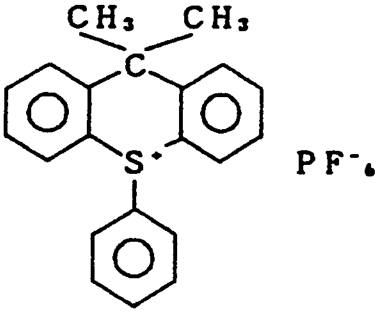

Cl
S
BF⁻₄

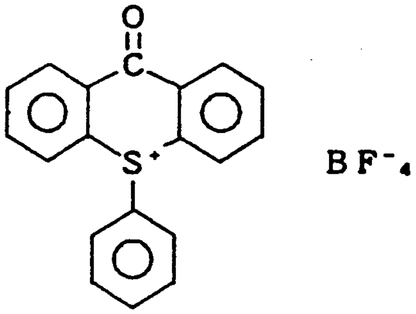

S+
CH₃
BF⁻₄

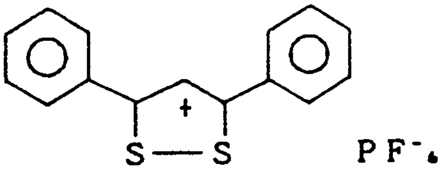

OCH₃
S+
ClO⁻₄

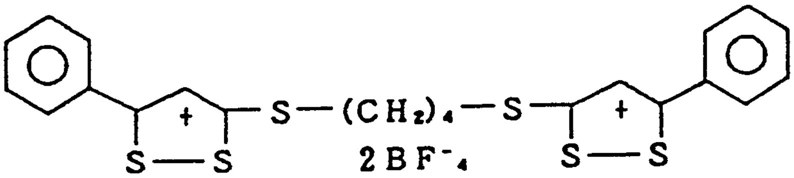

S+
AsF⁻₆

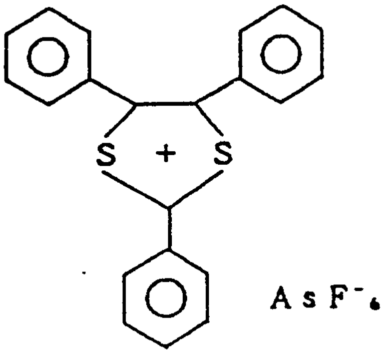

O
S+
AsF⁻₆

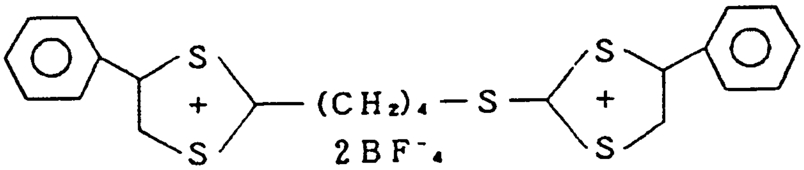

CH₃ CH₃
C
S+
PF⁻₆

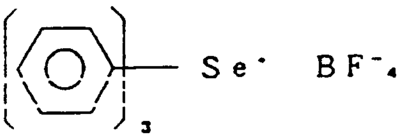

O
C
S+
BF⁻₄

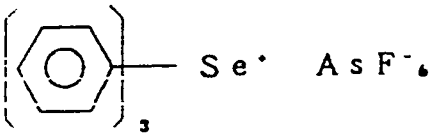

S
S
+
PF⁻₆

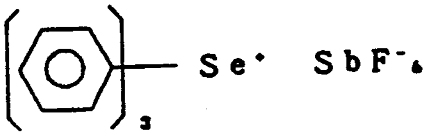

S
S
+
S—(CH₂)₄—S
2BF⁻₄
+
S
S

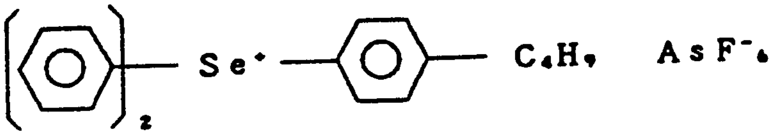

S
+
S
AsF⁻₆

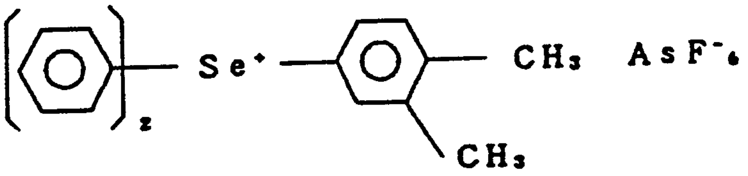

S
+
S
(CH₂)₄—S
2BF⁻₄
S
+
S

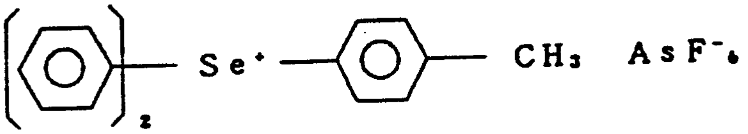

3
Se⁺
BF⁻₄

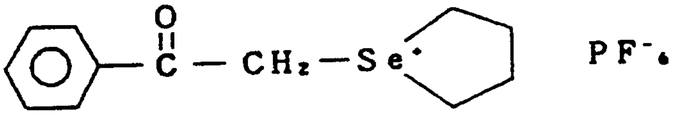

3
Se⁺
AsF⁻₆

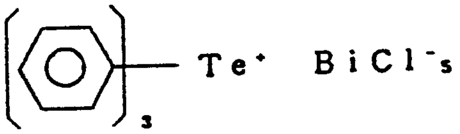

3
Se+
SbF6-


2
Se+
C4H9
AsF6-

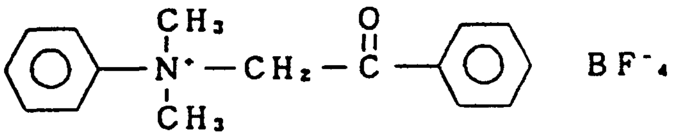

2
Se+
CH3
CH3
AsF6-

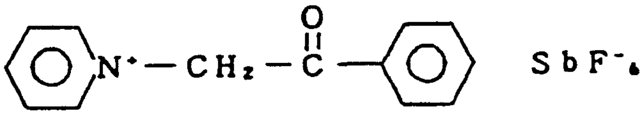

2
Se+
CH3
AsF6-

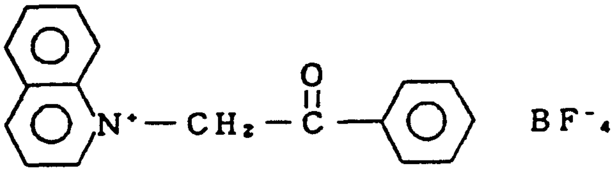

O
C
CH2
Se+
PF6-

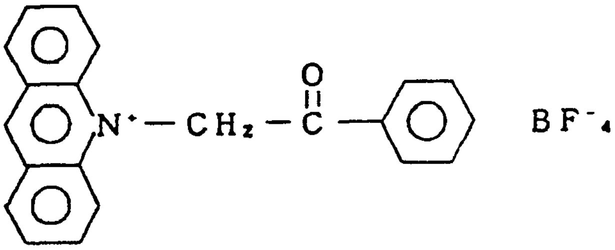

3
Te+
BiCl5-

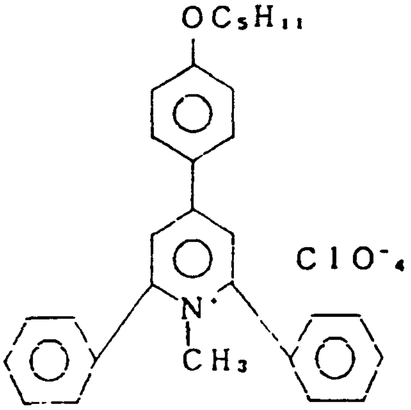
Aromatic onium salt of elements belonging to Group Va in the periodic table

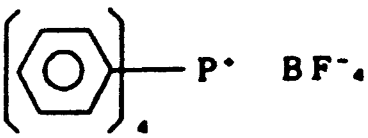


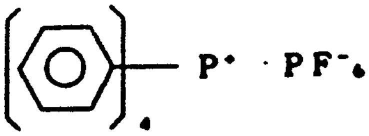


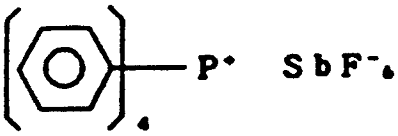


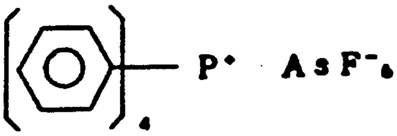


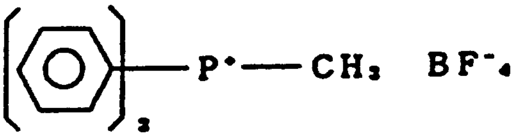


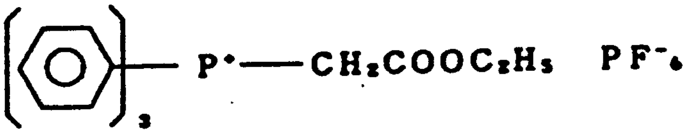

4
P^+
BF_4^-

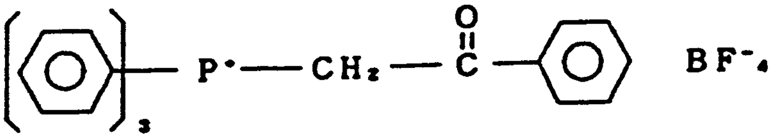

4
P^+
PF_6^-

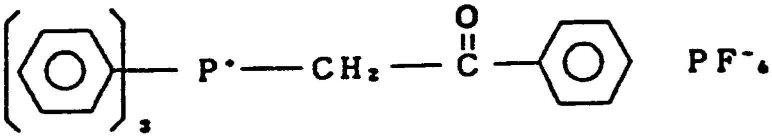

4
P^+
SbF_6^-

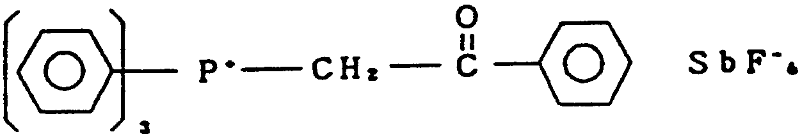

4
P^+
AsF_6^-

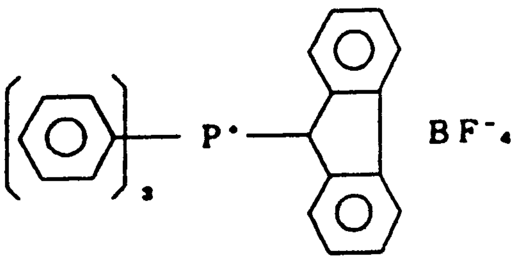

3
P^+
CH_3
BF_4^-

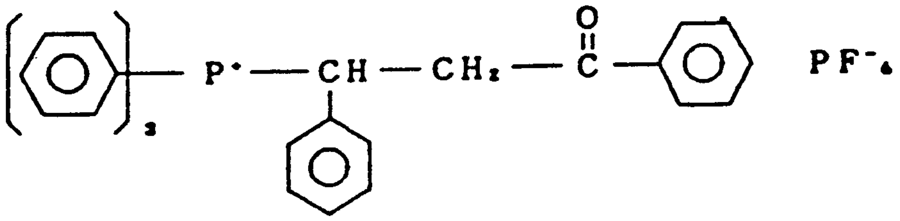

3
P^+
$CH_2COOC_2H_5$
PF_6^-

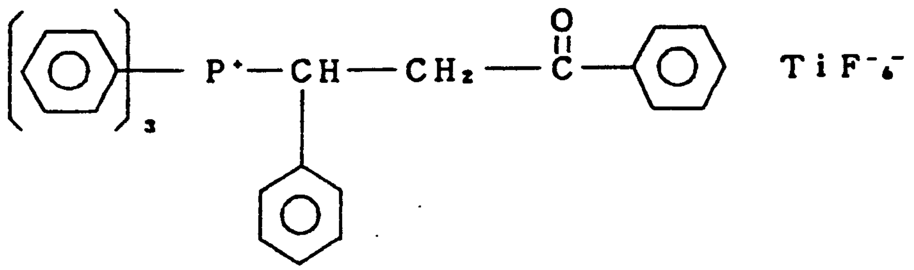

3
P^+
CH_2
O
C
BF_4^-

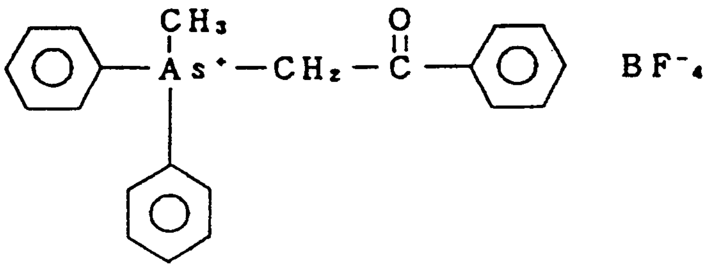

3
P^+
CH_2
O
C
PF_6^-

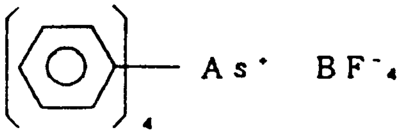

3
P^+
CH_2
O
C
SbF_6^-

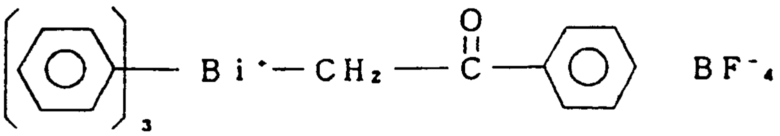












The compound having alcoholic hydroxyl groups used in the invention is colorless or light-colored liquid or solid, and has the property of improving a coloring speed at the time of light irradiation as long as it coexists with the electron donative chromatic organic compound and the photoactivator. The compound preferably used as the compound having alcoholic hydroxyl groups is an aliphatic alcohol of 6 or more carbon atoms, having a boiling point of 150°C or more; a polyhydric alcohol of 6 or more carbon atoms, having a boiling point of 150°C or more; an aromatic alcohol of 7 or more carbon atoms, having a boiling point of 150°C or more; and a macromolecular alcohol of from about 10,000 through about 300,000 molecular weight.

The more preferable compound is an aliphatic alcohol of 9 or more carbon atoms, having a boiling point of 200°C or more; an aromatic alcohol of 7 or more carbon atoms, having a boiling point of 200°C or more; a polyhydric alcohol of 6 or more carbon atoms, having a boiling point of 200°C or more; and a macromolecular alcohol of from about 10,000 through about 300,000 in molecular weight. Specific examples of such compounds include an aliphatic alcohol such as hexyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, eicosyl alcohol, docosyl alcohol, melissyl alcohol, oleyl alcohol, cyclohexanol, cyclopentanol, etc.;

an aromatic alcohol such as benzyl alcohol, β-phenylethyl alcohol, cinnamyl alcohol, triphenylcarbinol, etc.; a polyhydric alcohol such as ethylene glycol, diethylene glycol, ethylene glycol monoethyl ether, ethylene glycol monophenyl ether, ethylene glycol monobenzyl ether, propylene glycol, propylene glycol monobutyl ether, propylene glycol monoacrylate, propylene glycol monophenyl ether, butylene glycol, hexylene glycol, 2-ethyl-1,3-hexanediol, glycerol, glycerol monolaurate, glycerol monopalmitate, glycerol monostearate, glycerol dilaurate, pentaerythritol, mannitol, sorbitan, sorbitan monolaurate, sorbitan monoolate, sorbitan sesquistearate, etc.; and a macromolecular alcohol such as polyvinyl alcohol, polyvinyl acetal, polyvinyl butyral, cellulose acetate, hydroxyethyl cellulose, hydroxypropyl cellulose, cellulose acetate butylate, cellulose acetate phthalate, methyl cellulose, ethyl cellulose, polysiloxane-polycarbinol, etc.

The compound having oxyethylene groups used in the invention is colorless or light-colored liquid or solid, and although it is desired that the compound is miscible with the electron donative chromatic organic compound and the photoactivator, also the compound immiscible therewith can be used. The preferable compound is a compound of 100 or more in molecular weight, having 3 or more oxyethylene groups in a molecule, and the more preferable compound is a compound of 190 or more in molecular weight, having 6 or more oxyethylene groups in a molecule. Specific examples of such compounds include diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, diethylene glycol monophenyl ether, diethylene glycol monobenzyl ether, triethylene glycol, triethylene glycol monobutyl ether, triethylene glycol monophenyl ether, triethylene glycol dioctyl ether, tetraethylene glycol, tetraethylene glycol monoethyl ether, tetraethylene glycol monobutyl ether acetate, polyethylene glycol, oxyethylene-oxypropylene block copolymer, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan tristearate, polyoxyethylene sorbitan monoolate, polyoxyethylene sorbitan triolate, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octyl phenol ether, polyoxyethylene nonyl phenol ether, and polyethylene glycol diacrylate.

The compound having alcoholic hydroxyl groups and oxyethylene groups in one molecule has both the property of improving a coloring speed and the property of decoloring color developed by light irradiation.

The basic fine powder used in the invention is colorless or light-colored and immiscible with the electron donative chromatic organic compound or the photoactivator, having the average particle diameter of about 0.01 μm through about 100 μm, preferably about 0.1 μm through about 10 μm, and pH of 8 through 13. The words "immiscible with the electron donative chromatic organic compound or the photoactivator" means that solubility is 1% or less at room temperature.

Examples of the basic fine powder are generally a hydroxide of alkali metals such as lithium, sodium, potassium, etc., and alkaline-earth metals such as magnesium, calcium, barium, etc., and the carbonate thereof. Also, alkali-processed fine powder such as basic fine powder silica, basic montmorillonite, basic talc, basic lead sulfate, basic lead carbonate, etc. can be used.

The electron donative chromatic organic compound, the compound having alcoholic hydroxyl groups, the compound having oxyethylene groups, and the basic fine powder are available on the market as manufacturing products. Being hard to obtain (although sometimes available on the market), the photoactivator was synthesized on the basis of the above-mentioned literatures.

The weight proportion of the photoactivator to the electron donative chromatic organic compound is from 0.01 to 100 parts to 1 part, preferably from 0.1 to 10 parts to 1 part, and most preferably from 0.5 to 10 parts to 1 part.

The weight proportion of the compound having oxyethylene groups to the electron donative chromatic organic compound is from 0.01 to 100 parts to 1 part, preferably from 0.1 to 10 parts to 1 part, and most preferably from 0.5 to 5 parts to 1 part.

The weight proportion of the basic fine powder to electron donative chromatic organic compound is from 0.01 to 100 parts to 1 part, preferably from 0.1 to 100 parts to 1 part, and most preferably from 0.1 to 10 parts to 1 part.

The weight proportion of the compound having alcoholic hydroxyl groups to the photoactivator is from 0.01 to 200 parts to 1 part, preferably from 0.1 to 100 parts to 1 part, and most preferably from 0.1 to 20 parts to 1 part.

The photosensitive composition according to the present invention can be used in its original condition, and can be used also in various conditions in which a support material is coated, printed, or kneaded with it. In detail, the photosensitive composition (1), (2), (3) or (4) according to the invention can be used in the condition through the steps of: adding essential components and necessary additional components to proper solvent; dissolving or dispersing them at a temperature within a range from room temperature to about 100°C by using a stirrer, disperser, or the like, for the purpose of obtaining photosensitive composition solution; and enclosing the solution in a suitable vessel, printing with the solution on a support material, coating the solution on a support material, impregnating a support material with the solution, or the like, by the use of a printing machine, a writing instrument, etc., or the photosensitive composition according to the invention can be used in the condition through the steps of: kneading essential components and necessary components with being heated and fused; and cooling there up to room temperature.

The photosensitive composition can be used with various additional components added thereto in accordance with these various modes of use. For example, binders such as natural resin, synthetic resin, etc., sensitizers to improve color sensitivity, masking agent such as titanium white, alumina, etc., thickeners such as silica powder, etc., pH adjusters such as acid, alkali, etc., color tone adjusters such as a dye, a pigment, etc., plasticizers, various stabilizers, and the like, can be added according to demand.

The foregoing photosensitive compositions (1), (2), (3) and (4) can be obtained by application of additives at need, by dissolution or dispersion thereof in suitable solvent, or by evaporation of the solvent thereafter.

The photosensitive compositions obtained as described above are colored by ultraviolet radiation of 400 nm or less wavelength, and particularly, effectively colored by ultraviolet radiation of 250 to 350 nm wavelength. Sunlight, mercury-lamp light, black light, xenon-lamp light, ultraviolet laser light, and the like, are suitable as a light source. The compositions are spectrally sensitized by suitable sensitizers such as, for example, dye such as Acridine Orange (C.I. 46005), Acridine Yellow (C.I. 46025), Phosphine R (C.I. 46045), Benzoflavin (C.I. 46065), Setoflavin T (C.I. 49005), etc.; aromatic polynuclear compound such as Perylene, Anthracene, Coronene, Pyrene, Tetracene, etc.; and ketone compound such as Thioxanthon, Chlorothioxanthon, Benzophenon, 9-Fluorenon, Anthraquinon, etc., so that the compositions become colored by visible radiation (sunlight, or tungsten light) of 400 nm or more wavelength. There is no deterioration in properties even after long-term preservation for one year or more.

It is possible to obtain simply a coloring matter of color density, having a necessary color tone, by changing the kind of the electron donative chromatic organic compound.

As described above, the photosensitive composition according to the invention can overcome all the disadvantages of the conventional photosensitive composition, and it can be used under the conditions that it is applied onto paper, plastic sheet, metallic foil, various fiber, glass, ceramic, and the like, by being coated, printed, or impregnated thereon, and under the conditions that it is inserted between two support materials, or kneaded in support materials such as plastic, wax, or the like, and moreover, it can be produced in the form of ink to thereby use as ink or paint having a photosensitive property. Consequently, the photosensitive composition according to the invention is applicable widely to various industrial materials, recording materials, indicating media, ornamental materials, printing matters, daily necessaries, clothes, writing materials, toys, and so on.

Next, the present invention will be described in conjunction with the following examples. The examples, however, do not limit the scope of the invention. The term "part" used in the following examples means weight part.

EXAMPLE 1

NBP-1 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Co.)	0.25 part
Triphenylphenacylphosphonium tetrafluoroborate (photoactivator)	0.5 part
MS-300 (Trademark for stylene-metacrylic acid resin of Shinnittetsu Kagaku Co.)	1.5 parts
Toluene	6 parts
Methylethyl ketone	10 parts
Methanol	1.5 parts

After all components were stirred and dissolved, the components were coated on fine paper so as to constitute 4 to 5 g/m^2 solid matter, and consequently, color-producing paper having a photosensitive composition was obtained. When the color-producing paper was exposed to black light for 30 seconds, the exposure portion thereof became blue-colored on a white background.

The color-producing paper was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the paper was superior in color sensitivity and color density.

EXAMPLE 2

RLA (Trademark for electron donative chromatic organic compound of Hodogaya Kagaku Co.)	0.25 part
Diphenyliodonium tetrafluoroborate (photoactivator)	0.75 part
Methylethyl ketone	15 parts
Toluene	5 parts

After all components were stirred and dissolved, the components were impregnated on fine paper so as to constitute 1 to 2 g/m^2 solid matter, and consequently, color-producing paper having a photosensitive composition was obtained. When the color-producing paper was exposed to sunlight for 30 seconds, the paper became red-colored on a white background.

The color-producing paper was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the paper was superior in color sensitivity and color density.

EXAMPLE 3

S-205 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Kohgyoh Co.)	5 parts
Bis[4-(diphenylsulfonio)phenyl]sulfide-bis-hexafluorophosphate (photoactivator)	10 parts
Triphenyl phosphate	1 part
Toluene	30 parts
Methylethyl ketone	50 parts

After all components were stirred and dissolved, this ink was filled in a fiber pen, and consequently, a writing instrument was obtained. Holographs (writing traces) written on paper or plastic sheet with the writing instrument were illegible. When the paper or plastic sheet was however exposed to sunlight for 20 seconds, the holographic portion became black-colored. This showed the fact that the ink was useful as hidden ink.

The holographs with this ink were odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the holographs were superior in color sensitivity and color density.

EXAMPLE 4

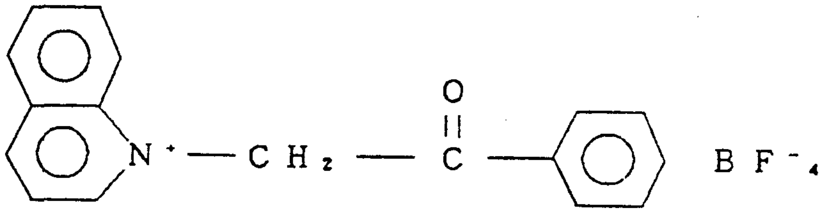
TH-107 (Trademark for electron donative chromatic organic compound of Hodogaya Kagaku Kohgyoh Co.)	0.25 part
Triphenylsulfonium hexafluorophosphate (photoactivator)	0.5 part
S-Lec BM-5 (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	1.5 parts
Methylethyl ketone	13 parts
Toluene	3 parts
Methanol	4 parts

After all components were stirred and dissolved, the components were coated on polyester film so as to constitute 4 g/m^2 solid matter, and consequently, film having a photosensitive composition was obtained. When the film was exposed to sunlight for 30 seconds, the exposed portion thereof became black-colored.

The film was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 5

NC-BK (Trademark for electron donative chromatic organic compound of Hodogaya Kagaku Co.)	5 parts
Compound expressed by the following formula (photoactivator)	10 parts



S-Lec BX-L (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	14 parts
Methylethyl ketone	71 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester film or fine paper so as to constitute from 2 to 4 g/m^2 solid matter, and consequently, sheet having a photosensitive composition was obtained. When the sheet was exposed to sunlight for 20 seconds, the exposed portion thereof became black-colored.

The sheet was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 6

Pergascript Red I-6B (Trademark for electron donative chromatic organic compound of Chiba Geigy A.G.)	5 parts
Bis[4-(diphenylsulfonio)phenyl]sulfide-bis-hexafluoroarsenate (photoactivator)	8 parts
Ethyl cellulose, N-4 (Trademark for cellulose resin of a compound having alcoholic hydroxyl groups of Hercules Co. of U.S.A.)	5 part
Methylethyl ketone	40 parts

A sheet having a photosensitive composition was obtained by the same way as in Example 1. When the sheet was exposed to sunlight for 20 seconds, the exposed portion thereof became red-colored.

The sheet was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 7

OR-55 (Trademark for electron donative chromatic organic compound of Yamada Kohgyoh Kagaku Co.)	5 parts
Bis[4-(diphenylsulfonio)phenyl]sulfide-bis-hexafluoroantimonate (photoactivator)	8 parts
β-phenylethyl alcohol (a compound having alcoholic hydroxyl groups)	1 part

MS-300 (Trademark for stylene-metacrylic acid copolymer resin of Shinnittetsu Kagaku Co.)	6 parts
Methylethyl ketone	50 parts
Toluene	20 parts

A sheet having a photosensitive composition was obtained by the same way as in Example 1. When the sheet was exposed to sunlight for 20 seconds, the exposed portion thereof became orange-colored.

The sheet was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 8

OR-55 (Trademark for electron donative chromatic organic compound of Yamada Kohgyoh Kagaku Co.)	0.25 part
Triphenylsulfonium hexafluorophosphate (photoactivator)	0.5 part
S-Lec BX-L (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	1.5 parts
Methylethyl ketone	15 parts
Methanol	3 parts

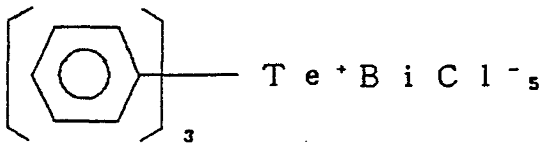
After all components were stirred and dissolved, the components were coated on polyester film so as to constitute

4 to 5 g/m^2 solid matter, and consequently, film having a photosensitive composition was obtained. Tackifiers were coated on the rear surface of the film, so that a label was obtained. When the label was adhered to a vessel, a writing material, a toy, or the like was exposed to sunlight for 20 seconds, the label became orange-colored.

The label was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 9

NBP-1 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Gohsei Co.)	5 parts
Compound expressed by the following formula (photoactivator)	10 parts



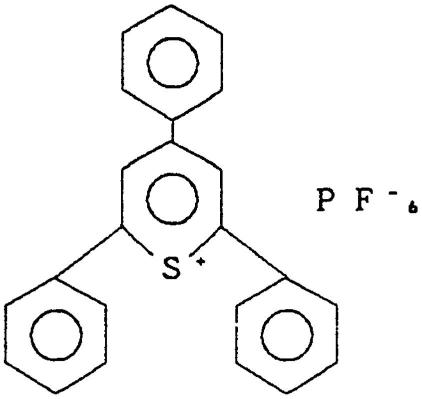
S-Lec BM-S (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	6 parts
Methyl ethyl ketone	30 parts
Toluene	20 parts

Sheet having a photosensitive composition was obtained in the same way as in Example 1. When the sheet was exposed to sunlight for 20 seconds, the exposed portion thereof became blue-colored.

The sheet was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 10

Pergascript Red I-6B (Trademark for electron donative chromatic organic compound of Chiba Geigy A.G.)	5 parts
Compound expressed by the following formula (photoactivator)	8 parts



Ethyl cellulose, N-4 (Trademark for cellulose resin of a compound having alcoholic hydroxyl groups of Hercules Co., U.S.)	5 parts

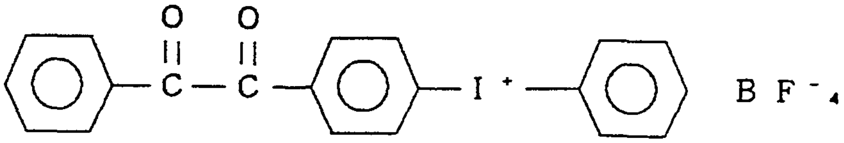
Methylethyl ketone	40 parts

Sheet having a photosensitive composition was obtained in the same way as in Example 1. When the sheet was exposed to sunlight for 20 seconds, the exposed portion thereof became red-colored.

The sheet was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 11

OR-55 (Trademark for electron donative chromatic organic compound of Yamada Kohgyoh Kagaku Co.)	5 parts
Compound expressed by the following formula (photoactivator)	8 parts



MS-300 (Trademark for stylene-metacrylic acid copolymer resin of Shinnittetsu Kagaku Co.)	6 parts
Methylethyl ketone	50 parts
Toluene	20 parts

Sheet having a photosensitive composition was obtained in the same way as in Example 1. When the sheet was exposed to sunlight for 20 seconds, the exposed portion thereof became orange-colored.

The sheet was odorless, and superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the film was superior in color sensitivity and color density.

EXAMPLE 12

PSD-G (Trademark for electron donative chromatic organic compound of Shinnisso Kako Co.)	0.25 part
Triphenylsulfonium hexafluorophosphate (photoactivator)	0.5 part
Light calcium carbonate fine powder (basic fine powder)	1 part
MS-300 (Trademark for stylene-metacrylic acid copolymer resin of Shinnittetsu Kagaku Co.)	1.5 parts
Toluene	8 parts
Methylethyl ketone	12 parts
Methanol	3 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester sheet so as to constitute 4 to 5 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained.

Tackifiers were coated on the rear surface of the sheet, so that a label was obtained. When the label was adhered to a writing material, a toy, or the like was exposed to sunlight for 20 seconds or more, the label became green-colored. When the label was left with interruption of light irradiation at room temperature for 24 hours thereafter, the label was returned to an original white color.

The label was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 13

NBP-1 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Co.)	0.25 part
Triphenylphenacylphosphonium tetrafluoroborate (photoactivator)	0.5 part
Acid sodium carbonate fine powder (basic fine powder)	1 part
Toluene	7 parts
Methylethyl ketone	10 parts
Methanol	3 parts

After all components were stirred and dissolved or dispersed, the components were coated on fine paper so as to constitute 5 to 8 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to black light for 30 seconds, the sheet became blue-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 14

R-DCF (Trademark for electron donative chromatic organic compound of Hodogaya Kagaku Co.)	0.25 part
Triphenylphenacylsulfonium tetrafluoro borate (photoactivator)	0.5 part
Light calcium carbonate fine powder (basic fine powder)	1.5 parts
S-Lec BM-5 (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	1.5 parts
Methylethyl ketone	15 parts
Toluene	5 parts
Methanol	5 parts

After all components were stirred and dissolved or dispersed, the components were applied on polyester sheet so as to constitute 5 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 30 seconds, the sheet became red-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 15

Red-40P (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Co.)	0.25 part
Diphenyl-4-thiophenoxyphenylsulfonium tetrafluoroborate (photoactivator)	0.5 part
Calcium carbonate fine powder (basic fine powder)	2.5 parts
S-Lec BM-5 (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	2 parts
Methylethyl ketone	15 parts
Toluene	5 parts
Methanol	5 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester sheet so as to constitute 5 to 6 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to a chemical lamp for 30 seconds, the sheet became red-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 16

OR-55 (Trademark for electron donative chromatic organic compound of Yamada Kagaku Co.)	0.25 part
Triphenylsulfonium tetrafluoroborate (photoactivator)	0.5 part
Magnesium carbonate fine powder (basic fine powder)	1.5 parts
Triphenyl phosphate	0.25 part
S-Lec BM-5 (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	2 parts
Methylethyl ketone	8 parts
Toluene	2 parts
Methanol	2 parts

After all components were stirred and dissolved or dispersed, the components were printed on fine paper by stencil printing, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 30 seconds, the printed portion became orange-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 17

PSD-170 (Trademark for electron donative chromatic organic compound of Shinnisso Kako Co.)	0.25 part
Diphenyliodonium tetrafluoroborate (photoactivator)	0.5 part
Light calcium carbonate fine powder (basic fine powder)	2.5 parts
S-Lec BX-L (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	2 parts
Methylethyl ketone	20 parts
Toluene	4 parts
Methanol	5 parts

After all components were stirred and dissolved or dispersed, the components were printed on fine paper by letterpress, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 30 seconds, the printed portion became black-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 18

NBP-1 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Co.)	0.25 part
Triphenylphenacylphosphonium tetrafluoroborate (photoactivator)	0.5 part
Newpol 50HB-2000 (Trademark for poly(oxyethyleneoxypropylene)glycol monoether of a compound having oxyethylene groups of Sanyo Kasei Co.)	0.25 part
Toluene	7 parts
Methylethyl ketone	10 parts
Methanol	3 parts

After all components were stirred and dissolved or dispersed, the components were impregnated on fine paper so as to constitute 2 to 3 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to black light for 30 seconds, the sheet became blue-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 19

PSD-HR (Trademark for electron donative chromatic organic compound of Shinnisso Kako Co.)	0.25 part
Triphenylsulfonium hexafluorophosphate (photoactivator)	0.75 part
Tween 80 (Trademark for polyoxyethylene sorbitan monooolate of a compound having oxyethylene groups of Kao-Atlas Co.)	0.5 part
Ethyl cellulose, N-4 (Trademark for cellulose resin of a compound having alcoholic hydroxyl groups of Hercules Co. of U.S.)	1.5 parts
Methylethyl ketone	10 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester sheet so as to constitute 5 to 8 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight or chemical lamp light for 30 seconds, the exposure portion thereof became red-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 20

NG-100 (Trademark for electron donative chromatic organic compound of Teikoku Kggaku Co.)	0.25 part
Triphenylsulfonium tetrafluoroborate (photoactivator)	0.5 part
PEG#600 (Trademark for polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 600, a produce of Nippon Yushi Co.)	0.5 part
Methylisobutyl ketone	12.5 parts
Toluene	12.5 parts

After all components were stirred and dissolved or dispersed, the components were filled in a pen body so as to constitute ink for a fiber pen.

When writing was made on paper or plastic sheet by the pen, an almost invisible latent image was obtained.

When sunlight was irradiated to the latent image portion for 15 seconds thereafter, the latent image became blue-colored. When it was left with interruption of light irradiation at room temperature for 24 hours thereafter, it was returned to an original white color. Although the appearance and disappearance of color were repeated 10 times, little deterioration in the property was seen.

EXAMPLE 21

Red-40P (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Co.)	0.25 part
Diphenyl-4-thiophenoxyphenylsulfonium tetrafluoroborate (photoactivator)	0.5 part
Emulgen 903 (Trademark for polyoxyethylenenonylphenol ether of a compound having oxyethylene groups of Kao-Atlas Co.)	0.5 part
S-Lec BM-5 (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	2 parts
Methylethyl ketone	15 parts
Toluene	5 parts
Methanol	5 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester sheet so as to constitute 5 to 6 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to a chemical lamp light for 30 seconds, the exposure portion thereof became red-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 22

OR-55 (Trademark for electron donative chromatic organic compound of Yamada Kagaku Co.)	0.25 part
Triphenylsulfonium hexafluorophosphate (photoactivator)	0.5 part
Uniox C-2300 (Trademark for polyethylene glycol castor oil ester of a compound having oxyethylene groups of Nippon Yushi Co.)	0.5 part
S-Lec BM-5 (Trademark for butyral resin of a compound having alcoholic hydroxyl groups of Sekisui Kagaku Co.)	2 parts
Methylethyl ketone	8 parts
Toluene	2 parts
Methanol	2 parts

After all components were stirred and dissolved or dispersed, the components were printed on fine paper by stencil printing, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 30 seconds, the printed portion became orange-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

EXAMPLE 23

PSD-170 (Trademark for electron donative chromatic organic compound of Shinnisso Kako Co.)	0.25 part
Diphenyliodonium tetrafluoroborate (photoactivator)	0.25 part
PEG#600 (Trademark for polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 600, a product of Nippon Yushi Co.)	0.5 part
S-Lec BX-L (Trademark for butyral resin of a compound having alcoholic hydroxyl groups, a product of Sekisui Kagaku Co.)	2 parts
Methylethyl ketone	20 parts
Toluene	4 parts
Methanol	5 parts

After all components were stirred and dissolved or dispersed, the components were printed on fine paper by letterpress, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 30 seconds, the printed portion became black-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 24

OR-55 (Trademark for electron donative chromatic organic compound of Yamada Kagaku Co.)	1 part
Bis[4-(diphenylsulfonio)phenyl]sulfide-bis-tetrafluoroborate (photoactivator)	5 parts
PEG#1000 (Trademark for polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 1000, a product of Sanyo Kasai Co.)	4 parts
MSK-PO (Trademark for calcium carbonate of basic fine powder, a product of Maruo Calcium Co.)	10 parts
S-Lec BX-L (Trademark for butyral resin of a compound having alcoholic hydroxyl groups, a product of Sekisui Kagaku Co.)	5 parts
Methylethyl ketone	25 parts

After all components were stirred and dissolved or dispersed, the components were applied on fine paper so as to constitute 5 to 8 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 15 seconds, the exposed portion became orange-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 25

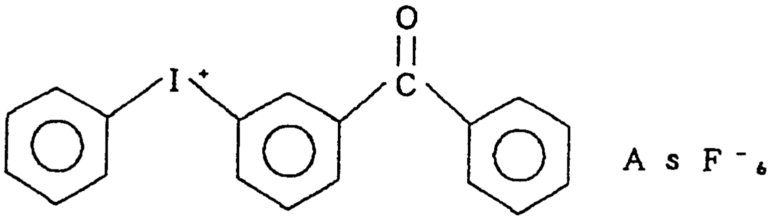
ATP (Trademark for electron donative chromatic organic compound of Yamada Kagaku Kohgyoh Co.)	1 part
Bis[4-(diphenylsulfonio)phenyl]sulfide-bis-hexafluoroarcenate (photoactivator)	4 parts
Amiet 302 (Trademark for polyoxyethylene-alkylamine of Kao Sekken Co.)	0.2 part
PEG#600 (Tradename of polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 600, a product of Sanyo Kasei Co.)	5 parts
Methylethyl ketone	25 parts
Methanol	5 parts

After all components were stirred and dissolved or dispersed, the components were filled in a pen body so as to constitute ink for a fiber pen.

When writing was made on paper or plastic sheet by the pen body, an almost invisible latent image was obtained. When sunlight was irradiated to the latent image portion for 15 seconds thereafter, the latent image became green-colored. When it was left with interruption of light irradiation at room temperature for 24 hours thereafter, it was returned to an original colorless condition. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

EXAMPLE 26

OR-55 (Trademark for electron donative chromatic organic compound of Yamada Kagaku Kohgyoh Co.)	1 part
Compound expressed by the following formula (photoactivator)	5 parts



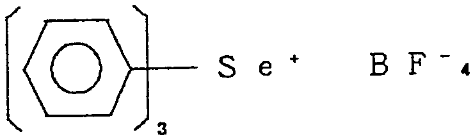
PEG#1000 (Trademark for polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 1000, a product of Sanyo Kasei Co.)	4 parts
MSK-PO (Trademark for calcium carbonate of basic fine powder, a product of Maruo Calcium Co.)	10 parts
S-Lec BX-L (Trademark for butyral resin of a compound having alcoholic hydroxyl groups, a product of Sekisui Kagaku Co.)	5 parts
Methylethyl ketone	25 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester sheet so as to constitute 5 to 8 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 15 seconds, the exposed portion became orange-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 27

NBP-1 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Gohsei Co.)	1 part
Compound expressed by the following formula (photoactivator)	4 parts

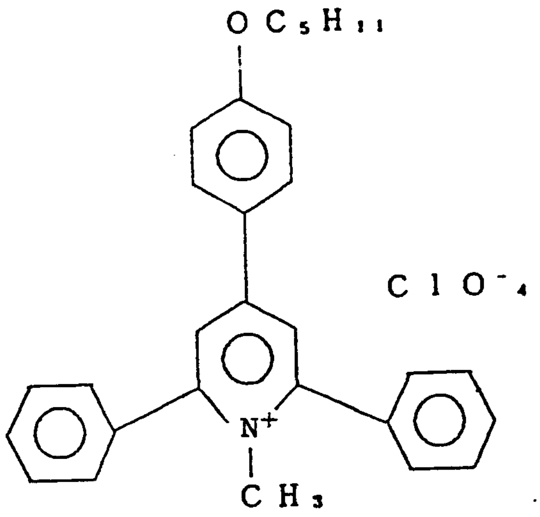


Rheodoll TW-0120 (Trademark for polyoxyethylene sorbitan monoolate of a compound having oxyethylene groups, a product of Kao Sekken Co.)	1 part
MSK-PO (Trademark for calcium carbonate of basic fine powder, a proudct of Maruo Calcium Co.)	10 parts
Ethyl cellulose, N-4 (Trademark for cellulose resin of a compound having alcoholic hydroxyl groups, a product of Hercules Co. of U.S.)	6 parts
Methylethyl ketone	30 parts

A sheet having photochromic property was obtained in the same way as in Example 26. When the sheet was exposed to sunlight for 15 seconds, the exposed portion became blue-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

EXAMPLE 28

NC-BK (Trademark for electron donative chromatic organic compound of Hodogaya Kagaku Co.)	1 part
Compound expressed by the following formula (photoactivator)	5 parts



PEG#600 (Trademark for polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 600,

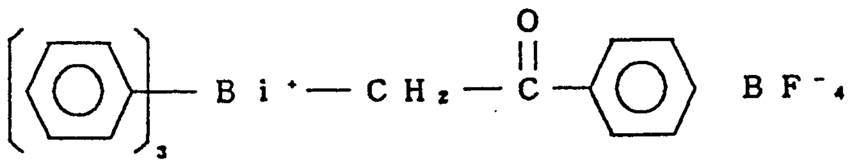
a product of Sanyo Kasei Co.)	3 parts
MSK-PO (Trademark for calcium carbonate of basic fine powder, a product of Maruo Calcium Co.)	9 parts
Triphenyl phosphate	1 part
Ethyl cellulose, N-4 (Trademark for cellulose resin of a compound having alcoholic hydroxyl groups, a product of Hercules Co. of U.S.)	6 parts
Methylethyl ketone	35 parts

A sheet having photochromic property was obtained in the same way as in Example 27. When the sheet was exposed to sunlight for 15 seconds, the exposed portion became black-colored. When the sheet was left with interruption of light irradiation at room temperature for 12 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 29

ATP (Trademark for electron donative chromatic organic compound of Yamada Kagaku Kohgyoh Co.)	1 part
Compound expressed by the following formula (photoactivator)	4 parts



Amiet 302 (Trademark for polyoxyethylene-alkylamine of a compound having oxyethylene groups, a product of Kao Sekken Co.)	0.2 part
PEG#600 (Trademark for polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 600, a product of Sanyo Kasei Co.)	5 parts
Methylethyl ketone	25 parts
Methanol	5 parts

After all components were stirred and dissolved or dispersed, the components were filled in a pen body so as to constitute ink for a fiber pen.

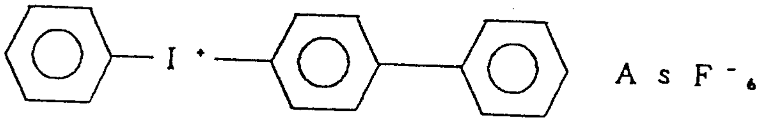
When writing was made on paper or plastic sheet by the pen body, an almost invisible latent image was obtained.

When sunlight was irradiated to the latent image portion for 15 seconds thereafter, the latent image became green-colored. When it was left with interruption of light irradiation at room temperature for 12 hours thereafter, it was returned to an original colorless condition. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

EXAMPLE 30

NC-BK (Trademark for electron donative chromatic organic compound of Hodogaya Kagaku Co.)	1 part

Compound expressed by the following formula (photoactivator)	4 parts



MSK-PO (Trademark for calcium carbonate of basic fine powder, a product of Maruo Calcium Co.)	10 parts
MS-300 (Trademark for stylene-metacrylic acid resin, a product of Shinnittetsu Kagaku Co.)	5 parts
MIBK (ethylisobutyl ketone)	50 parts
Methylethyl ketone	10 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester sheet or fine paper so as to constitute 5 to 8 g/m^2 solid matter, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 15 seconds, the exposed portion became black-colored. When the sheet was left with interruption of light irradiation at room temperature for 12 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 31

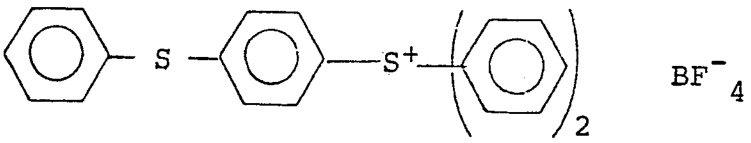
NBP-1 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Co.)	0.25 part
Triphenylphenacylphosphonium tetrafluoroborate (photoactivator)	0.5 part
Newpol 50HB-2000 (Trademark of poly(oxyethyleneoxypropylene) glycol monoether of a compound having oxyethylene groups, a product of Sanyo Kasei Co.)	0.25 part
Oleyl alcohol (a compound having alcoholic hydroxyl groups)	0.2 part
Toluene	7 parts
Methylethyl ketone	10 parts
Methanol	3 parts

After all components were stirred and dissolved or dispersed, the components were impregnated on polyester sheet so as to constitute 3 to 5 g/m^2 solidity, and consequently, white sheet having photochromic property was obtained. When the sheet was exposed to black light for 30 seconds, the sheet became blue-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original white color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 32

S-205 (Trademark for electron donative chromatic organic compound of Yamada Kagaku Co.)	0.5 part
Compound expressed by the following formula (photoactivator)	1 part



PEG#1540 (Trademark for polyethylene glycol of a compound having oxyethylene groups, having an average molecular weight of 1540, a product of Sanyo Kasei Co.)	1.5 parts
MSK-PO (Trademark for calcium carbonate of basic fine powder, a product of Maruo Calcium Co.)	3.5 parts
Amisol SME (Trademark for wax, a product of Kawaken Fine chemical Co.)	10 parts

After all components were heated to 100 to 120°C and dispersed by an attritor (grinder), the components were poured into a test tube of 9 mm diameter and left at room temperature, and consequently, a colorless crayon was obtained.

Although letters, pictures, and the like were drawn on a notebook with the crayon, they were invisible.

When sunlight was irradiated to the notebook for 30 seconds, the letters, pictures, and the like became black-colored. When it was left with interruption of light irradiation at room temperature for 24 hours thereafter, it was returned to an original colorless condition. Although the appearance and disappearance of color were repeated 10 times, little deterioration in the property was seen.

EXAMPLE 33

A colorless crayon was obtained in the same way as in Example 32, except that Pergascript Red I-6B was used instead of S-205.

Although letters, pictures, and the like were drawn on a notebook with the crayon, they were invisible.

When sunlight was irradiated to the notebook for 30 seconds, the letters, pictures, and the like became red-colored. When it was left with interruption of light irradiation at room temperature for 24 hours thereafter, it was returned to an original colorless condition. Although the appearance and disappearance of color were repeated 10 times, little deterioration in the property was seen.

EXAMPLE 34

A colorless crayon was obtained in the same way as in Example 32, except that Green 24P was used instead of S-205.

Although letters, pictures, and the like were drawn on a notebook with the crayon, they were invisible.

When sunlight was irradiated to the notebook for 30 seconds, the letters, pictures, and the like became green-colored. When it was left with interruption of light irradiation at room temperature for 24 hours thereafter, it was returned to an original colorless condition. Although the appearance and disappearance of color were repeated 10 times, little deterioration in the property was seen.

EXAMPLE 35

A colorless crayon was obtained in the same way as in Example 32, except that NBP-1 was used instead of S-205.

Although letters, pictures, and the like were drawn on a notebook with the crayon, they were invisible.

When sunlight was irradiated to the notebook for 30 seconds, the letters, pictures, and the like became blue-colored. When it was left with interruption of light irradiation at room temperature for 24 hours thereafter, it was returned to an original colorless condition. Although the appearance and disappearance of color were repeated 10 times, little deterioration in the property was seen.

EXAMPLE 36

A colorless crayon was obtained in the same way as in Example 32, except that OR-55 was used instead of S-205.

Although letters, pictures, and the like were drawn on a notebook with the crayon, they were invisible.

When sunlight was irradiated to the notebook for 30 seconds, the letters, pictures, and the like became orange-colored. When it was left with interruption of light irradiation at room temperature for 24 hours thereafter, it was returned to an original colorless condition. Although the appearance and disappearance of color were repeated 10 times, little deterioration in the property was seen.

EXAMPLE 37

NBP-1 (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Gohsei Co.)	0.25 part
Triphenylsulfonium hexafluorophosphate (photoactivator)	0.5 part
MIRJ 52 (Trademark for polyoxyethylene stearate of a compound having oxyethylene groups, a product of Kao-Atlas Co.)	0.5 part
Oil Pink#312 (Trademark for red dye, a product of Orient Kagaku Co.)	0.05 part
MS-300 (Trademark for stylene-metacrylic acid copolymer resin, a product of Shinnittetsu Kagaku Co.)	1.5 parts
Toluene	8 parts
Methylethyl ketone	12 parts
Methanol	3 parts

After all components were stirred and dissolved or dispersed, the components were coated on polyester sheet so as to constitute 4 to 5 g/m^2 solid matter, and consequently, red sheet having photochromic property was obtained. Tackifiers were applied on the rear surface of the sheet, whereby a label was obtained. When the label was adhered to a writing material, a toy, or the like was exposed to sunlight for 20 seconds or more, the label became violet-colored. When the label was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original red color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The label was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 38

Pergascript Red I-6B (Trademark for electron donative chromatic organic compound of Chiba Geigy A.G.)	1 part
Bis[4-(diphenylsulfonio)phenyl]sulfide-bis-tetrafluoroborate (photoactivator)	5 parts
MS-1 (Trademark for calcium carbonate of basic fine powder, a proudct of Maruo Calcium Co.)	12 parts
S-Lec BX-L (Trademark for butylal resin of a compound having alcoholic hydroxyl groups, a product of Sekisui Kagaku Co.)	5 parts
Oil Yellow#107 (Trademark for yellow dye, a product of Orient Kagaku Co.)	0.2 part
Methylethyl ketone	25 parts

A yellow sheet having photochromic property was obtained in the same way as in Example 37. When the sheet was exposed to sunlight for 15 seconds, the exposed portion became green-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original yellow color. Although the appearance and disappearance of color were repeated 10 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties.

EXAMPLE 39

Red-40P (Trademark for electron donative chromatic organic compound of Yamamoto Kagaku Co.)	0.25 part
Triphenylsulfonium perchlorate (photoactivator)	0.5 part
S-Lec BM-S (Trademark for butyral resin of a compound having alcoholic hydroxyl groups, a product of Sekisui Kagaku Co.)	1.5 parts
Oil Yellow#107 (Trademark for yellow dye, a product of Orient Kagaku Co.)	0.05 part
Toluene	9 parts
Methylethyl ketone	25 parts

After all components were stirred and dissolved or dispersed, the components were applied on fine paper by letterpress, and consequently, a yellow sheet having photochromic property was obtained. When the sheet was exposed to sunlight for 30 seconds, the printed portion became green-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original yellow color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the paper was superior in color sensitivity and color strength.

EXAMPLE 40

NC-Y-2-1 (Trademark for electron donative chromatic organic compound of Hodogaya Kagaku Co.)	0.25 part
Triphenylsulfonium tetrafluoroborate (photoactivator)	0.5 part
Triphenyl phosphate	0.25 part
S-Lec BM-5 (Trademark for butyral resin of a compound having alcoholic hydroxyl groups, a product of Sekisui Kagaku Co.)	1.5 parts
Basic fine powder silica	0.5 part
Oil Pink#312 (Trademark for red dye, a product of Orient Kagaku Co.)	0.1 part
Methylethyl ketone	7 parts
Toluene	2 parts
Methanol	2 parts

After all components were stirred and dissolved or dispersed, the components were printed on fine paper by stencil print, and consequently, a red sheet having photochromic property was obtained. When the sheet was exposed to high-pressure mercury-vapor lamp for 30 seconds, the printed portion became green-colored. When the sheet was left with interruption of light irradiation at room temperature for 24 hours thereafter, the sheet was returned to an original red color. Although the appearance and disappearance of color were repeated 20 times, little deterioration in the property was seen.

The sheet was superior in heat-proof, humidity-proof, and preservation properties. Moreover, gases or air bubbles were not generated at the time of exposure, and the paper was superior in color sensitivity and color density.

Thus the photosensitive compositions according to the present invention have abundant kinds of color productions, are superior in heat-proof, humidity-proof, and preservation properties, and can be used as a useful material in a wide field.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

WHAT IS CLAIMED IS:

1. A photosensitive composition comprising an electron donative chromatic organic compound, and a photoactivator selected from the group consisting of an aromatic halonium salt, an aromatic onium salt of elements belonging to Group VIa in the periodic table and an aromatic onium salt of elements belonging to Group Va in the periodic table.

2. A photosensitive composition as claimed in claim 1, further comprising a compound having alcoholic hydroxy groups.

3. A photosensitive composition as claimed in claim 1, further comprising at least one of a compound having oxyethylene groups and basic fine powder.

4. A photosensitive composition as claimed in claim 3, further comprising a compound having alcoholic hydroxy groups.

5. A photosensitive composition as claimed in claim 1, wherein said electron donative chromatic organic compound is selected from the group consisting of triphenylmethanephthalides, fluorans, phenothiazines, indolylphthalides, leucoauramines, rhodamine lactams, rhodamine lactones, indolines, triphenylmethanes, azaphthalides, chromenoindols, and triazenes.

6. A photosensitive composition as claimed in claim 1, wherein said electron donative chromatic organic compound is

selected from the group consisting of triphenylmethanephthalides, fluorans, indolylphtalides, leucoauramines, rhodamine lactams, triphenylmethanes, and azaphtalides.

7. A photosensitive composition as claimed in claim 1, wherein said photoactivator is selected from the group consisting of an aromatic halonium salt (a salt of an aromatic halonium and a halogen-containing complex ion of Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, B, P and As); a salt of an aromatic onium of elements belonging to Group VIa in the periodic table (O, S, Se, and Te) and a halogen containing complex ion of Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, B, P and As; a salt of an aromatic onium of elements belonging to Group Va in the periodic table (N, P, As, Sb, and Bi) and a halogen-containing complex ion of Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, B, P, and As; and a salt of an aromatic onium and a perchloric acid.

8. A photosensitive composition as claimed in claim 1, wherein said photoactivator is selected from the group consisting of an aromatic iodonium salt (a salt of an aromatic iodonium and a halogen-containing complex ion of Sb, B, P and As); a salt of an aromatic onium of elements belonging to Group VIa in the periodic table (S) and a halogen-containing complex ion of Sb, B, P, and As; a salt of an aromatic onium of elements belonging to Group Va in the periodic table (N and P) and a halogen-containing complex

ion of Sb, B, P, and As; and a salt of an aromatic onium and a perchloric acid.

9. A photosensitive composition as claimed in claim 1, wherein said photoactivator is selected from the group consisting of a salt of an aromatic iodonium and BF_4^-; a salt of an aromatic iodonium and PF_6^-; a salt of an aromatic sulfonium and BF_4^-; and a salt of an aromatic sulfonium and PF_6^-.

10. A photosensitive composition as claimed in claim 2, wherein said compound having alcoholic hydroxyl groups is selected from the group consisting of an aliphatic alcohol of 6 or more carbon atoms, having a boiling point of 150°C or more; a polyhydric alcohol of 6 or more carbon atoms, having a boiling point of 150°C or more; an aromatic alcohol of 7 or more carbon atoms, having a boiling point of 150°C or more; and a macromolecular alcohol of from about 10,000 through about 300,000 molecular weight.

11. A photosensitive composition as claimed in claim 2, wherein said compound having alcoholic hydroxyl groups is selected from the group consisting of an aliphatic alcohol of 9 or more carbon atoms, having a boiling point of 200°C or more; an aromatic alcohol of 7 or more carbon atoms, having a boiling point of 200°C or more; a polyhydric alcohol of 6 or more carbon atoms, having a boiling point of 200°C or more; and a macromolecular alcohol of from about

10,000 through about 300,000 in molecular weight.

12. A photosensitive composition as claimed in claim 3, wherein said compound having oxyethylene groups is a compound of 100 or more in molecular weight, having 3 or more oxyethylene groups in a molecule.

13. A photosensitive composition as claimed in claim 3, wherein said compound having oxyethylene groups is a compound of 190 or more in molecular weight, having 6 or more oxyethylene groups in a molecule.

14. A photosensitive composition as claimed in claim 3, wherein said basic fine powder is selected from the group consisting of a hydroxide of alkali metals, such as lithium, sodium, potassium, etc., and alkaline-earth metals, such as magnesium, calcium, barium, etc.; the carbonate thereof; and basic fine powder silica, basic montmorillonite, basic talc, basic lead sulfate, and basic lead carbonate.

15. A photosensitive composition as claimed in claim 4, wherein said compound having alcoholic hydroxyl groups is selected from the group consisting of an aliphatic alcohol of 6 or more carbon atoms, having a boiling point of 150°C or more; a polyhydric alcohol of 6 or more carbon atoms, having a boiling point of 150°C or more; an aromatic alcohol of 7 or more carbon atoms, having a boiling point of 150°C or more; and a macromolecular alcohol of from about 10,000 through about 300,000 in molecular weight.

16. A photosensitive composition as claimed in claim 4, wherein said compound having alcoholic hydroxyl groups is selected from the group consisting of an aliphatic alcohol of 9 or more carbon atoms, having a boiling point of 200°C or more; an aromatic alcohol of 7 or more carbon atoms, having a boiling point of 200°C or more; a polyhydric alcohol of 6 or more carbon atoms, having a boiling point of 200°C or more; and a macromolecular alcohol of from about 10,000 through about 300,000 in molecular weight.

17. A photosensitive composition as claimed in claim 1, wherein the weight proportion of said photoactivator to said electron donative chromatic organic compound is from 0.01 to 100 parts to 1 part.

18. A photosensitive composition as claimed in claim 3, wherein the weight proportion of said compound having oxyethylene groups to said electron donative chromatic organic compound is from 0.01 to 100 parts to 1 part.

19. A photosensitive composition as claimed in claim 3, wherein the weight proportion of said basic fine powder to said electron donative chromatic organic compound is from 0.01 to 100 parts to 1 part.

20. A photosensitive composition as claimed in claim 2, wherein the weight proportion of said compound having alcoholic hydroxyl groups to said photoactivator is from 0.01 to 200 parts to 1 part.

21. A photosensitive composition as claimed in claim 4, wherein the weight proportion of said compound having alcoholic hydroxyl groups to said photoactivator is from 0.01 to 200 parts to 1 part.