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(54) High sensitive silver halide photographic light-sensitive material.

(57) A silver halide photographic light-sensitive material having a support and provided thereon the hydrophilic colloid layers including a silver halide emulsion layer is disclosed. Said silver halide emulsion layer comprises a silver halide emulsion prepared by carrying out desalination of the excessive salts at pH of not higher than 6 after formation of the silver halide grains, and by adding a sensitizing dye to the silver halide emulsion prior to chemical sensitization of the silver halide grains.

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Description

HIGH SENSITIVE SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material capable of providing a high quality image, and in particular to a silver halide photographic light-sensitive material comprising less fogging and a higher sensitivity, and capable of providing a high quality image that has good graininess and sharpness, even in rapid processing.

BACKGROUND OF THE INVENTION

Recently, a higher sensitivity is required of the silver halide photographic light-sensitive material in accordance with advance in photographic techniques. The higher sensitivity is required in such fields as camera for higher shutter speed, color and black-and-white print paper for more rapid processing, printing for digitalization and rationalization, medical service for reduction of exposure to X-ray.

For example, in a medical radiography, ortho-type sensitive materials that are ortho-sensitized to a wavelength region of 540 - 550 nm are more commonly used instead of conventional regular type materials sensitive to a wavelength of 450 nm. These sensitized materials have a wider sensitive wavelength range as well as higher sensitivity, and therefore can contribute to reduction of adverse effects on a human body because of reduction of exposure to X-ray.

There have been made various research and development on a sensitizing technique for a photographic sensitive emulsion, and a lot of useful methods have been found. One of them is a method using a sensitizing dye, i.e. spectral sensitization.

One example of a spectral sensitization method is addition of a dye in formation of silver halide grains, as is disclosed in U.S. Patent Nos. 2,735,766, 3,628,960, and 4,225,666. The relevant methods are disclosed in further detail in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) Nos. 184142/1983, 196278/1986, 103149/1986, and 205929/1986.

These techniques can provide the photographic materials comprising good sensitizing efficiency and high sensitivity however, they have problems to some extent such as fogging, graininess in rapid processing, and a pressure resistance (a roller mark resistance).

SUMMARY OF THE INVENTION

An object of the present invention is to provide a silver halide photographic light-sensitive material comprising higher spectral sensitivity and an excellent pressure resistance, and capable of providing an image of excellent graininess. Another object of the invention is to provide a silver halide photographic light-sensitive material capable of providing an image of excellent sharpness and graininess even in rapid processing.

These objects of the invention can be achieved by a silver halide photographic light-sensitive material having a support and provided thereon, the hydrophilic colloid layers including at least one light-sensitive silver halide emulsion layer, wherein the light-sensitive material is characterized by that at least one emulsion layer comprises a silver halide emulsion prepared by removing excessive salts at pH of not higher than 6 after formation of silver halide grains and adding a sensitizing dye prior to chemical sensitization of the silver halide grains.

DETAILED DESCRIPTION OF THE INVENTION

The silver halide photographic light-sensitive material of the invention comprises a support having thereon the hydrophilic colloid layers including at least one light-sensitive silver halide emulsion layer.

This material may be a two-sided light-sensitive material having each at least one silver halide emulsion layer on both sides of the support, or may be a single-sided light-sensitive material having at least one silver halide emulsion layer on only one side of the support. In the single-sided light-sensitive material, a backing layer comprising of a hydrophilic colloid layer may be provided on a side opposite to the side having the emulsion layer.

In the invention, silver halide may be any of silver bromide, silver bromoiodide, silver bromochloroiodide, silver bromochloride, and silver chloride. The preferred silver halide is silver bromoiodide or silver bromochloroiodide each having 30 mol% or less of silver iodide. The particularly preferred is silver bromoiodide having 2 to 25 mol% of silver iodide.

The silver halide grains may have a regular crystal such as cube, octahedron, and tetradecahedron, or an irregular crystal such as sphere or twinned crystal.

The silver halide grains may have either a uniform composition of silver halide or a multilayered construction in which a core and outer layers have different compositions of silver halide, and have preferably the multilayered construction consisting of the core having a higher silver iodide content and the outer layers having a lower silver iodide content.

The silver halide emulsions used in the invention may be either monodispersed or multidispersed.

The silver halide emulsions can be prepared by conventional methods.

Two or more types of silver halide emulsions independently prepared may be blended to make an emulsion of the invention.

The silver halide emulsion of the invention is preferably grown from a seed emulsion.

The silver halide emulsion comprising of the regular grains is can be prepared by controlling pAg and pH during grain formation.

The silver halide emulsion is subjected to desalination after completion of growth of the silver halide grains in order to remove excess salts.

Various methods are available as a desalination process. One typical method is a flocculation method where a flocculant is added to a silver halide emulsion for decantation of supernatant.

The desalination process may be performed either only once or several times. When this process is repeated several times, a flocculant may be added either every time or only at first.

In the invention, pH of the emulsion in desalination is preferably not higher than 6, and more preferably 2 to 5. pH is controlled in the above range in flocculating and settling silver halide grains after adding a flocculant, and in repeating the same after the flocculated and settled silver halide grains are dispersed again. pH may be adjusted to not higher than 6 either before or after addition of a flocculant, preferably after addition thereof.

The flocculation method includes a sulfuric acid method, an organic solvent method, an organic gelatin flocculant method, a gelatin derivative method, and a high-molecular flocculant method.

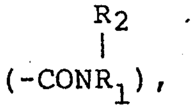
A gelatin derivative preferably used as a flocculant is a modified gelatin having substituted amino groups of not less than 50% (hereinafter referred to as a gelatin flocculant).

The examples of a substituent bonded to the amino group and the synthesis methods of the gelatin flocculant are described in U.S. Patent Nos. 2,691,582, 2,614,928, and 2,525,753.

The examples of the useful substituent are as follows;

(1) an acyl group such as alkylacyl, arylacyl, acetyl, and benzoyl;
(2) a carbamoyl group such as alkylcarbamoyl, and arylcarbamoyl;
(3) a sulfonyl group such as alkylsulfonyl, and arylsulfonyl;
(4) a thiocarbamoyl group such as alkylthiocarbamoyl, and arylthiocarbamoyl;
(5) a linear or branched alkyl group having 1 to 18 carbon atoms; and
(6) an aryl group such as phenyl, naphthyl, and an aromatic heterocyclic group.

The preferred gelatin flocculant comprises an amino group substituted by an acyl group ($-COR_1$) or a carbamoyl group



$$(-CO\overset{R_2}{\overset{|}{N}}R_1),$$

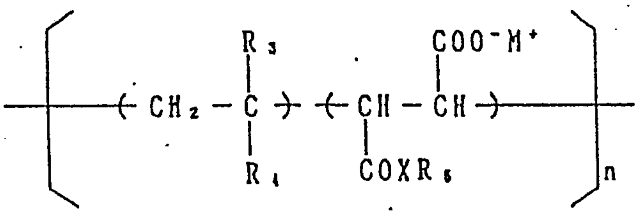
wherein R_1 represents an aliphatic group such as an alkyl group having 1 to 18 carbon atoms or an allyl group, an aryl group or an aralkyl group such as phenethyl group; R_2 represents a hydrogen atom, an aliphatic group, an aryl group, or an aralkyl group.

Preferably, R_1 is an aryl group and R_2 is a hydrogen atom.

An addition amount of the gelatin flocculant is 0.3 to 10 parts (by weight) per part of a protective colloid, and preferably 1 to 5 parts.

In the invention, after addition of the gelatin flocculant, pH is adjusted to not higher than 6, and preferably to 2 to 5. An acid used for adjusting pH includes an organic acid such as acetic acid, citric acid, and salicylic acid; and an inorganic acid such as nitric acid, sulfuric acid, and phosphoric acid. Together with the gelatin flocculant, heavy metal ions may be added, such as magnesium ion, cadmium ion, lead ion, and zirconium ion.

The high-molecular flocculant used in the invention is represented by the following Formula (I).

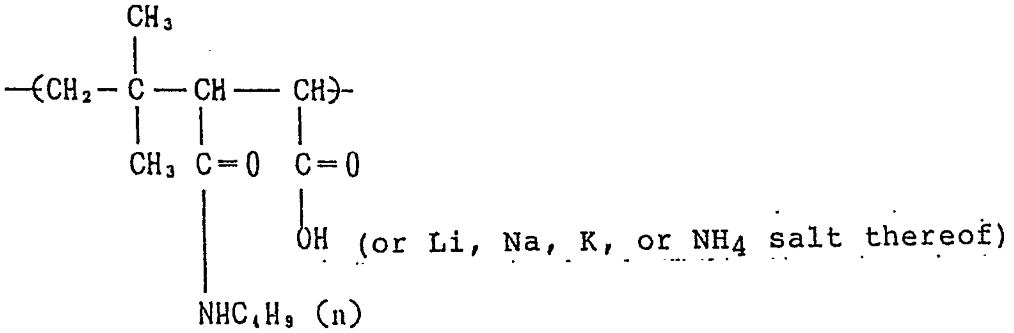


$$\left[-\left(CH_2-\overset{R_3}{\underset{R_4}{C}}\right)-\left(\underset{COXR_5}{CH}-\overset{COO^-M^+}{CH}\right)- \right]_n$$

wherein R_3 and R_4 independently represent a hydrogen atom, an aliphatic group, an aryl group and an aralkyl group; R_5 represents a hydrogen atom, an aliphatic group, an aryl group, an aralkyl group, or M; X represents -O-, or -NH-; M represents a hydrogen atom, an alkali metal atom, a quaternary ammonium group, or a quaternary phosphonium group; n is an integer of 10 to 10^4; either of two terminal beondages of Chain B may be linked to a tertiary carbon having R_3 and R_4 in Chain A; X may form a nitrogen-containing ring together with R_5, provided that X is -NH-.

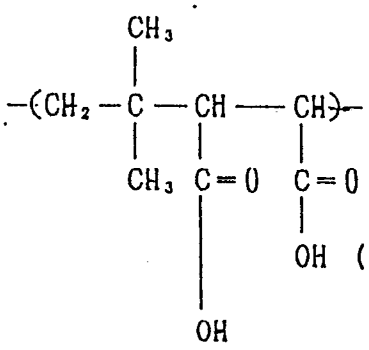
The examples of a high molecular compound represented by Formula (I) are as follows.

P－1



$$-\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\underset{\underset{NHC_4H_9\,(n)}{C=O}}{CH}-\underset{\underset{OH}{C=O}}{CH}\right)- \text{ (or Li, Na, K, or } NH_4 \text{ salt thereof)}$$

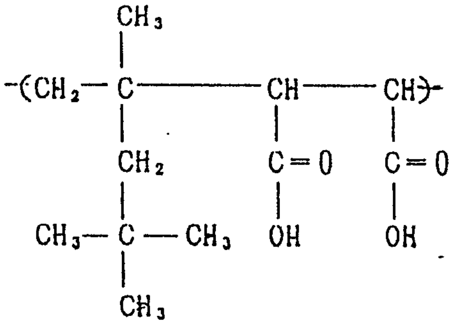
P − 2



$\mathrm{-\!(CH_2-C(CH_3)_2-CH(COOH)-CH(COOH))\!-}$

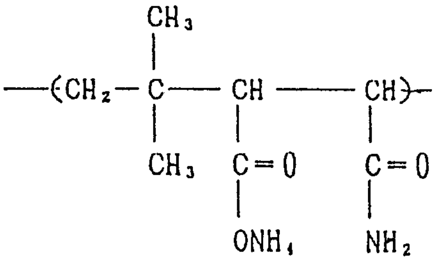
(or Li, Na, K, or NH_4 salt thereof)

P − 3



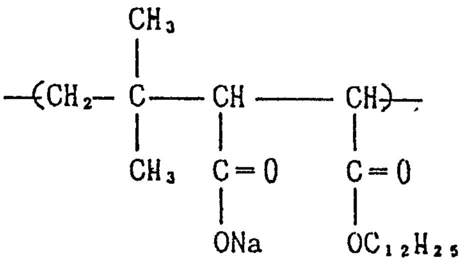
(or Li, Na, K, or NH_4 salt thereof)

P − 4



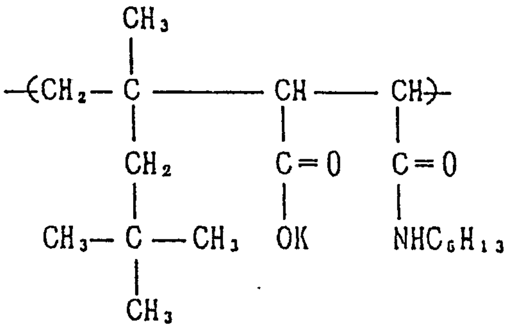
$\mathrm{-\!(CH_2-C(CH_3)_2-CH(COONH_4)-CH(CONH_2))\!-}$

P − 5



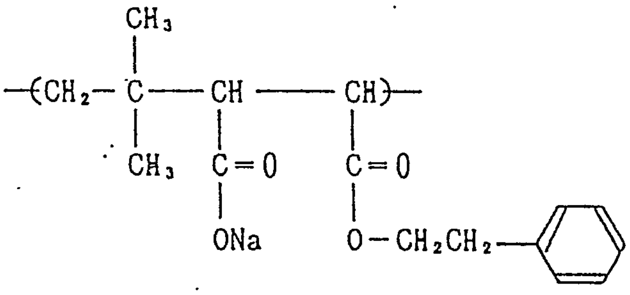
$$-\!\left(CH_2-C(CH_3)_2-CH(COONa)-CH(COOC_{12}H_{25})\right)\!-$$

P − 6

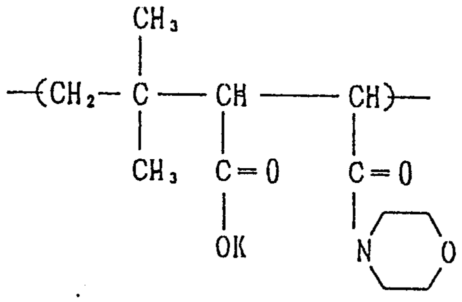


$$-\!\left(CH_2-C(CH_3)(CH_2C(CH_3)_3)-CH(COOK)-CH(CONHC_6H_{13})\right)\!-$$

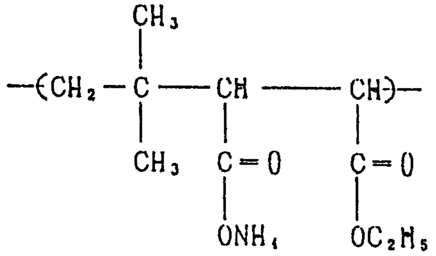
P − 7



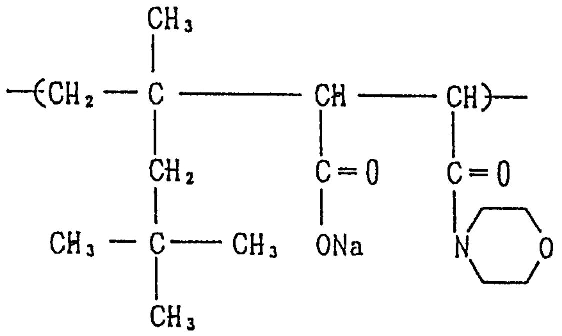
P-8



P-9



P-10

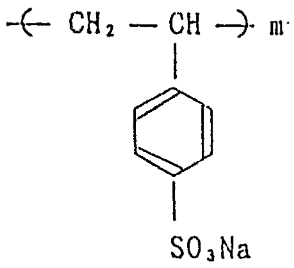


These high-molecular flocculants can be synthesized by a method, for example, described in "Kogyo Kagaku Zasshi (Industrial Chemistry Magazine)", Vol. 60, pp.1004 (1957).

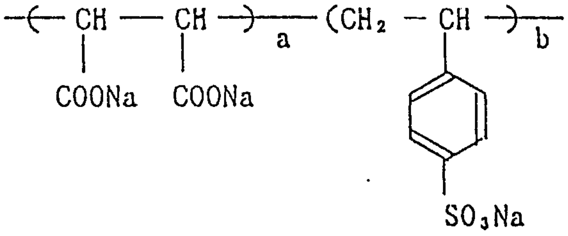
A molecular weight of these high molecular compounds is preferably 10^3 to 10^6, and more preferably 3×10^3 to 2×10^5. An addition amount thereof in a weight ratio to a protective colloid is preferably 1/50 to 1/4, and more preferably 1/40 to 1/10. An addition way thereof is the same as in the preceding gelatin flocculant.

The other typical polymer flocculants are shown below;

A-1

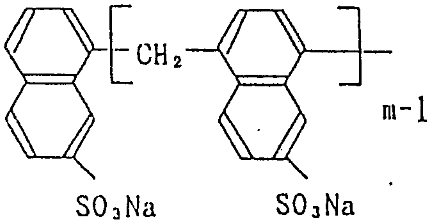


A-2



a:b=1:9~9:1 (molar ratio)

A-3



wherein m represents a degree of polymerization, and a molecular weight of these flocculants ranges from 1,000 to 200,000.

An addition amount thereof is 3 to 50 wt%, and preferably 3 to 20 wt% of gelatin in a silver halide emulsion.

After formation of the silver halide grains, the silver halide emulsion of the invention is subjected to spectral sensitization and chemical sensitization.

In spectral sensitization, a spectral sensitizing dye is used. The preferred spectral sensitizing dyes are described in Japanese Patent O.P.I. Publication No. 80237/1986, and Japanese Patent O.P.I. Publication No. 257947/1987.

In the present invention, the spectral sensitizing dye is added in formation of a silver halide grain or in desalination for removing excess salts; it is added prior to chemical sensitization, and preferably before completion of desalination. It is added more preferably while an addition of a silver ion is in a range of 70 to 100% in forming a silver halide grain, or in desalination.

If the silver halide emulsion of the invention is prepared via a seed emulsion, the spectral sensitizing dye is not added in preparing the seed emulsion.

The spectral sensitizing dye is added to the emulsion preferably at pH of 4 to 10 besides adding in desalination, and more preferably at pH of 6 to 9. It is added preferably at pAg of 5 to 11.

Two or more of the spectral sensitizing dyes may be combinedly used. In this case, two or more spectral sensitizing dyes may be added either at once or independently and separately.

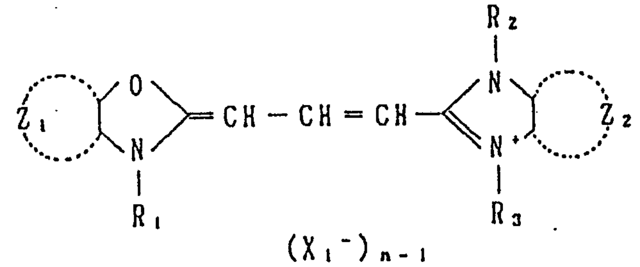
It may be added in proportion to a surface area of the growing silver halide grains.

An addition amount of the spectral sensitizing dye is 1 mg to 1 g, and preferably 5 to 500 mg per mol silver.

It is preferable to add potassium iodide prior to adding of the spectral sensitizing dye.

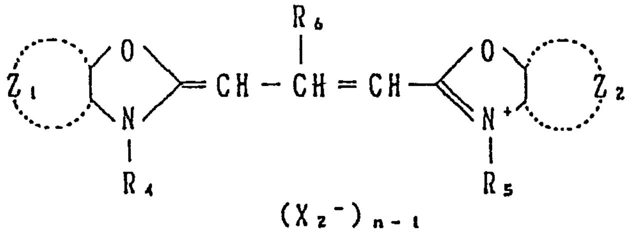
In the invention, at least one spectral sensitizing dye selected from the compounds represented by Formulas (II), (III) and (IV) is preferably added.

Formula (II)



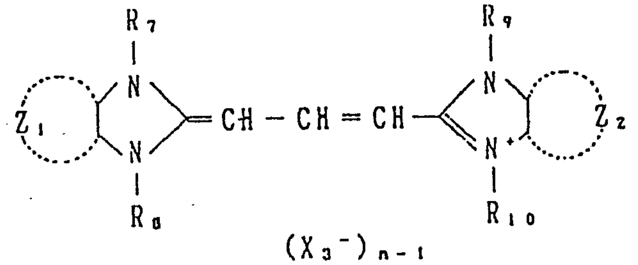
wherein R_1, R_2, and R_3 independently represent an alkyl group, an alkenyl group and an aryl group, provided that at least one of R_1 and R_3 is a sulfoalkyl or carboxyalkyl group; X_1^- represents an anion; Z_1 and Z_2 independently represent a non-metal atomic group needed for completing a carbon ring; n represents 1 or 2, provided that n is 1 when an intramolecular salt is formed.

Formula (III)



wherein R_4 and R_5 independently represent the same groups as those defined for R_1, R_2 and R_3 in Formula (II), provided that at least one of R_4 and R_5 is a sulfoalkyl or carboxyalkyl group; R_6 represents a hydrogen atom, a lower alkyl group, or an aryl group; X_2^- represents an anion; Z_1 and Z_2 independently represent the same as that defined for Z_1 and Z_2 in Formula (II); n represents 1 or 2, provided that n is 1 when an intramolecular salt is formed.

Formula (IV)



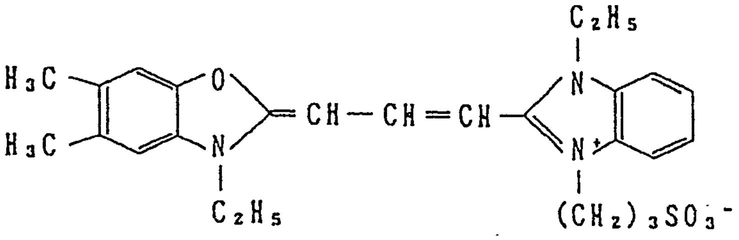
wherein R_7 and R_9 independently represent a lower alkyl group; R_8 and R_{10} independently represent a lower alkyl group, a hydroxyalkyl group, a sulfoalkyl group, or a carboxyalkyl group; X_3^- represents an anion; Z_1 and Z_2 independently represent the same as defined for Z_1 and Z_2 in Formula (II); n represents 1 or 2, provided that n is 1 when an intramolecular salt is formed.

In the above formulas, the carbon ring formed by each of Z_1 and Z_2 is preferably an aromatic ring such as a benzene and naphthalene ring;

the alkyl group includes a lower alkyl group such as methyl, ethyl, n-propyl and butyl groups; the substituted alkyl group includes a vinylmethyl group; the hydroxyalkyl group includes 2-hydroxyethyl and 4-hydroxybutyl; the carboxyalkyl group includes 2-carboxyethyl, 3-carboxypropyl and 2-(2-carboxyethoxy)ethyl; the sulfoalkyl group includes 2-sulfoethyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, and 2-hydroxy-3-sulfopropyl; the alkenyl group includes allyl, butynyl, octenyl and oleyl; the aryl group includes phenyl and carboxyphenyl; the anion represented by X_1, X_2 and X_3 includes a chlorine ion, a bromine ion, an iodine ion, a thiocyan III ion, a sulfate ion, a perchlorate ion, a p-toluenesulfonate ion, and an ethylsulfate ion.

The examples of a compound represented by Formula (II) are listed below.

1



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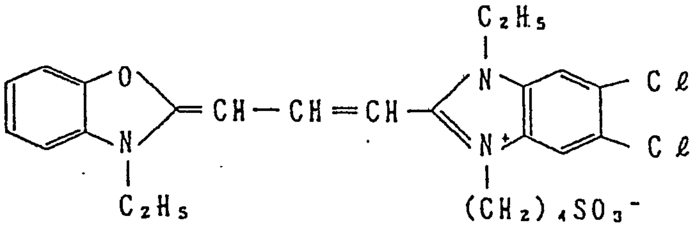

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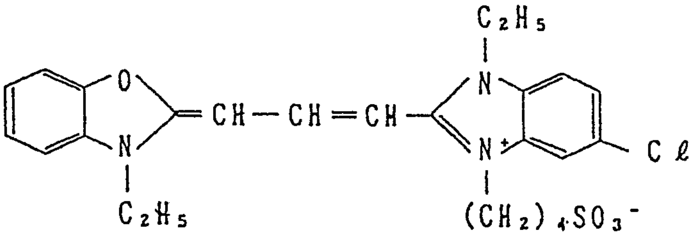

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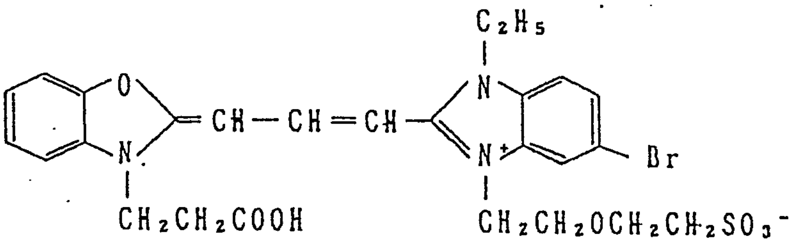

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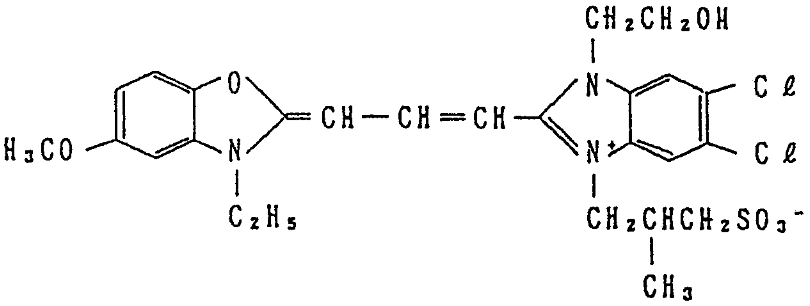

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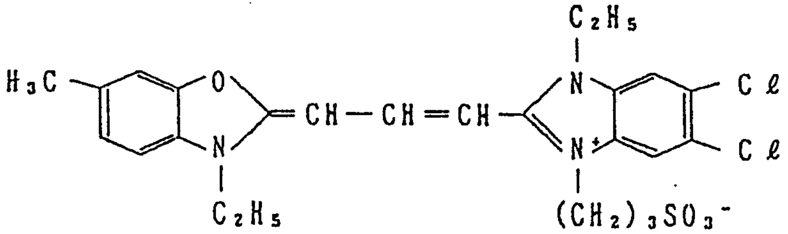

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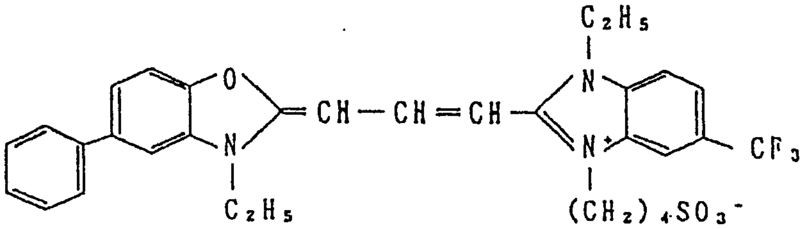

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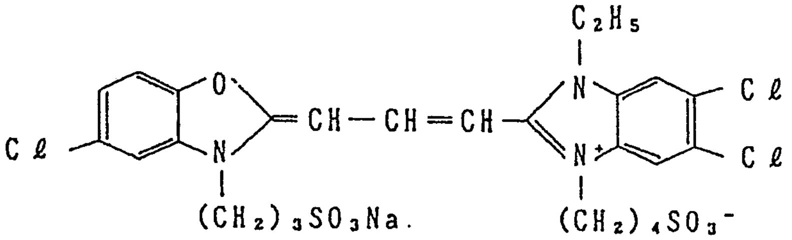

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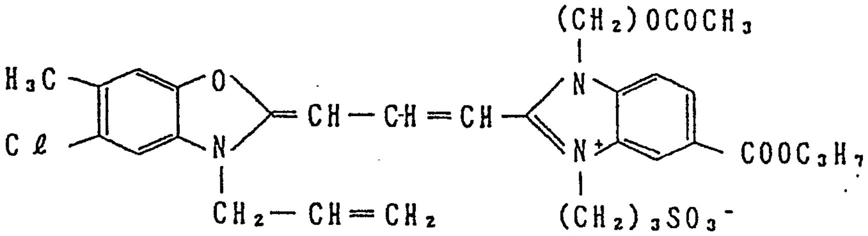

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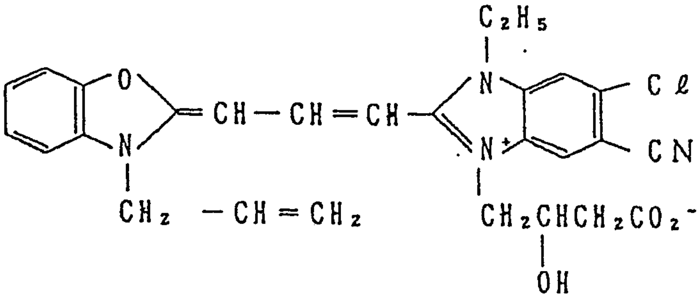

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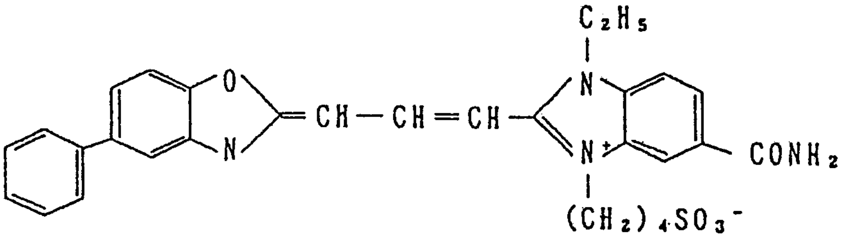

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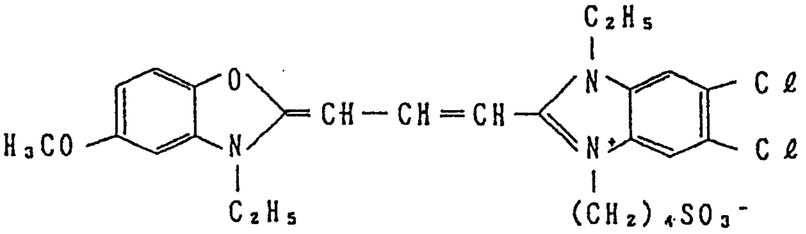

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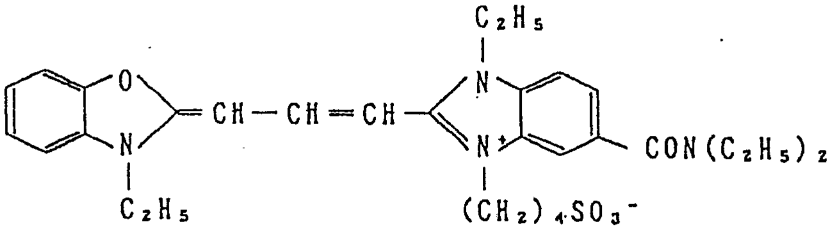

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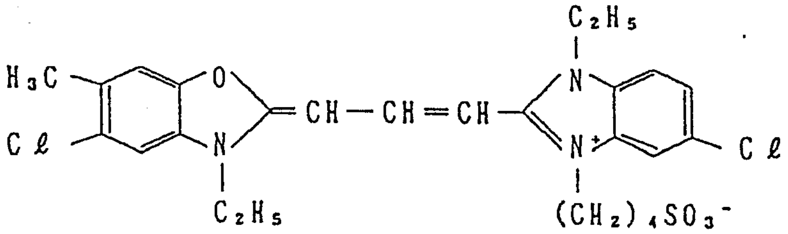

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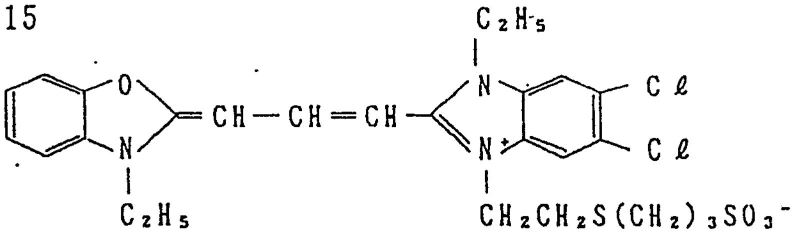

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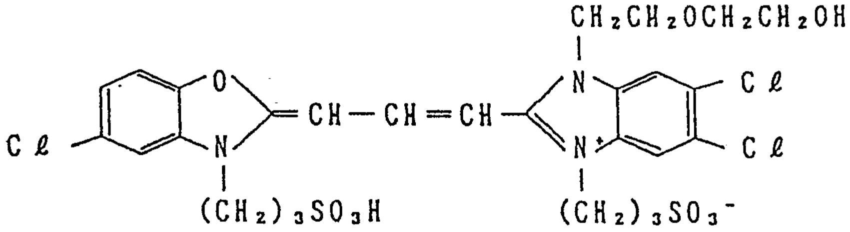

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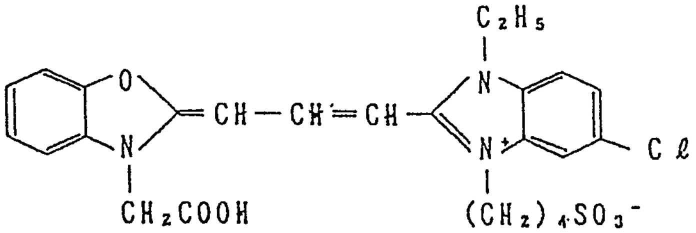

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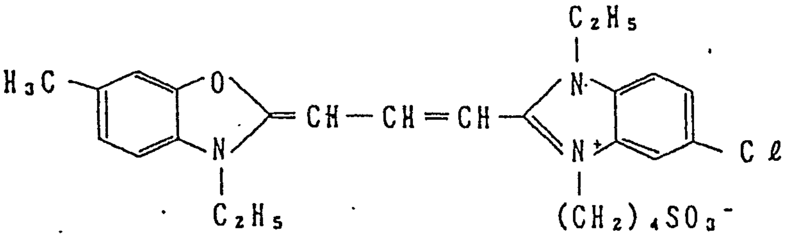

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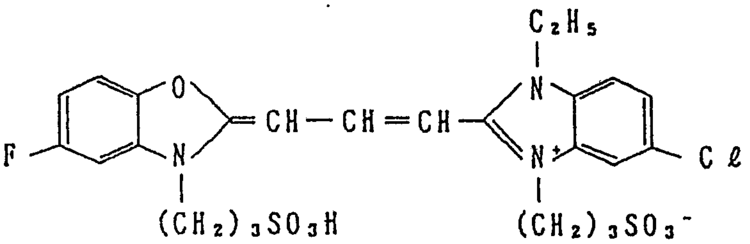
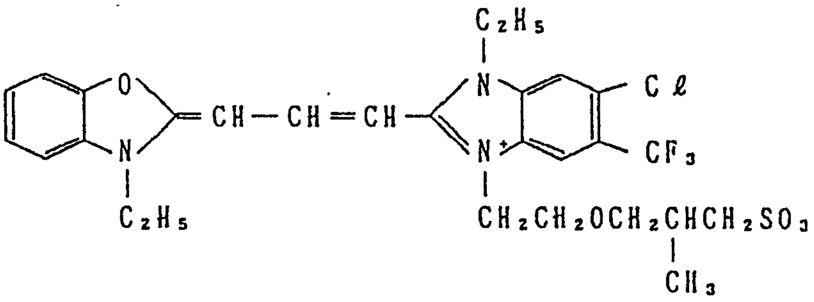
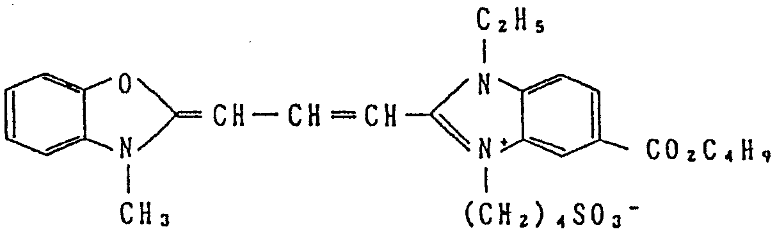

C₂H₅
O
N
N⁺
F
Cℓ
CH — CH = CH
(CH₂)₃SO₃H
(CH₂)₃SO₃⁻

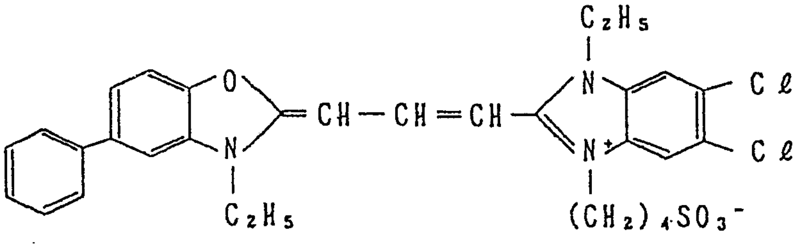
20


C₂H₅
O
N
N⁺
Cℓ
CF₃
CH — CH = CH
C₂H₅
CH₂CH₂OCH₂CHCH₂SO₃
CH₃

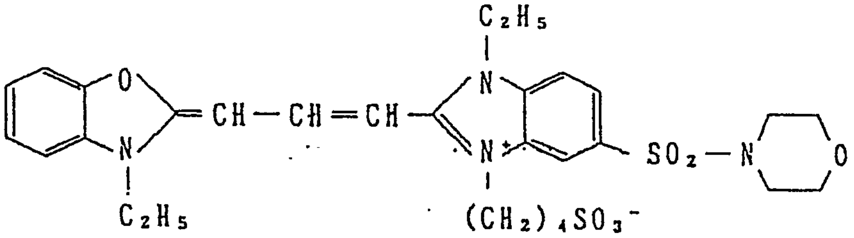
21.


C₂H₅
O
N
N⁺
CO₂C₄H₉
CH — CH = CH
CH₃
(CH₂)₄SO₃⁻

22


C₂H₅
O
N
N⁺
Cℓ
Cℓ
CH — CH = CH
C₂H₅
(CH₂)₄SO₃⁻

23



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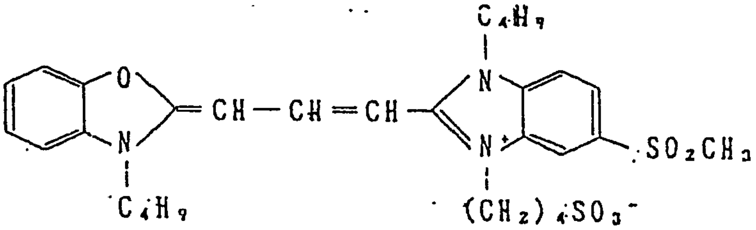

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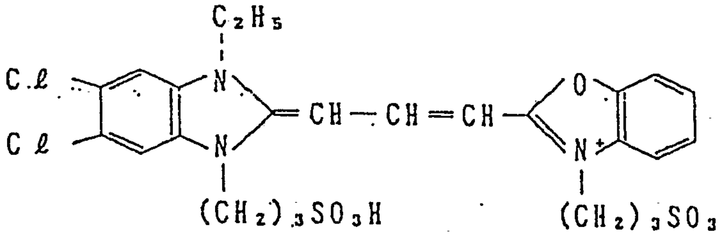

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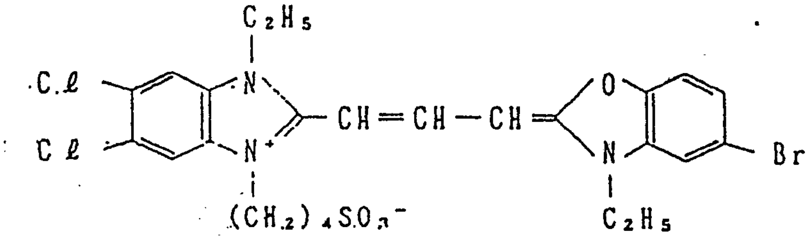

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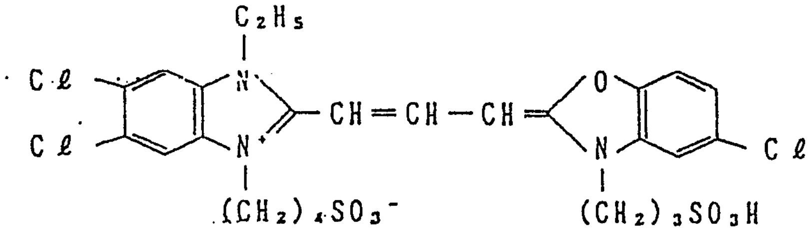

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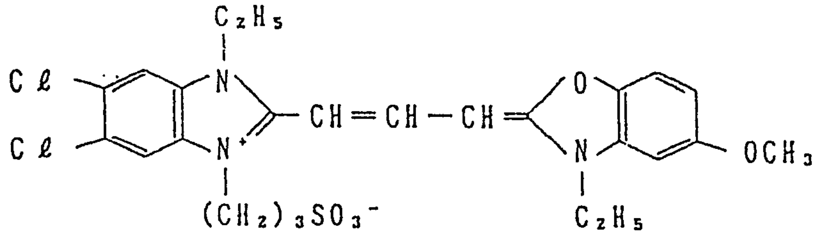

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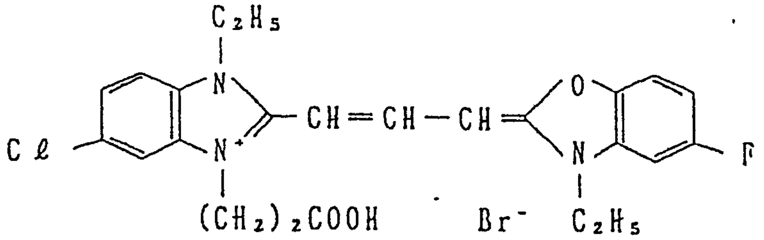

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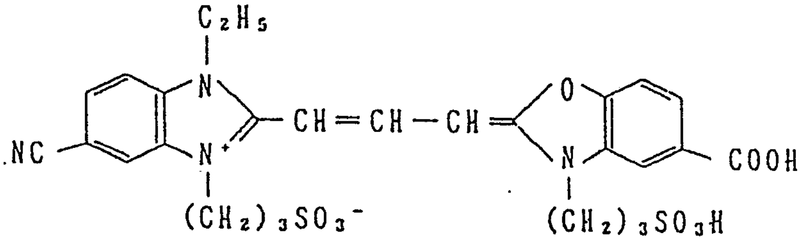

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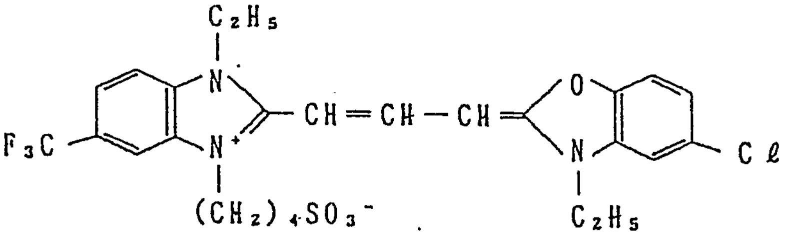

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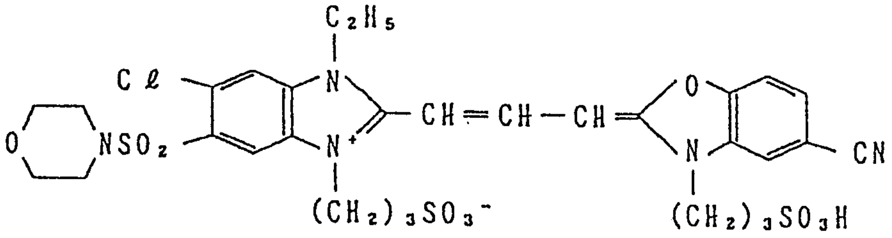

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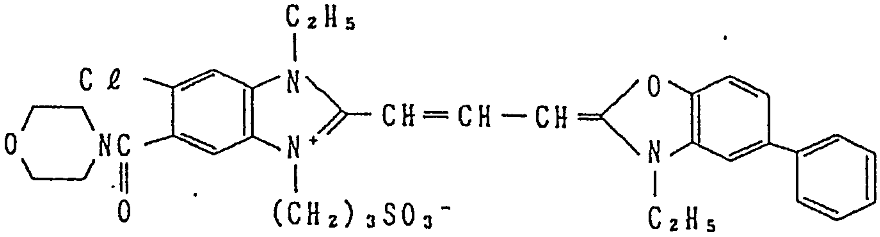

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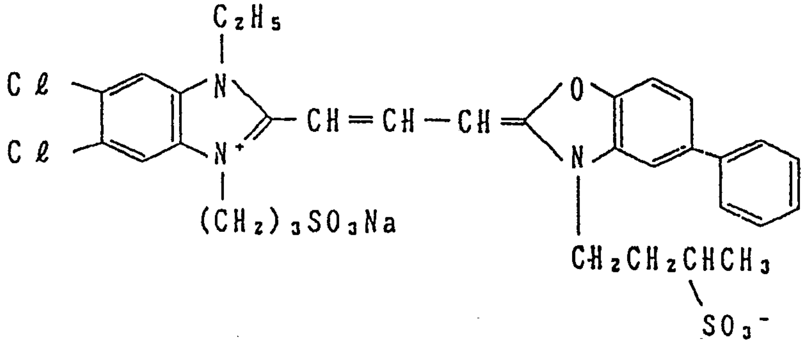
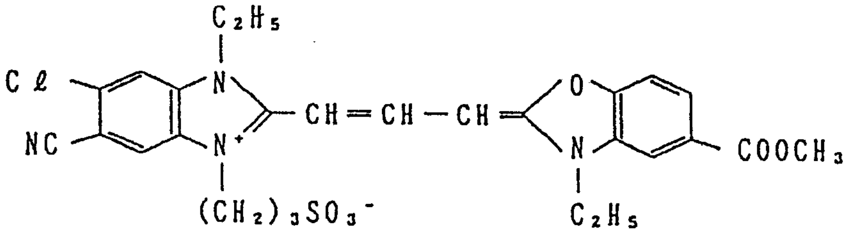
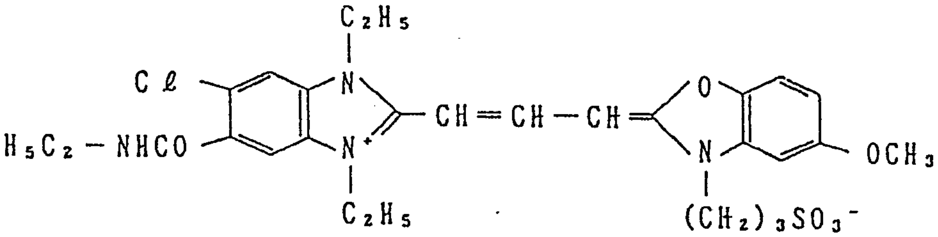

C₂H₅
Cℓ
Cℓ
N
N⁺
(CH₂)₃SO₃Na
CH=CH—CH=
O
N
CH₂CH₂CHCH₃
SO₃⁻

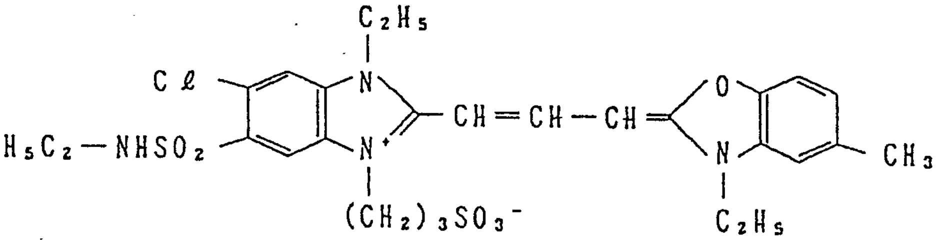
35


C₂H₅
Cℓ
NC
N
N⁺
(CH₂)₃SO₃⁻
CH=CH—CH=
O
N
COOCH₃
C₂H₅

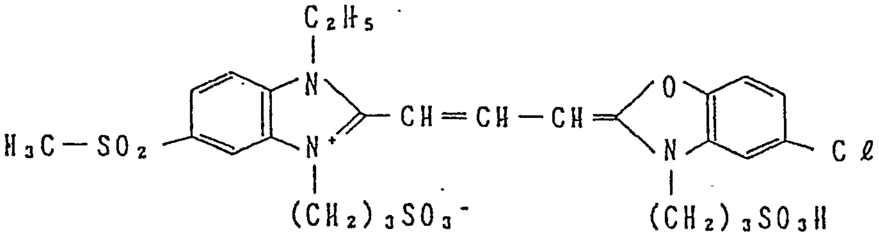
36


C₂H₅
Cℓ
H₅C₂—NHCO
N
N⁺
C₂H₅
CH=CH—CH=
O
N
OCH₃
(CH₂)₃SO₃⁻

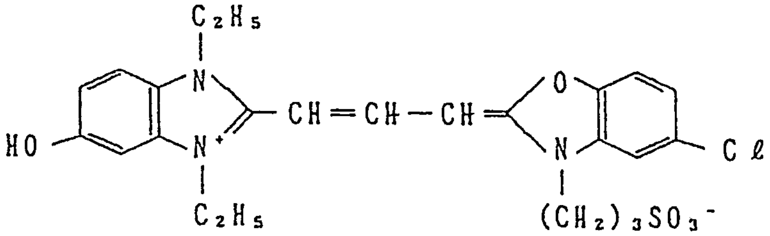
37


C₂H₅
Cℓ
H₅C₂—NHSO₂
N
N⁺
(CH₂)₃SO₃⁻
CH=CH—CH=
O
N
CH₃
C₂H₅

38



39



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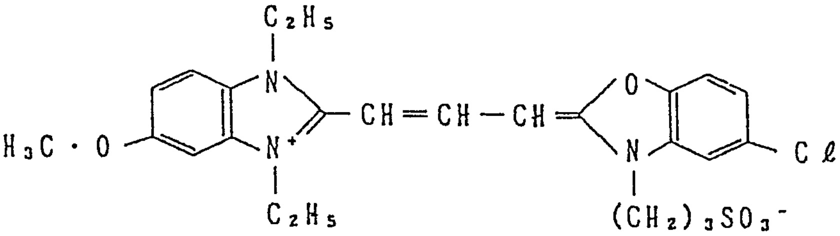
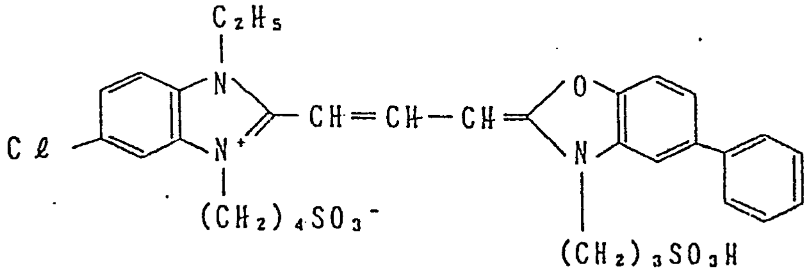
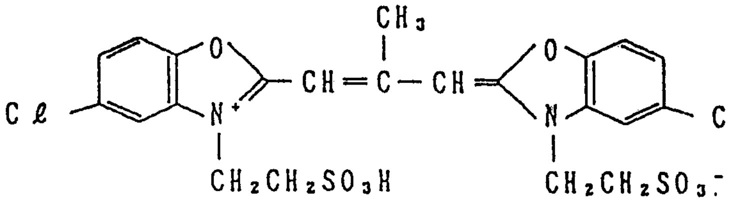


41

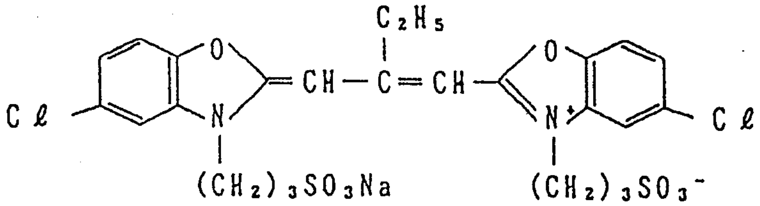


The examples of a compound represented by Formula (II) are listed below.

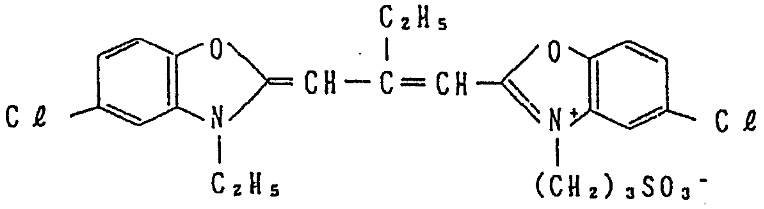
42



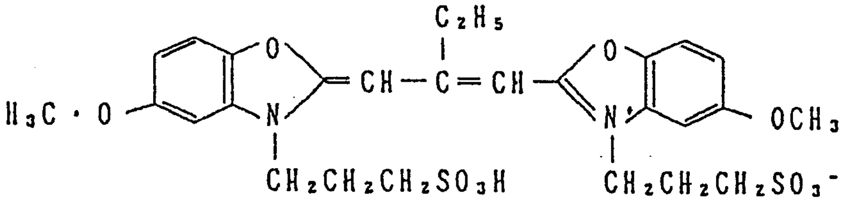
43



44



45



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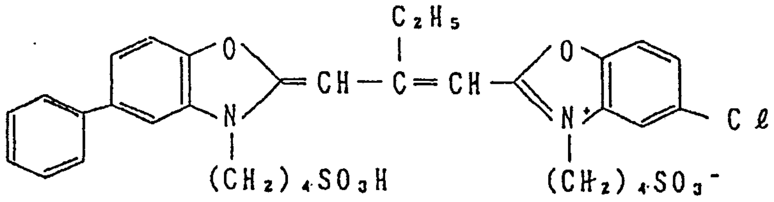

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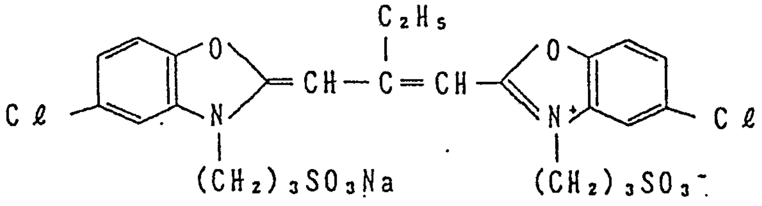

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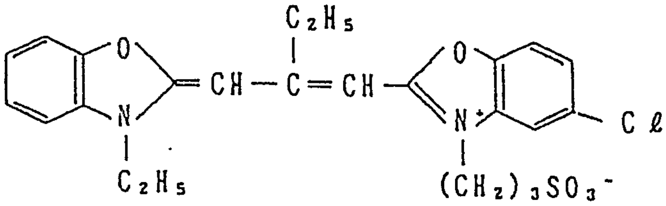

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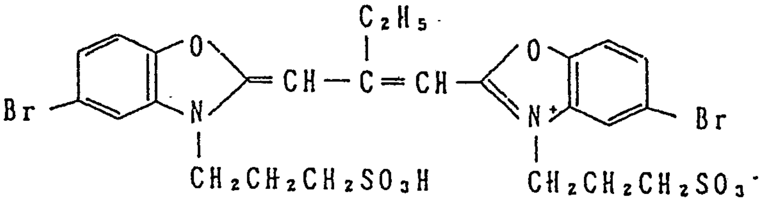

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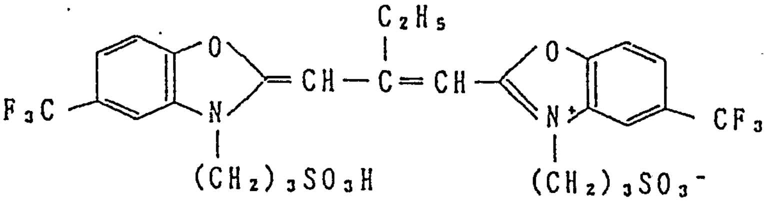

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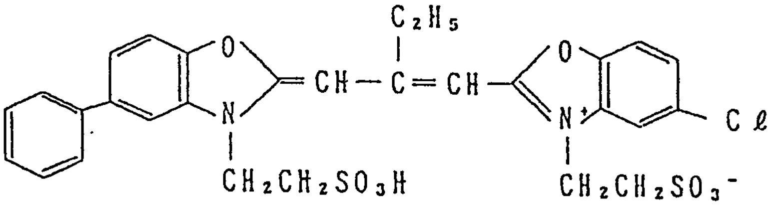
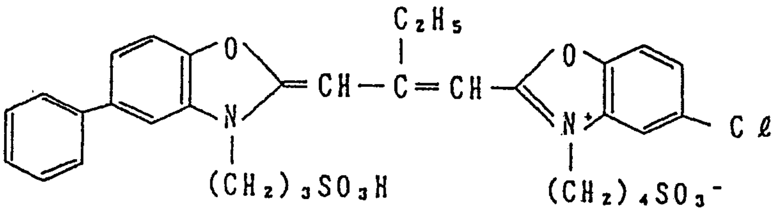
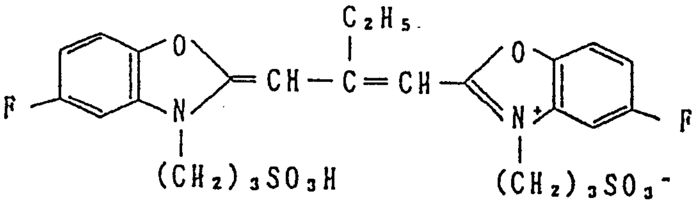


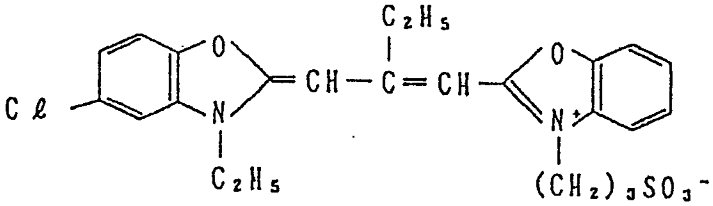
52


C2H5
O
CH
C
CH
O
N
N+
Cℓ
(CH2)3SO3H
(CH2)4SO3-

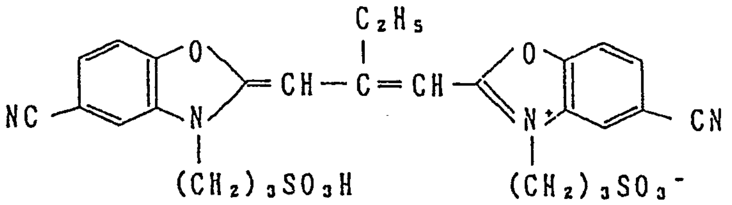
53


C2H5
O
CH
C
CH
O
F
N
N+
F
(CH2)3SO3H
(CH2)3SO3-

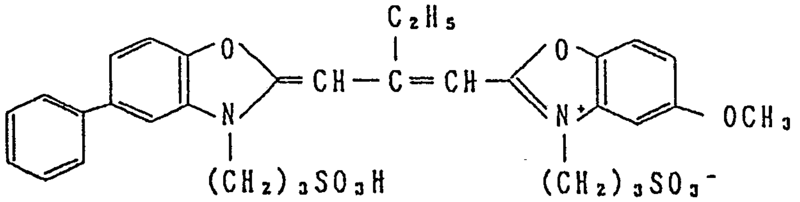
54.


C2H5
O
CH
C
CH
O
Cℓ
N
N+
C2H5
(CH2)3SO3-

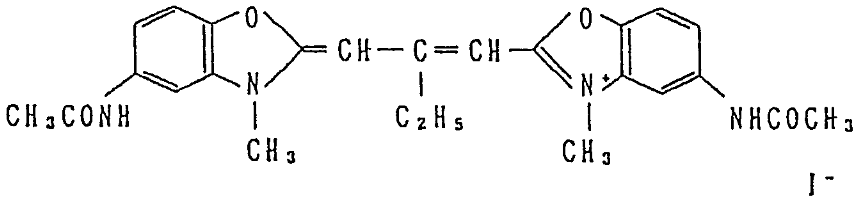
55


C₂H₅
O
CH—C=CH
NC
N
(CH₂)₃SO₃H
O
N⁺
CN
(CH₂)₃SO₃⁻

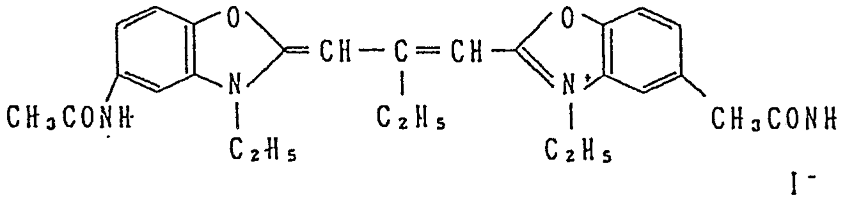
56


C₂H₅
O
CH—C=CH
N
(CH₂)₃SO₃H
O
N⁺
OCH₃
(CH₂)₃SO₃⁻

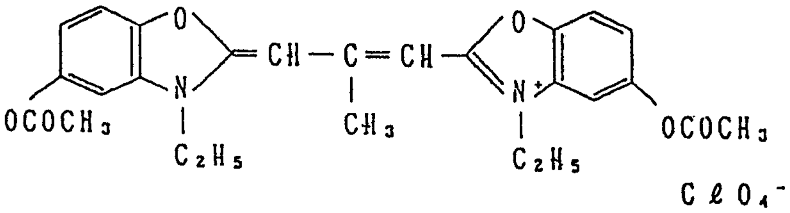
57.


O
CH—C=CH
CH₃CONH
N
CH₃
C₂H₅
O
N⁺
NHCOCH₃
CH₃
I⁻

58


O
CH—C=CH
CH₃CONH
N
C₂H₅
C₂H₅
O
N⁺
CH₃CONH
C₂H₅
I⁻

59



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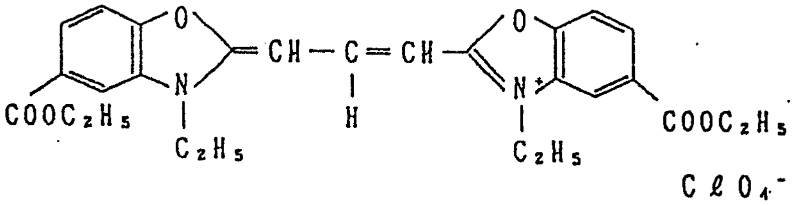

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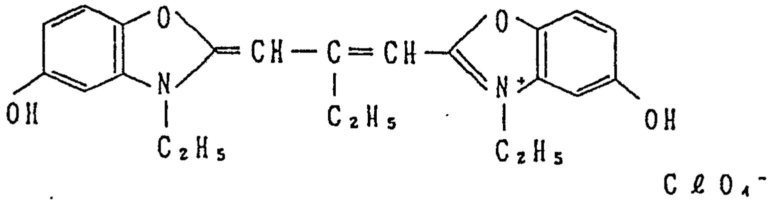

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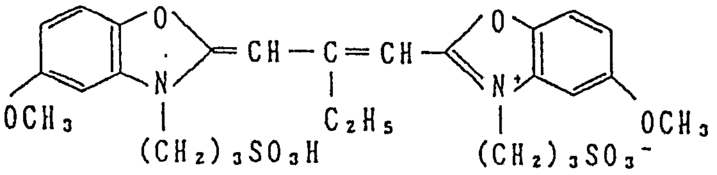

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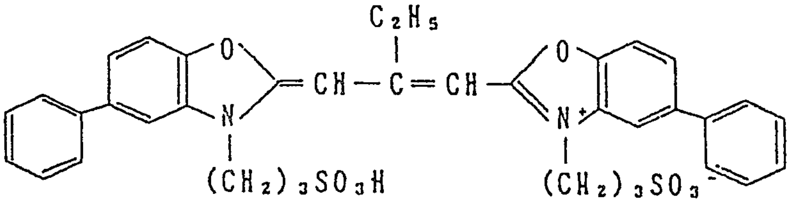

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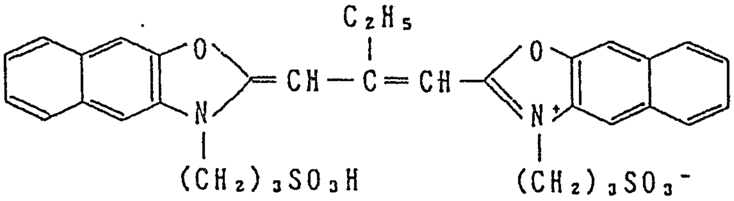

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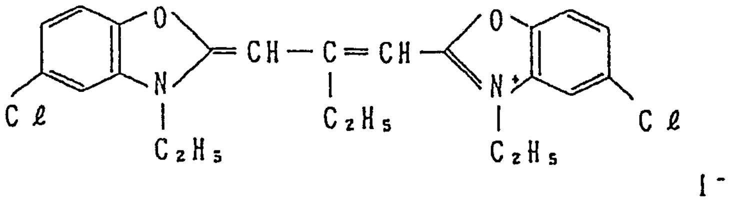
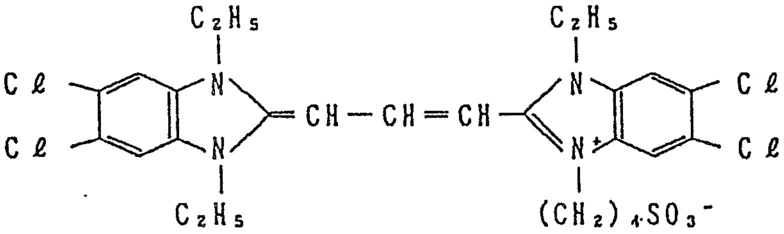
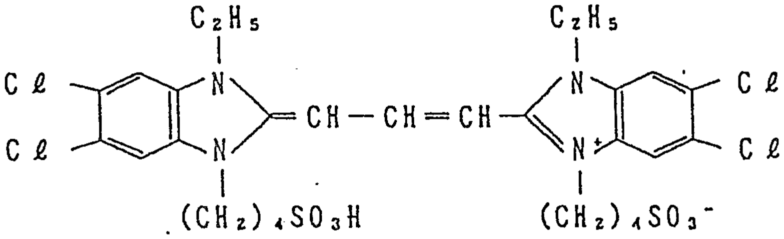


The examples of a compound represented by Formula (IV) are listed below.

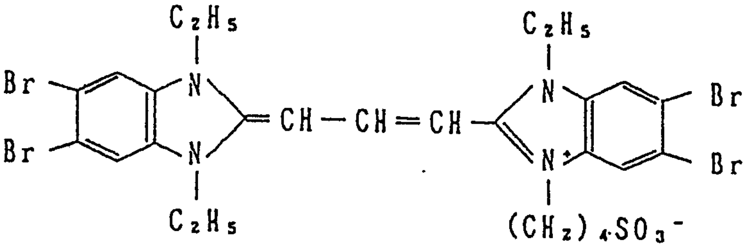
66



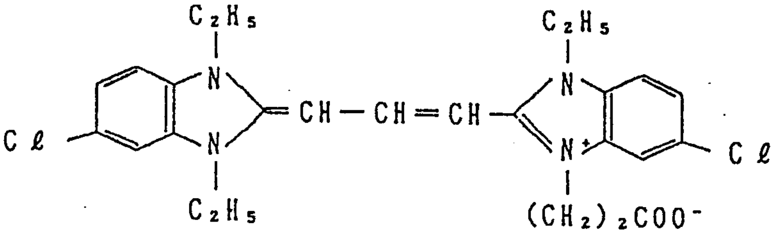
67



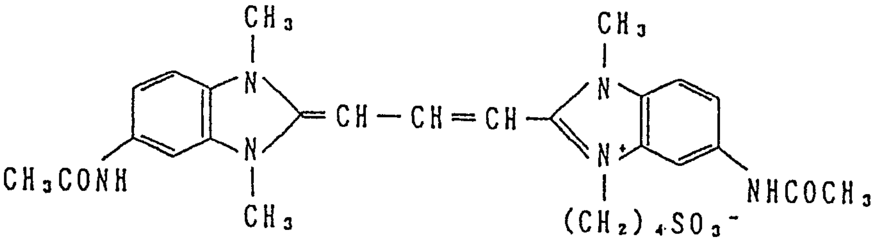
68



69



70



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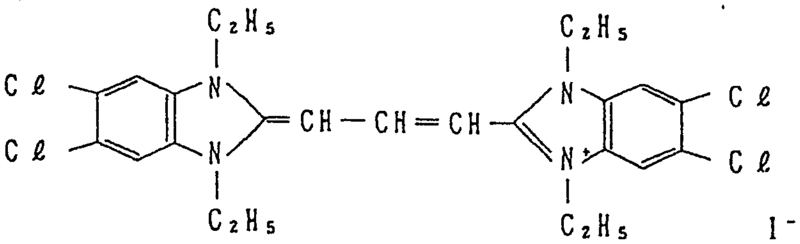
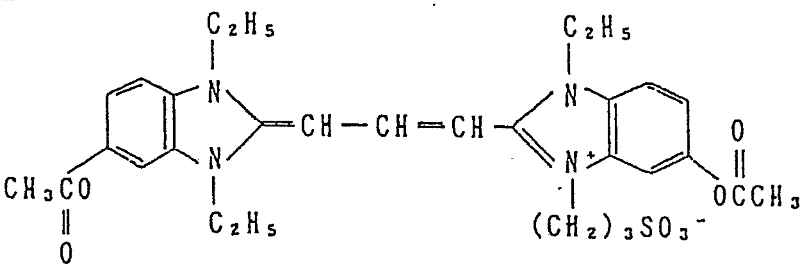
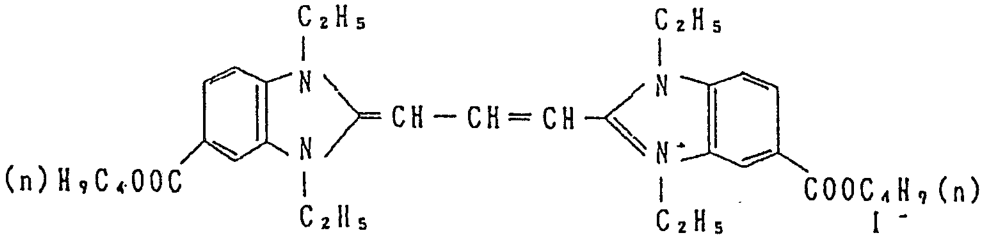


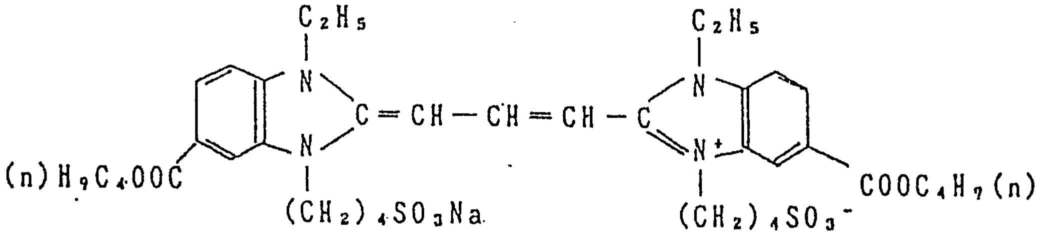
72



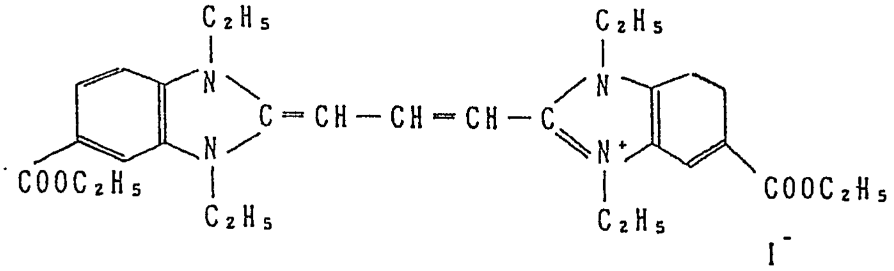
73



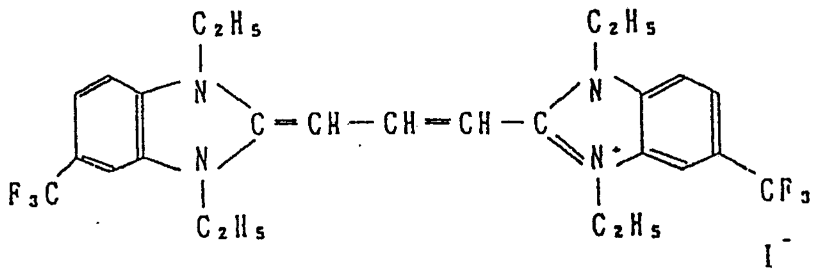
74



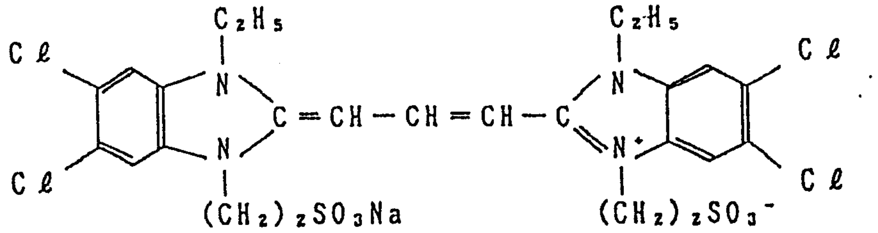
75



76

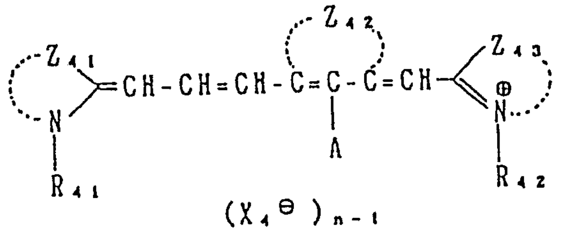


77



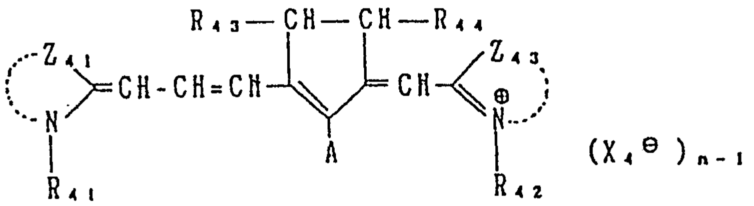
Further, in the invention, at least one selected from the compounds represented by Formula (V) is added preferably as a spectral sensitizing dye.

Formula (V)

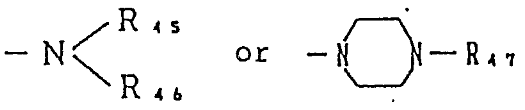


wherein Z_{41} and Z_{43} independently represent a non-metal atom group necessary for forming a benzothiazole, benzoxazole, naphtothiazole, and naphthooxazole nucleus each allowed to have a substituent including a halogen atom, an alkyl group having 1 to 4 carbon atoms, and an alkoxy group having 1 to 4 carbon atoms; R_{41} and R_{42} independently represent a saturated or unsaturated aliphatic group such as methyl, 2-hydroxyethy, 2-methoxyethyl, carboxymethyl, 2-sulfoethyl, 3-sulfopropyl, vinylmethyl, benzyl, phenethyl, and p-sulfophenethyl; Z_{42} represents a five- or six-membered carbon ring; if Z_{42} is a six-membered ring, A represents a hydrogen atom; if Z_{42} is a five-membered ring, Formula (V) is represented by Formula (V-a) below.

Formula (V-a)



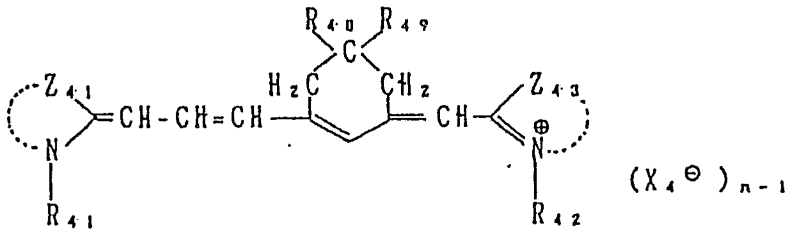
wherein A represents



; R_{43} and R_{44} represent independently a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a halogen atom, and an alkoxy group having 1 to 4 carbon atoms; R_{45} and R_{46} represent independently an alkyl group having 1 to 12 carbon atoms, an alkoxycarbonyl-alkyl group, and an aryl group; R_{47} represents an alkyl group having 1 to 12 carbon atoms, an aryl group having 6 to 10 carbon atoms, or an alkoxycarbonyl group with an alkoxy group having 1 to 4 carbon atoms.

Formula (V) is represented by following Formula (V-b), provided that Z_{42} is a six-membered ring;

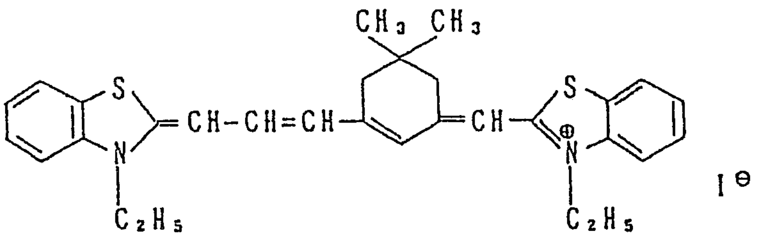
Formula (V-b)



wherein R_{48} represents a hydrogen atom or a methyl group; R_{49} represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, or an aryl group having a single ring; $X_4^{\ominus}$ represents an anion such as a chloride ion, a perchlorate ion, a benzenesulfonate ion, a p-toluenesulfonate ion, a methylsulfate ion, an ethylsulfate ion, and a tetrafluoroborate ion; n represents 1 or 2, provided that n is 1 when an intramolecular salt is formed.

The examples of a compound represented by Formula (V) are listed below.

78



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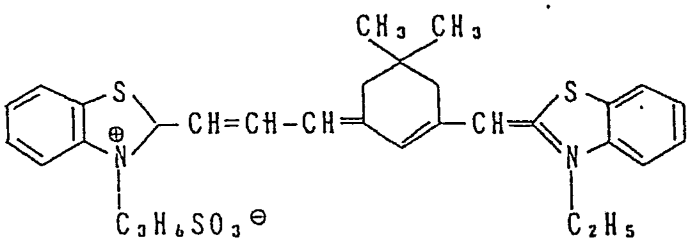
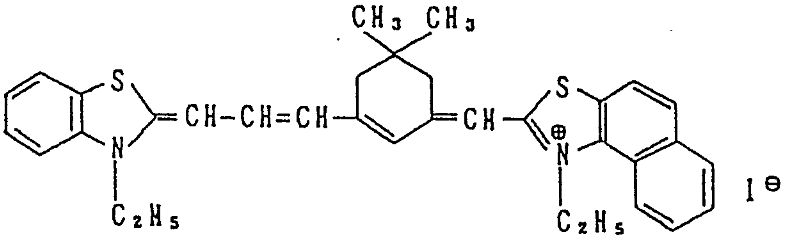
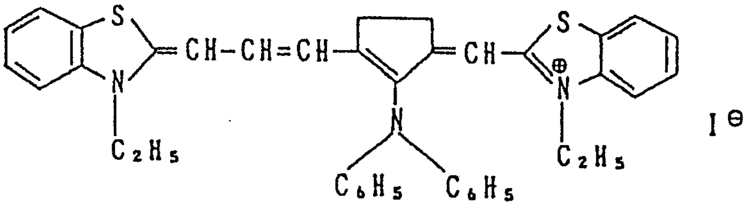


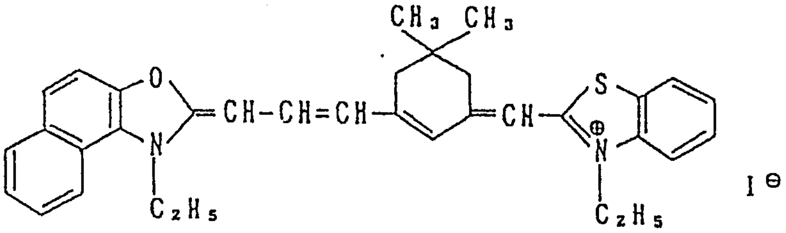
80


CH₃ CH₃
S
CH-CH=CH
CH
N
C₂H₅
I⊖

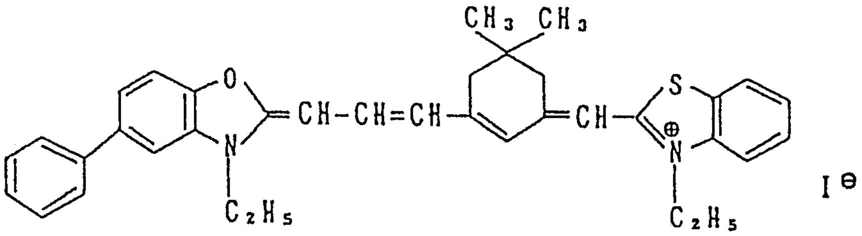
81


S
CH-CH=CH
CH
N
C₂H₅
C₆H₅
I⊖

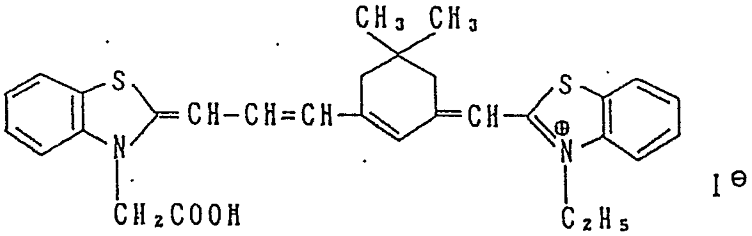
82


CH₃ CH₃
O
S
CH-CH=CH
CH
N
C₂H₅
I⊖

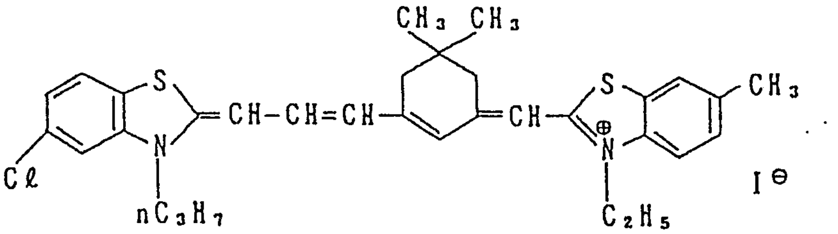
83


CH₃ CH₃
O
S
CH-CH=CH
CH
N
C₂H₅
I⊖

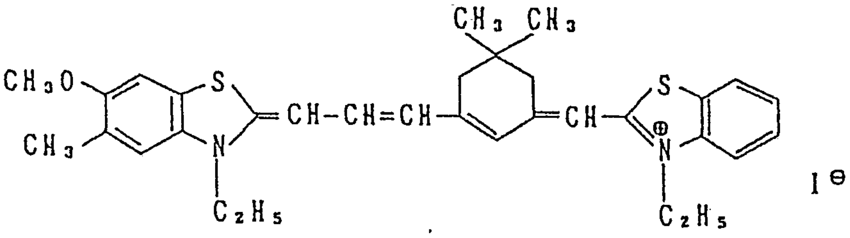
84


CH3 CH3
S
CH-CH=CH
CH
S
N
N⊕
CH2COOH
C2H5
I⊖

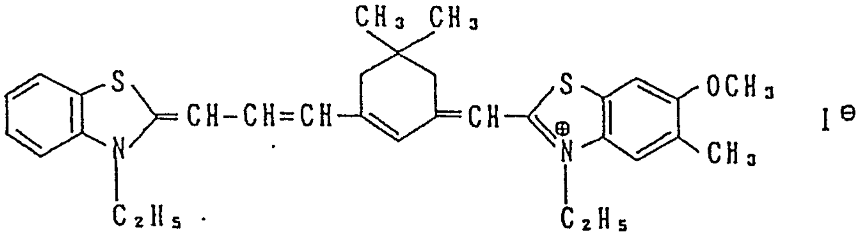
85


CH3 CH3
S
CH-CH=CH
CH
S
CH3
N
N⊕
Cl
nC3H7
C2H5
I⊖

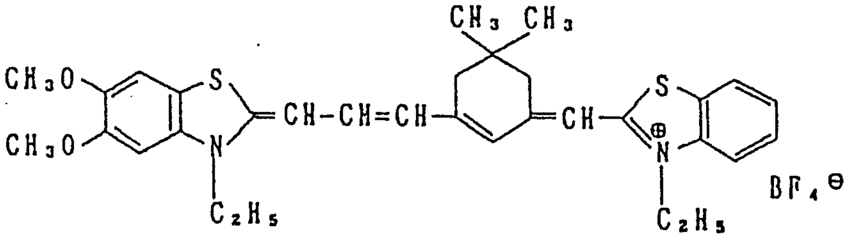
86


CH3 CH3
CH3O
CH3
S
CH-CH=CH
CH
S
N
N⊕
C2H5
C2H5
I⊖

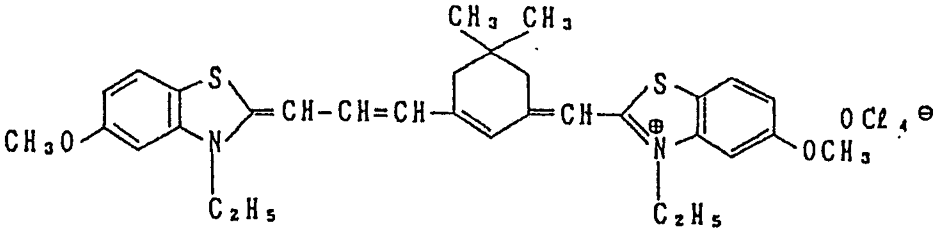
87


CH3 CH3
S
CH-CH=CH
CH
S
OCH3
CH3
N
N⊕
C2H5
C2H5
I⊖

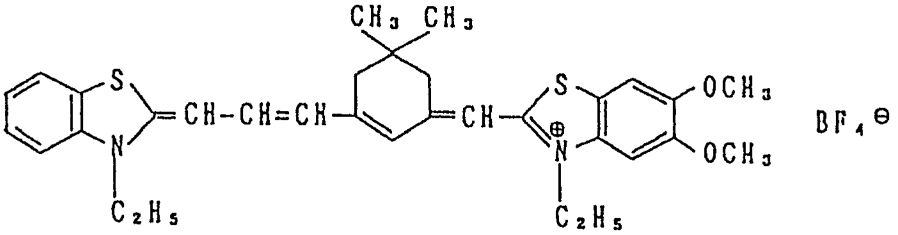
88


CH₃ CH₃
CH₃O
CH₃O
S
N
C₂H₅
CH-CH=CH
CH
S
N⊕
C₂H₅
BF₄⊖

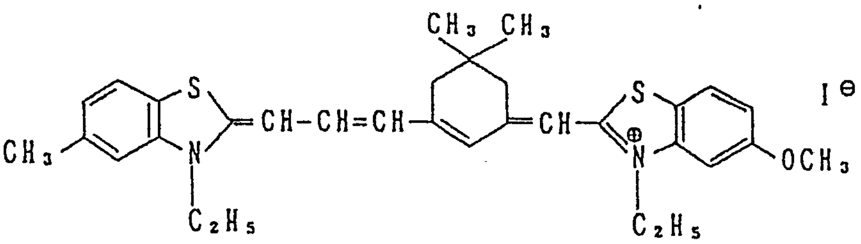
89


CH₃ CH₃
CH₃O
S
N
C₂H₅
CH-CH=CH
CH
S
N⊕
C₂H₅
OCH₃
OCℓ₄⊖

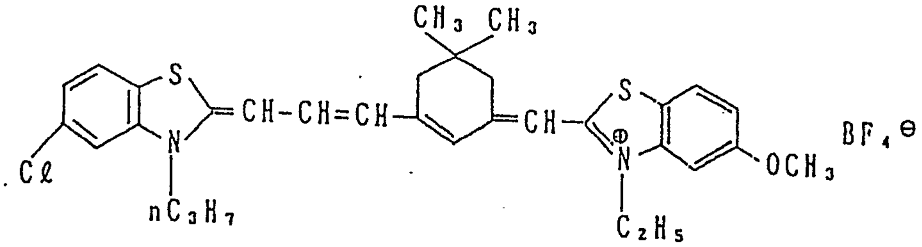
90


CH₃ CH₃
S
N
C₂H₅
CH-CH=CH
CH
S
N⊕
C₂H₅
OCH₃
OCH₃
BF₄⊖

91


CH₃ CH₃
CH₃
S
N
C₂H₅
CH-CH=CH
CH
S
N⊕
C₂H₅
OCH₃
I⊖

92



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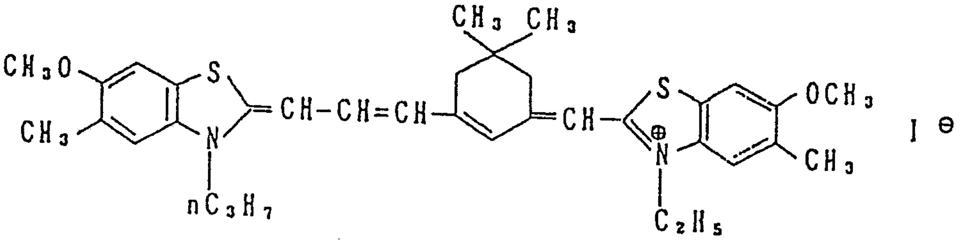

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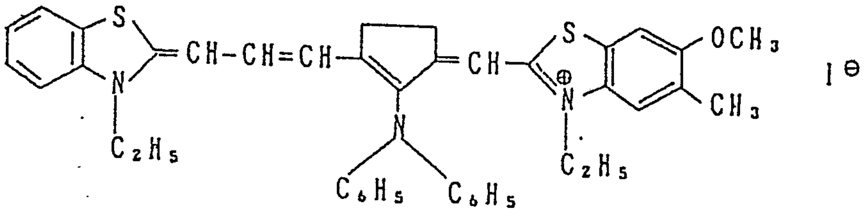

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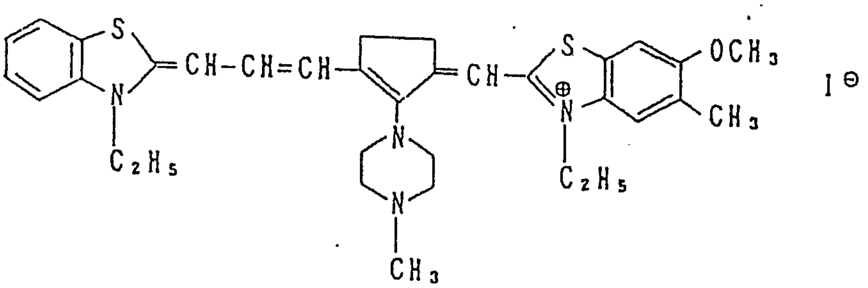

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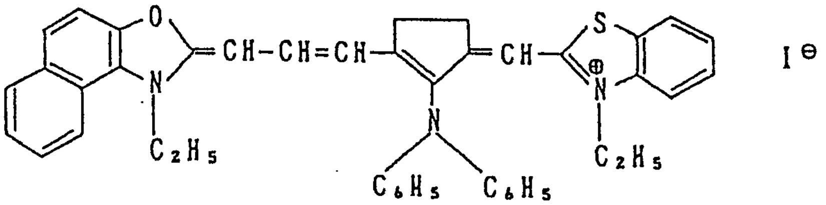

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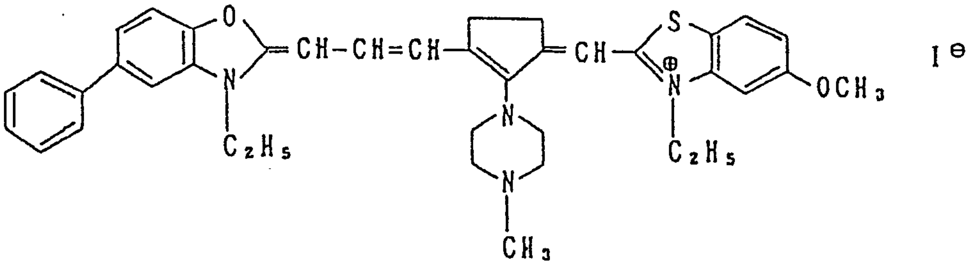

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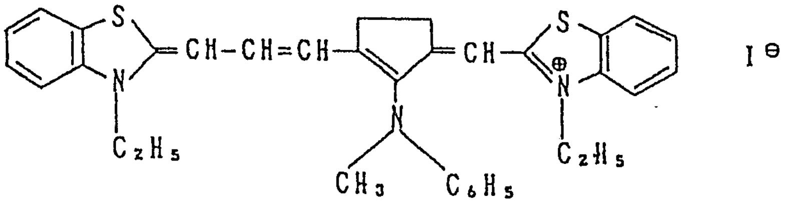

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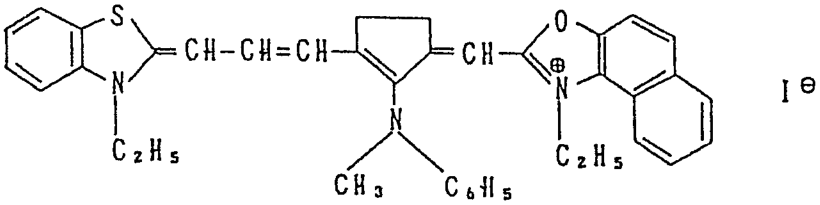

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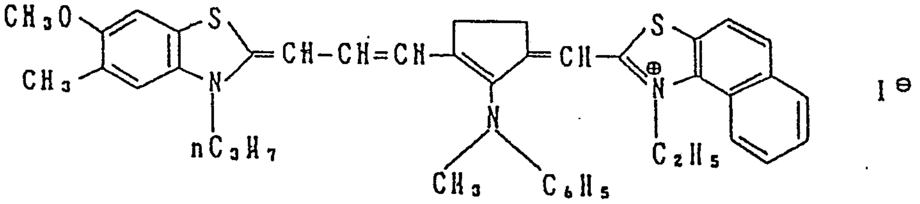

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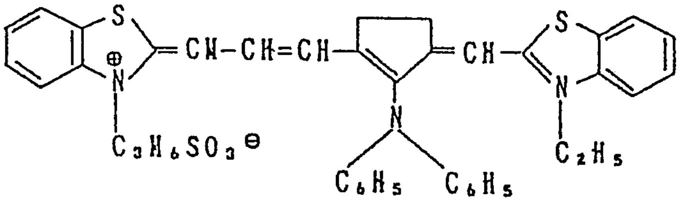

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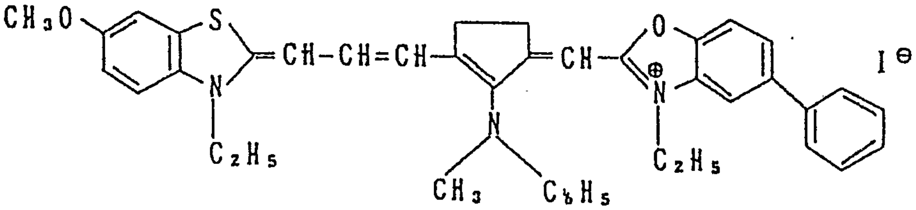

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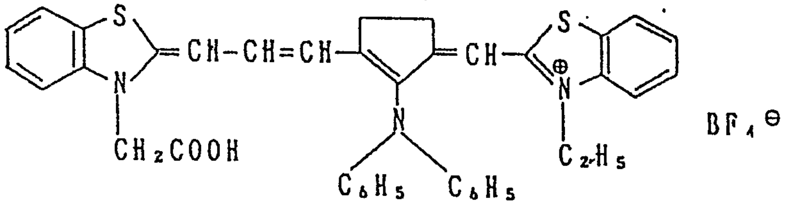

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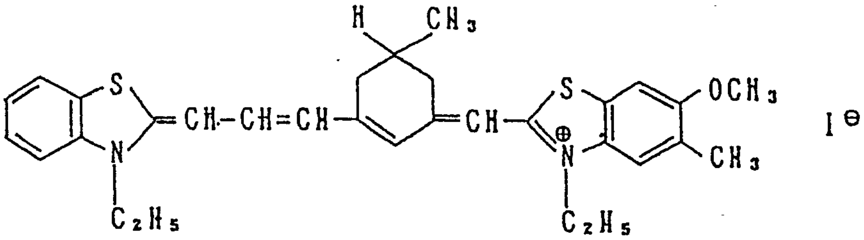

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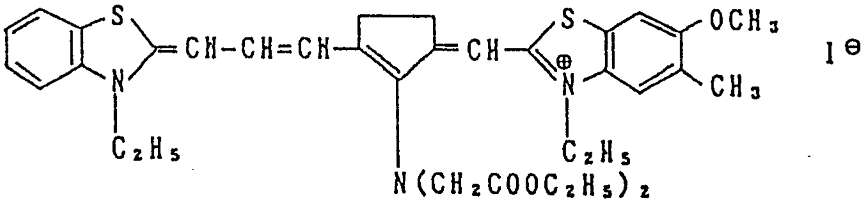

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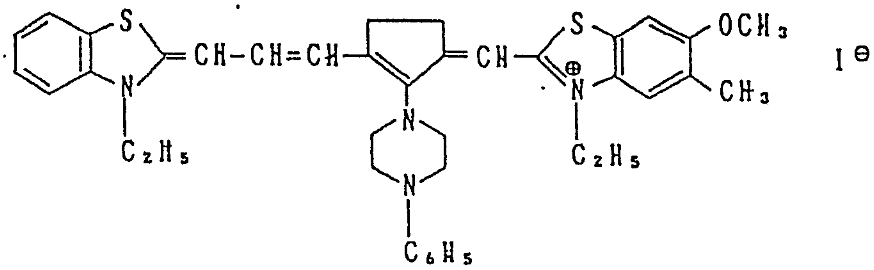

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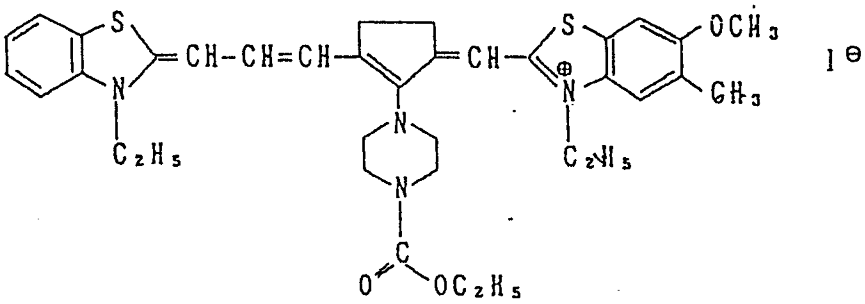

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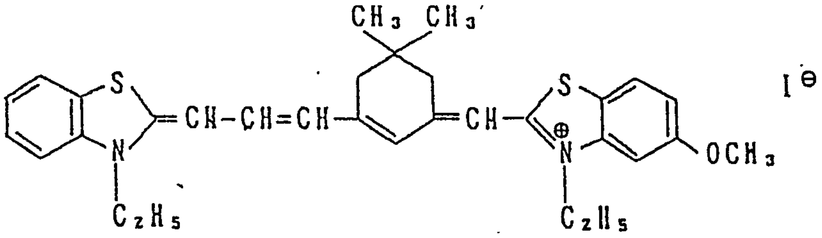

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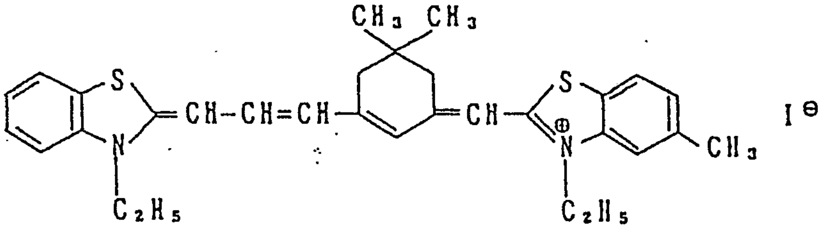

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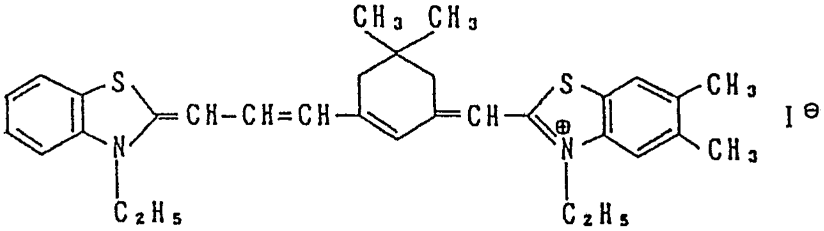

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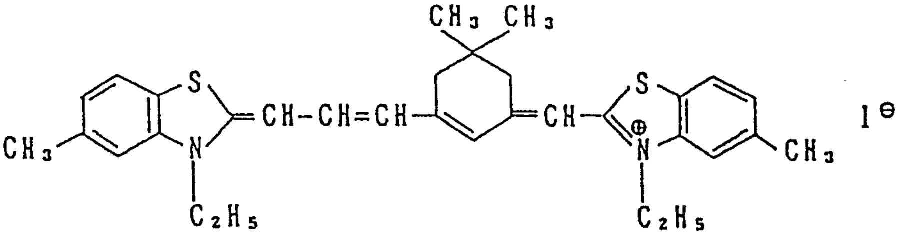

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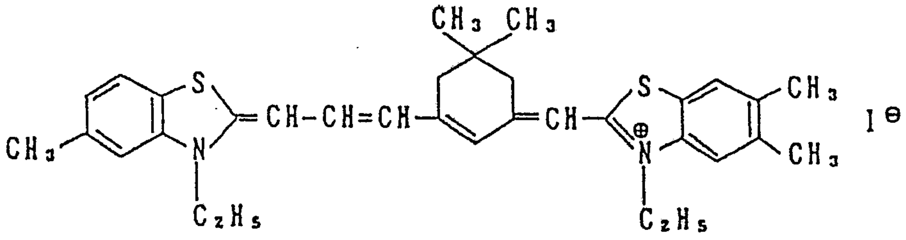
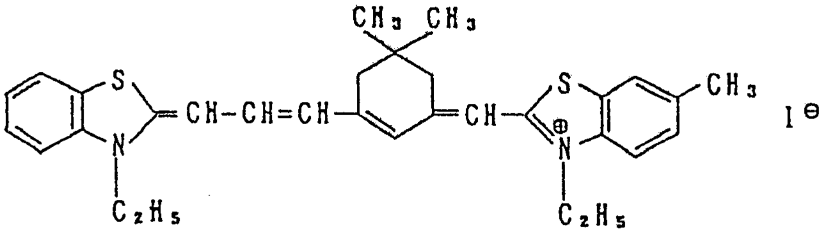


113



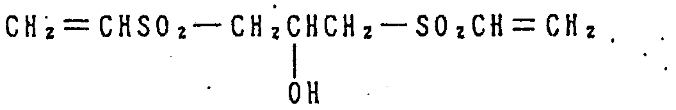
In the silver halide photographic light-sensitive material of the invention, at least one of the hydrophilic colloid layers is hardened with a vinylsulfone type hardener.

A layer hardened with the vinylsulfone type hardener is arbitrarily selected; it may be a silver halide emulsion layer, or another hydrophilic colloid layers such as a protective layer, an intermediate layer and a subbing layer. A protective layer is hardened preferably with the vinylsulfone hardener.

The examples of the vinylsulfone hardener used in the invention include an aromatic compound disclosed in West German Patent No. 1,100,942; an alkyl compound having a hetero-atom bond disclosed in Japanese Patent Examined Publication Nos. 29622/1969 and 25373/1972; sulfonamide and sulfonate disclosed in Japanese Patent Examined Publication No. 8736/1972; 1,3,5-tris[β-(vinylsulfonyl)-propionyl]-hexahydro-s-triazine disclosed in Japanese Patent O.P.I. Publication No. 24435/1974; and an alkyl compound disclosed in Japanese Patent O.P.I. Publication No. 44164/1976.

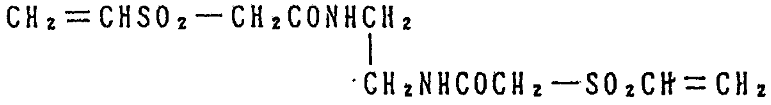
The examples of the vinylsulfone hardener are listed below.

H - 1



$CH_2{=}CHSO_2{-}CH_2CH(OH)CH_2{-}SO_2CH{=}CH_2$

H - 2



$CH_2{=}CHSO_2{-}CH_2CONHCH_2CH_2NHCOCH_2{-}SO_2CH{=}CH_2$

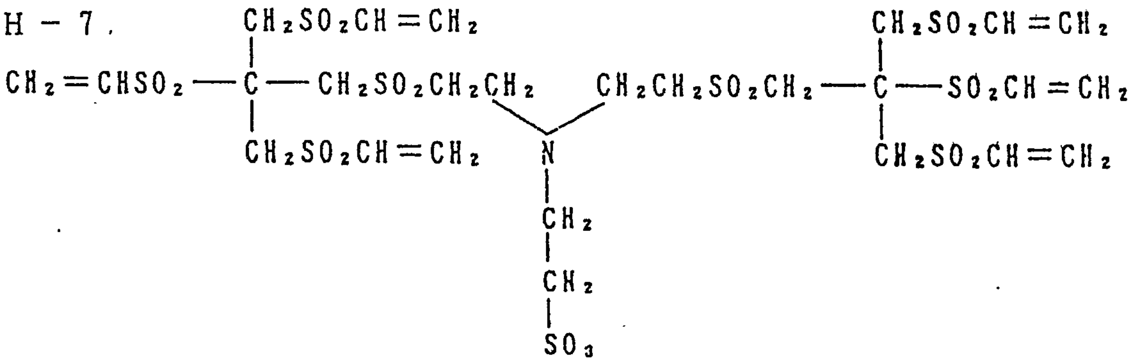
H - 3 $CH_2{=}CHSO_2{-}CH_2OCH_2{-}SO_2CH{=}CH_2$

H - 4 $CH_2{=}CHSO_2{-}(CH_2)_4O(CH_2)_4{-}SO_2CH{=}CH_2$

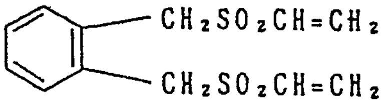
H - 5 $CH_2{=}CHSO_2{-}CH_2{-}CH_2{-}SO_2CH{=}CH_2$

H - 6 $(CH_2CHSO_2CH_2)_4C$

H - 7.



H - 8

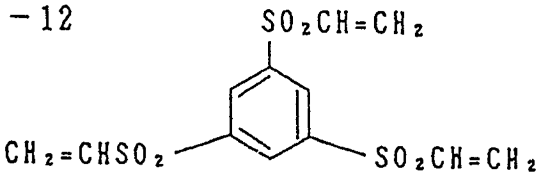


H - 9 $CO(CH_2CH_2SO_2CH{=}CH_2)_2$

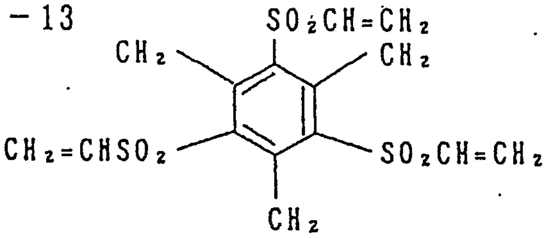
H - 10 $NH(CH_2CH_2SO_2CH{=}CH_2)_2$

H - 11

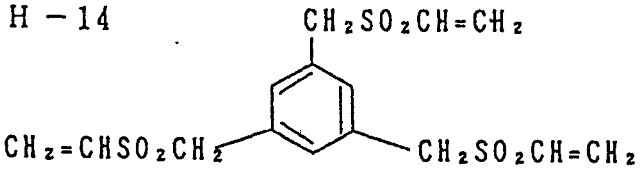
H - 12



H - 13



H - 14

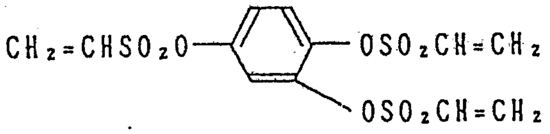


H - 15 $CH_3C(CH_2OCH_2SO_2CH{=}CH_2)_3$

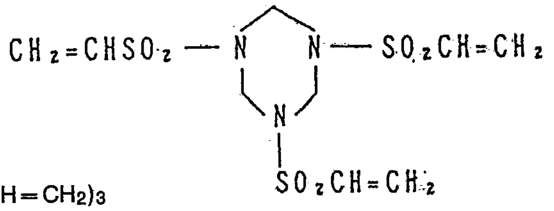
H - 16 $C(CH_2OCH_2SO_2CH{=}CH_2)_4$

H - 17 $N(CH_2CH_2OCH_2SO_2CH{=}CH_2)_3$

H - 18

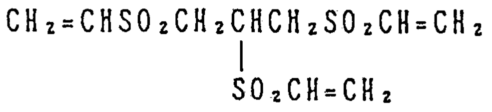


H - 19



H - 20 $C_2H_5C(CH_2SO_2CH=CH_2)_3$
H - 21 $C_8H_{17}C(CH_2SO_2CH=CH_2)_3$

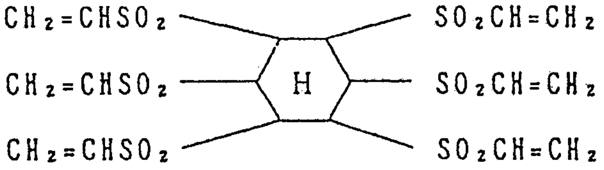
H - 22



$CH_2=CHSO_2CH_2\underset{SO_2CH=CH_2}{CH}CH_2SO_2CH=CH_2$

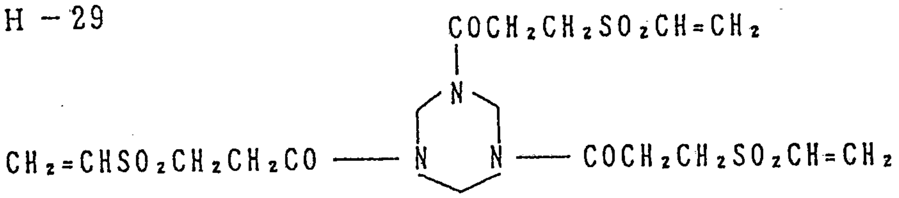
H - 23 $(CH_2=CHSO_2CH_2)_3CCH_2Br$
H - 24 $(CH_2=CHSO_2CH_2)_2CHCH(CH_2SO_2CH=CH_2)_2$
H- 25 $(CH_2=CHSO_2CH_2)_3CCH_2OCH_2C(CH_2SO_2CH=CH_2)_2$
H - 26 $C(CH_2SO_2CH=CH_2)_4$

H - 27



H - 28 $(CH_2=CHSO_2CH_2)_3CCH_2SO_2CH_2CH_2Cl$

H - 29



H - 30 $CH_2=CHSO_2(CH_2)_4SO_2CH=CH_2$

In addition to the above compounds, the vinylsulfone hardener useful in the invention includes a compound prepared by reacting the exemplified compounds having at least three vinylsulfone groups in a molecular structure, such as example compounds H-12 to H-29, with a compound having a hydrophilic group and a group capable of reacting with a vinylsulfone group, such as diethanolamine, thioglycolic acid, sodium methylglycinate, and sodium 2-aminoethanesulfonate.

A chemical sensitization includes a gold sensitization, a sensitization with a VIII family metal ion, a sulfur sensitization, a reduction sensitization, a sensitization with a thioether compound, and a combination thereof. The useful chemical sensitizers include a sulfur sensitizer such as sodium thiosulfate, allylthiocarbamide, thiourea, thiosulfate, and cystine; a noble metal sensitizer such as potassium chloroaurate, aurathiosulfate, and potassium chloropalladate; and a reduction sensitizer such as tin chloride and phenyl hydrazine.

Additionally, the emulsion of the invention and the other emulsions that constitutes the light-sensitive material of the invention may incorporate conventional additives such as a whitening agent, an anti-fogging agent, an UV absorbent, and a surfactant.

Besides a silver halide emulsion layer, the light-sensitive material of the invention may have a non-light-sensitive layer such as a protective layer, an intermediate layer and an antihalation layer.

The light-sensitive material of the invention is prepared by coating an emulsion with a conventional method on a conventional support such as a baryta paper, a polyethylene-coated paper, a polypropylene paper, a glass sheet and a cellulose acetate film, via a subbing layer and an intermediate layer.

The light-sensitive material of the invention can be used for black-and-white and color photograph, and for the various applications such as general purpose, printing and radiograph. Especially, it exhibits an optimum performance in a high-sensitivity light-sensitive material comprising silver bromoiodide.

Also, it works very well in a ultra-rapid processing, wherein total processing time necessary for transporting a film from an inlet of an automatic processor to an exit of a drying unit thereof (total length of processing line ÷ line velocity) is 20 to 60 seconds.

In the light-sensitive material of the invention, the excellent results can be achieved in processing time of 3 and a half minutes or less, and more excellent results in processing time of 90 seconds or less.

EXAMPLES

The present invention is hereunder described in detail with the examples. It should naturally be understood that the scope of the invention is not limited to these examples.

Example 1

According to Processes 1 through 6 below, a silver halide emulsion was prepared.

Process 1

A monodispersed seed emulsion containing silver bromoiodide grains having an average grain size of 0.3 µm and an iodide content of 2 mol% was prepared by a double jet method keeping a temperature at 60° C, pH and pAg at 60° C, 2 and 8, respectively. A twinned crystal of not more than 1% by number was observed therein with an electronmicroscope.

The above seed emulsion dispersed in aqueous gelatin solution was cooled to 40° C, and then adjusted to pH of 9.5 with ammonia water and acetic acid. Then, it was further grown in the following manner.

Process 2

After pAg of the above seed emulsion was adjusted to 7.3 with ammoniac silver ion solution, an ammoniac silver ion solution and a solution containing potassium iodide and potassium bromide were added by a double jet method while keeping pH and pAg constant to form a silver bromoiodide stratum containing 30 mol% of silver iodide.

Process 3

pH and pAg were adjusted to 9 and 9.0, respectively, with acetic acid and potassium bromide, and then an ammoniac silver ion solution and a potassium bromide solution were added simultaneously to grow silver halide grains up to 90% of a final size, wherein pH was gradually dropped from 9.0 to 8.2.

Process 4

pAg was adjusted to 11 by adding a potassium bromide solution, and then an ammoniac silver ion solution and a potassium bromide solution were added gradually lowering pH to 8 to grow the silver halide grains to prepare emulsion containing a silver bromoiodide grain having a silver iodide content of 2 mol% and an average size of 0.7 µm.

Process 5

Next, the above emulsion was subjected to each of following four desalination processes (a) through (d) to remove excessive soluble salts.

Desalination process (a)

To the above emulsion were added at 40° C and pH adjusted as shown in Table 1 an exemplified compound A-3 of 5.5 g/mol of AgX and $MgSO_4$ of 8.5 g/mol of AgX, and then the suspension was stirred for 3 minutes. After standing and decanting, water of 40° C was added. $MgSO_4$ of 20 g/mol of AgX was further added, and the suspension was stirred for 3 minutes. It was again subjected to decantation following standing. The same was repeated once again, and then gelatin of 15 g/mol of AgX, and water were added to make total quantity 450 mℓ/mol of AgX. The emulsion was dispersed stirring further for 20 minutes at 55° C.

Desalination process (b)

To the above emulsion was added at 40° C an example compound P-4 of 6 g/mol of AgX, and the suspension was stirred for 3 minutes. pH was adjusted to 3 to 3.5 with 50 wt% an aqueous acetic acid solution, and the suspension was subjected to decantation following standing. Water of 40° C was added, and the suspension was stirred. Then, it was subjected once again to decantation following standing. Decantation was repeated twice, and then gelatin of 15 g/mol of AgX, and water were added to make total quantity 450 mℓ/mol of AgX. The emulsion was dispersed stirring further for 20 minutes at 55° C.

Desalination process (c)

To the emulsion was added at 40° C 60% benzoyl-modified gelatin of 50 g/mol of AgX, and pH was adjusted to 5.0 with 56 wt% aqueous acetic acid solution. The suspension was allowed to stand and subjected to decantation. After adding water of 40° C and adjusting pH to 6.0 with potassium hydroxide, the suspension was stirred and subjected to standing and decanting following adjustment of pH to 4.5 with a 56 wt% aqueous acetic acid solution. Decantation was repeated twice, and then gelatin of 15 g/mol of AgX, potassium hydroxide of 1 g/mol of AgX, and water were added to make total quantity 450 mℓ/mol of AgX. The emulsion was dispersed stirring further for 20 minutes at 55° C.

Desalination process (d)

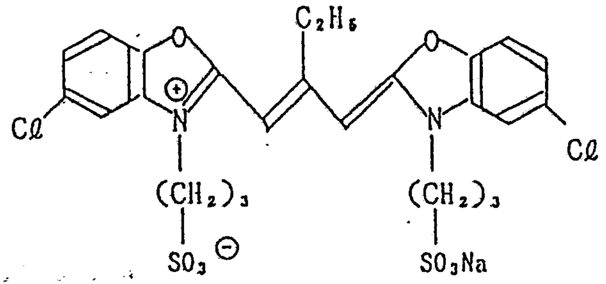
pH of the emulsion was adjusted to 4.5, and 50 wt% aqueous magnesium sulfate solution of 15 g/mol of AgX was added. After standing, the suspension was subjected to decantation, and this decantation was repeated twice. Then, gelatin of 15 g/mol of AgX, and water were added to make total quantity 450 mℓ/mol of AgX. The emulsion was dispersed stirring further for 20 minutes at 55° C.

Process 6

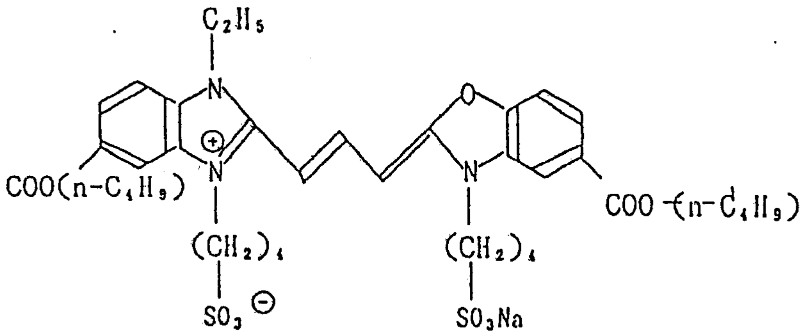
The emulsion prepared in Process 5 was subjected to chemical sensitization with chloroauric acid and hypo at 55° C, and then 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added to prepare a light-sensitive emulsion.

In preparing the emulsion, were added a sensitizing dye (A) of 300 mg per mol of AgX and a sensitizing dye (B) of 15 mg per mol of AgX in various processes as shown in Table 1.

Sensitizing dye (A)



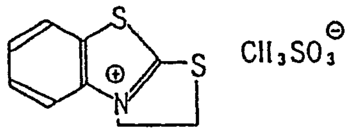
Sensitizing dye (B)



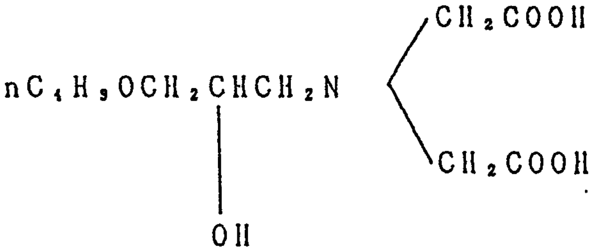
The above processes 2 through 4 were respectively subdivided into modes I and II like 2-I and 2-II; the above sensitizing dyes were added during addition of an ammoniac silver ion solution and a halide solution in case of I and after addition thereof in case of II.

Similarly, process 5 was subdevided into I, II and III; the sensitizing dyes were added during addition of an exemplified compound A-3 in case of I, during addition of $MgSO_4$ in case of II, and during second addition of $MgSO_4$ in case of III.

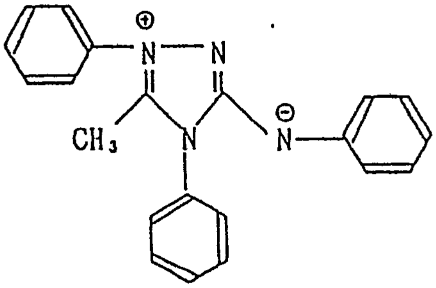
To each of the above light-sensitive emulsions were added in term of per mol AgX, 400 mg of t-butyl-catecol, 1.0 g of polyvinyl pyrrolidone (molecular weight, 10,000), 2.5 g of styrene-maleic acid anhydride copolymer, 10 g of trimethylpropane, 5 g of diethylene glycol, 50 mg of nitrophenyl-triphenylphosphonium chloride, 4 g of ammonium 1,3-dihydroxybenzene-4-sulfonate, 5 mg of sodium 2-mercaptobenzoimidazole-5-sulfonate, 70mg of



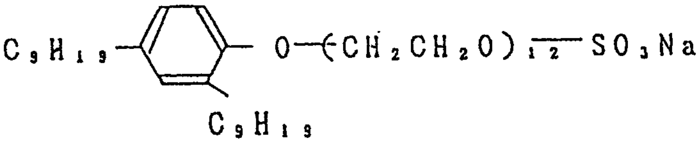
1g of



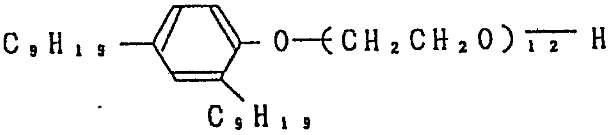
10 mg of 1,1-dimethylol-1-bromo-1-nitromethane and 150 mg of



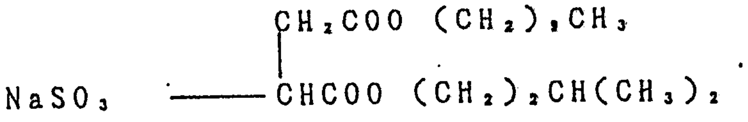
Additionally, into a protective layer were incorporated the following compounds per gram of gelatin;



12mg

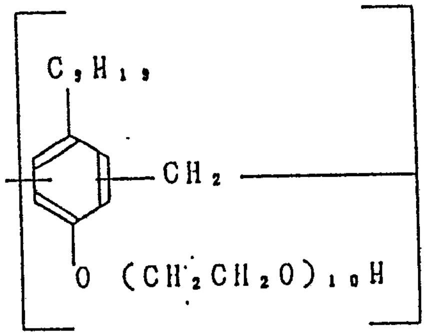


2 mg



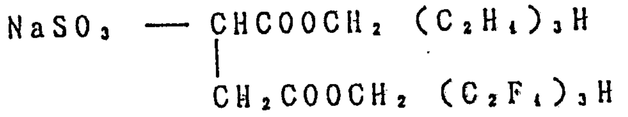
$$NaSO_3-\underset{\displaystyle CHCOO(CH_2)_2CH(CH_3)_2}{\overset{\displaystyle CH_2COO(CH_2)_9CH_3}{|}}$$

7 mg



n (a mixture where n is 2 to 5)

15 mg



$$NaSO_3-\underset{\displaystyle CH_2COOCH_2(C_2F_4)_3H}{\overset{\displaystyle CHCOOCH_2(C_2F_4)_3H}{|}}$$

5 mg

$F_{19}C_9-O(CH_2CH_2O)_{10}CH_2CH_2OH$ 3 mg

Matting agent comprising of polymethyl methacrylate with an average grain size of 7 μm	7 mg
Colloidal silica with an average grain size of 0.013μ	70 mg
Formalin	20 mg
Glyoxal	30 mg
2-hydroxy-4,6-dichlorotriazine sodium	30 mg

The emulsion was uniformly coated on both faces of a subbed and blue-colored polyethylene terephthalate film base of thickness 180μ, and dried to prepare Sample Nos. 1 through 44, each of which was evaluated as follows.

(1) Sensitometry

A sample was sandwiched between two sheets of KS for radiography made by Konica Corporation and was exposed to X-ray via Penetrometer Model B made by Konica Medical. Then, the sample was processed in a developer XD-90 in 90 seconds with an automatic developer Model KX-500 made by Konica Corporation. The sensitivities of the processed samples were evaluated. The sensitivity is expressed by a reciprocal of an exposure necessary for giving a fog + 1.0 density, and by a value relative to that of Sample 1, which is set at 100.

(2) Pressure resistance

Resistance for roller marks (pressure marks caused by rollers of an automatic developer) in processing was evaluated as follows; an unexposed sample was processed in 45 or 90 seconds by an X-ray automatic developer having opposed type rollers with heavily roughened surfaces, and the developed sample was observed visually and classified to five grades: 5: no roller marks; 4: only a few roller marks; 3: some roller marks; 2: many roller marks; 1: heavy roller marks.

(3) Graininess

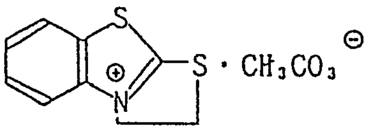
A sample uniformly exposed to light and developed was observed visually in an area of 20 cm x 20 cm having a black density of 0.6 to 0.8, and classified to five grades: 5: very excellent; 4: good; 3: practicable; 2: roughened within practicability; 1: no practicable due to roughness.

Additionally, a rectangular wave chart was exposed on each sample, and MTF was measured by a contrast method. MTF is a value in a spatial frequency of 20 lines/mm.

The evaluation results of (1) to (3) are shown in Table 1.

The compositions of the developer and fixer used for processing a light-sensitive material were as follows:

Developer

Potassium sulfite	68.75 g
Sodium hydroxyethylethylenediaminetriaacetate	8 g
1,4-dihydroxybenzene	27 g
Boric acid	10 g
5-methylbenzoimidazole	0.035 g
1-phenyl-5-mercaptotetrazole	0.015 g
Sodium metabisulfite	5.0 g
Acetic acid (90%)	12.8 g
Diethylene glycol	16.0 g
1-phenyl-3-pyrazolidone	1.2 g
5-nitroindazole	0.14 g
	0.001 g
Glutaraldehyde	3.08 g
Potassium bromide	4.0 g
5-methylbenzotriazole	0.05 g

Water was added to one liter, and pH was adjusted to 10.40 with potassium hydroxide.

Fixer

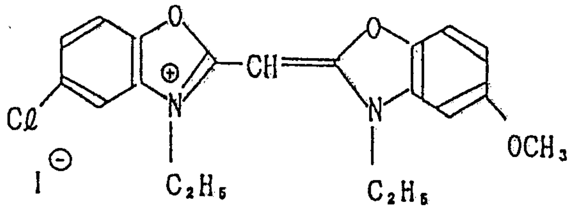
Ammonium thiosulfate	140 g
Sodium sulfite	7.3 g
Sodium acetate ·	15.5 g
Aluminum sulfate $10\text{-}18H_2O$	27.7 g
Sulfuric acid (50 wt%)	6.0 g
Citric acid	0.9 g
Boric acid	7.0 g
Glacial acetic acid	5.1 g
Disodium ethylenediaminetetraacetate	5 g

Water was added to one liter, and pH was adjusted to 4.3 with sulfuric acid (50 wt%).

Example 2

The emulsions were prepared in the same manner as Example 1, except that the following sensitizing dye (C) was used instead of sensitizing dyes (A) and (B) used in Example 1.

(C)



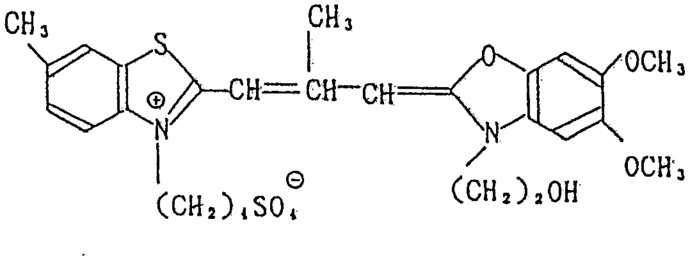
An addition amount of this sensitizing dye was 400 mg per mol silver.

Samples 45 to 90 were prepared and evaluated in the same manners as Example 1. The evaluation results are summarized in Table II.

Example 3

The emulsions were prepared in the same manner as Example 1, except that the following sensitizing dye (D) was used instead of sensitizing dyes (A) and (B).

(D)



An addition amount of this sensitizing dye was 300 mg per mol silver.

Samples 91 to 131 were prepared and evaluated in the same manners as Example 1. The evaluation results are summarized in Table III.

Example 4

The emulsions E1 and E2 each having a different average grain size were prepared by processes 1 through 6 in Example 1. E1 and E2 had the same AgI content of 2 mol% and the average silver halide grain sizes of 0.55 µm and 0.80 µm, respectively. Sensitizing dye (A) of 300 mg per mol silver and sensitizing dye (B) of 15 mg per mol silver were added to the emulsions in the processes as shown in Table IV.

Samples 132 to 190 were prepared and evaluated in the same manners as Example 1. The evaluation results are summarized in Table IV.

Example 5

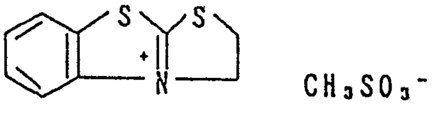
Sample Nos. 191 through 227 were prepared and evaluated in the same manners as Example 1, except that formalin used in Example 1 was replaced with a hardener specified in Table V. Desalination was carried out by process (a). The evaluation results are summarized in Table V.

Example 6

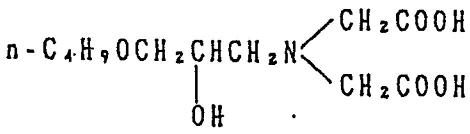
The emulsions were prepared in the same manner as Example 1, except that the sensitizing dyes used in Example 1 was replaced with an exemplified compound 31 of 20 mg per mol Ag.

The following additives were added to the above emulsions

Trimethylolpropane	9 g
Nitrophenyl-triphenylphosphonium chloride	3.0 mg
Ammonium 1,3-dihydroxybenzene-4-sulfonate	1 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	10 mg
2-mercaptobenzothiazole	10 mg



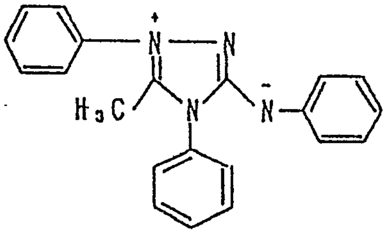
35 mg



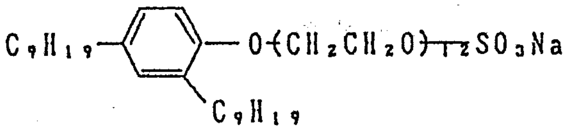
$$n\text{-}C_4H_9OCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2N\left\langle\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}\right.$$

1 g

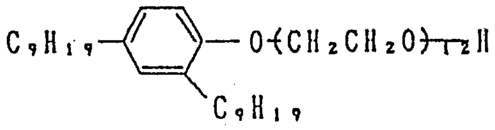
1,1-dimethylol-1-bromo-1-nitromethane



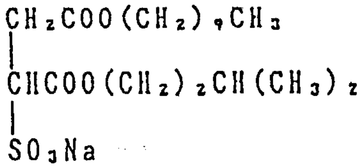
In addition, a protective layer solution containing gelatin, matting agent, sodium dodecylbenzenesulfonate and the like was prepared. Further, the following compounds were added thereto.



10 mg,



2 mg

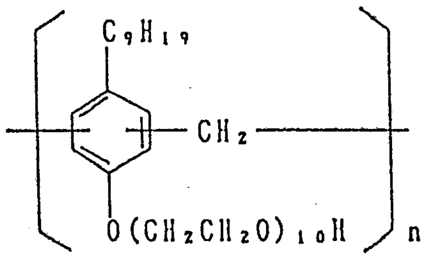


$$\begin{array}{l} CH_2COO(CH_2)_9CH_3 \\ | \\ CHCOO(CH_2)_2CH(CH_3)_2 \\ | \\ SO_3Na \end{array}$$

7 mg

C_9F_{19}-$O(CH_2CH_2O)_{10}$-CH_2CH_2OH 2 mg

$C_8F_{17}SO_3K$ 3 mg



15 mg

(a mixture where n is 2 to 5)

Sodium chloride	50 mg
Matting agent comprising of polymethyl methacrylate having an average grain size of 5 µm	7 mg
Colloidal silica having an average grain size of 0.013µ	70 mg

To comparative examples were added, as a hardener, 2 mℓ of formalin (35%) and 1.5 mℓ of aqueous glyoxal solution (40%). The hardeners specified in Table VI were added to the samples of the invention.

Samples 228 to 248 were prepared in the same manner as Example 1.

Each of the samples was slit into 3.5 cm strips, and each strip was subjected to wedgewise exposure via an 820 nm interference filter in 10^{-5} second with a a xenon flash. Next, it was processed at 35°C in a developer XD-SR in 45 seconds with an automatic developer for radiograph Model SRX-501 made by Konica Corporation.

The sensitivities of the developed samples were evaluated. The sensitivity of each sample is expressed by a reciprocal of an exposure necessary for giving fog + 1.0 density, and by a value relative to that of Sample 228, which is set at 100. The evaluation results are summarized in Table VI.

As can be understood from the data in Table VI, the samples of the invention comprise less fogging and high sensitivity.

Table 1 (1/3)

	Sample No.	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalination method	Sensitivity	Roller marks		Image quality	
						45"	90"	Graininess	MTF
Comparative	1	1	1	(a) (pH8)	100	1	1	1	27
"	2	1	1	" (pH4)	90	1	1	1	32
"	3	2-I	2-I	" (pH8)	80	1	1	1	37
Invention	4	"	3-I	" (pH4)	152	5	4	4	52
"	5	"	4-II	(b)	160	4	5	5	55
"	6	"	"	(c)	158	5	5	5	66
Comparative	7	3-I	3-I	(a) (pH8)	80	1	2	1	22
Invention	8	"	"	" (pH4)	140	5	5	5	67
"	9	"	"	(b)	145	4	5	4	67
"	10	"	"	(c)	157	5	5	5	66
Comparative	11	"	4-II	(a) (pH8)	160	5	5	5	65
Invention	12	"	"	(b)	177	4	5	4	57
"	13	"	"	(c)	180	4	5	5	59
Comparative	14	3-II	1	(a) (pH8)	100	1	2	2	23
"	15	"	"	(c)	80	2	2	2	19
"	16	"	2-I	(2) (pH8)	95	1	1	1	37

Table 1 (2/3)

	Sample No.	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalination method	Sensitivity	Roller marks		Image quality	
						45"	90"	Graininess	MTF
Invention	17	3-II	2-I	(a) (pH6)	114	4	5	5	60
"	18	"	"	" (pH2)	173	5	4	4	55
"	19	"	3-II	(b)	160	5	5	5	57
"	20	"	"	(c)	156	5	5	5	59
Comparative	21	"	6	"	70	1	1	1	30
"	22	4-I	2-I	(a) (pH7)	60	2	1	1	29
Invention	23	"	"	(") (pH2)	173	5	5	4	60
"	24	"	3-I	(b)	181	4	5	4	65
"	25	"	"	(c)	179	4	5	4	63
"	26	"	5-I	(a) (pH4)	163	4	4	5	64
"	27	4-II	4-II	"	111	5	5	5	66
"	28	"	"	(c)	134	5	5	5	64
"	29	5-I	3-I	(a) (pH4)	150	5	4	5	59
"	30	"	5-I	(b)	166	5	5	5	58
"	31	"	"	(c)	172	5	4	5	57
"	32	5-II	5-I	(a) (pH4)	183	5	5	5	55

Table 1 (3/3)

	Sample No.	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalination method	Sensitivity	Roller marks		Image quality	
						45"	90"	Graininess	MTF
Invention	33	5-II	5-I	(b)	192	5	5	4	54
"	34	"	"	(c)	183	5	5	5	59
Comparative	35	6	6	(a) (pH8)	55	1	1	1	25
Invention	36	2-I	4-II	(d)	150	5	5	5	57
"	37	"	5-I	"	162	5	4	4	58
"	38	3-I	3-I	"	140	5	5	5	57
"	39	3-I	4-II	"	150	5	5	5	62
"	40	3-II	3-II	"	170	5	5	4	60
Comparative	41	"	6	"	70	2	2	2	40
Invention	42	4-I	3-I	"	177	5	4	4	59
"	43	5-I	5-I	"	180	5	5	4	58
"	44	"	5-II	"	145	5	5	5	62

Table 2 (1/3)

	Sample No.	sensitizing dye	Desalination method	Sensitivity	Roller marks		Image quality	
					45"	90"	Graininess	MTF
Comparative	45	1	(a) (pH8)	100	1	1	1	35
"	46	"	" (pH6)	85	2	1	1	35
"	47	"	(b)	40	2	2	2	40
"	48	2-I	(a) (pH8)	124	4	5	4	58
Invention	49	"	" (pH6)	133	4	4	5	60
"	50	"	(b)	142	5	5	4	62
"	51	"	(c)	150	4	5	4	66
"	52	2-II	(a) (pH4)	192	4	5	4	59
"	53	"	(c)	183	5	4	5	62
Comparative	54	3-I	(a) (pH8)	80	1	1	1	33
Invention	55	"	(b)	187	5	5	5	63
"	56	"	(c)	178	4	5	5	65
"	57	3-II	(a) (pH4)	117	4	5	5	67
"	58	"	(") (pH2)	193	5	5	5	50
"	59	"	(b)	152	5	4	5	55
"	60	"	(c)	163	5	5	4	62

Table 2 (2/3)

	Sample No.	sensitizing dye	Desalination method	Sensitivity	Roller marks		Image quality	
					45"	90"	Graininess	MTF
Invention	61	4-I	(a) (pH6)	177	5	5	5	55
"	62	"	(c)	149	5	5	4	60
Comparative	63	4-II	(a) (pH8)	75	1	2	1	20
Invention	64	"	" (pH4)	147	4	5	5	66
"	65	"	(b)	163	5	5	5	65
"	66	"	(c)	168	5	5	4	66
Comparative	67	5-I	(a) (pH8)	60	1	1	1	32
Invention	68	"	" (pH6)	170	4	5	5	50
"	69	"	" (pH2)	172	5	4	4	55
"	70	5-I	(b)	177	4	5	5	58
"	71	"	(c)	176	5	5	4	59
"	72	5-II	(b) (pH6)	150	5	5	5	62
"	73	"	(b)	162	5	5	4	65
"	74	"	(c)	170	5	4	5	66
Comparative	75	5-III	(a) (pH8)	85	1	1	1	29

Table 2 (3/3)

	Sample No.	sensitizing dye	Desalination method	Sensitivity	Roller marks		Image quality	
					45"	90"	Graininess	MTF
Invention	76	5-III	(b)	169	5	5	5	55
"	77	"	(c)	142	5	5	5	59
Comparative	78	6	(a) (pH8)	100	1	1	1	30
"	79	"	" (pH4)	70	1	2	2	34
"	80	"	(b)	65	1	2	1	35
"	81	1	(d)	70	1	2	2	42
Invention	82	2-1	"	140	5	5	5	58
"	83	2-II	"	150	5	4	5	57
"	84	3-I	"	148	5	4	5	62
"	85	3-II	"	157	5	5	4	60
"	86	4-II	"	160	5	5	5	65
"	87	5-I	"	167	5	4	5	67
"	88	5-II	"	170	5	5	4	62
"	89	5-III	"	175	5	4	5	60
Comparative	90	6	"	80	2	2	1	38

Table 3 (1/3)

	Sample No.	sensitizing dye	Desalination method	Sensitivity	Roller marks		Image quality	
					45"	90"	Graininess	MTF
Comparative	91	1	(a) (pH8)	50	1	1	1	32
"	92	"	(c)	45	2	1	1	35
"	93	2-I	(a) (pH8)	63	1	1	1	30
Invention	94	"	" (pH4)	113	4	5	5	50
"	95	"	(b)	160	4	4	4	60
"	96	2-II	(a) (pH4)	173	5	4	5	55
"	97	"	(c)	150	5	5	4	60
"	98	3-I	(a) (pH6)	142	4	4	4	57
"	99	"	(b)	145	4	5	4	58
"	100	"	(c)	138	4	5	5	62
"	101	3-II	(b)	129	5	5	5	65
"	102	"	(c)	163	5	5	5	60
Comparative	103	4-I	(a) (pH8)	92	2	2	1	20
Invention	104	"	(b)	119	5	5	4	57
"	105	"	(c)	157	5	5	5	58
"	106	4-II	(a) (pH6)	163	5	5	5	55

Table 3 (2/3)

	Sample No.	sensitizing dye	Desalination method	Sensitivity	Roller marks		Image quality	
					45"	90"	Graininess	MTF
Invention	107	4-II	(b)	167	4	4	5	60
"	108	"	(c)	170	5	5	5	62
"	109	5-I	(a) (pH6)	165	5	5	4	67
"	110	"	" (pH4)	153	4	4	5	66
"	111	"	" (pH2)	157	4	5	4	72
"	112	"	(c)	149	4	4	5	77
Comparative	113	5-II	(a) (pH8)	85	1	1	1	33
Invention	114	"	" (pH6)	138	4	5	4	75
"	115	"	(b)	139	5	5	4	58
"	116	5-II	(c)	142	5	5	4	62
"	117	5-III	(a) (pH6)	125	5	5	4	55
"	118	"	(a) (pH4)	126	5	5	5	58
"	119	"	(c)	134	5	5	5	59
Comparative	120	6	(a) (pH6)	30	1	2	2	25
"	121	"	" (pH2)	25	1	1	1	27
"	122	"	(b)	50	1	1	1	37

Table 3 (3/3)

	Sample No.	sensitizing dye	Desalination method	Sensitivity	Roller marks		Image quality	
					45"	90"	Graininess	MTF
Invention	123	6	(c)	47	2	1	1	25
"	124	1	(d)	70	1	2	2	38
Invention	125	2-I	"	150	5	5	5	57
"	126	3-I	"	140	4	4	4	56
"	127	3-II	"	145	4	4	5	62
"	128	4-I	"	167	5	4	5	63
"	129	5-I	"	170	5	5	4	60
"	130	5-III	"	178	4	4	4	67
Comparative	131	6	"	72	1	1	1	40

Table 4 (1/3)

	Sample No.	E-1				E-2				Sensi-tivity	Roller marks		Image quality	
		Blending ratio	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalina-tion method	Blending ratio	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalina-tion method		45"	90"	Graini-ness	MTF
Comparative	132	30	1	1	(a) (pH8)	70	1	1	(a) (pH6)	75	1	1	1	25
"	133	"	"	"	(b)	"	"	"	" (pH2)	63	1	1	1	20
Invention	134	"	2-I	2-I	(a) (pH6)	"	2-I	3-I	(c)	123	5	4	4	60
Comparative	135	"	"	2-II	(b)	"	"	"	(a) (pH8)	83	1	2	2	32
Invention	136	"	"	4-I	(c)	"	"	4-II	(c)	134	4	5	5	62
Comparative	137	"	"	5-II	(a) (pH8)	"	"	"	"	75	2	1	1	37
Invention	138	"	"	"	" (pH4)	"	3-I	3-I	(a) (pH6)	155	5	5	4	57
"	139	4-I	2-I	"	" (pH4)	"	"	"	(b)	170	5	5	4	58
"	140	"	"	"	(c)	"	"	3-II	(a) (pH2)	173	5	5	4	55
"	141	"	"	5-I	(b)	"	"	"	(c)	167	5	5	5	59
Comparative	142	"	5-I	3-I	(a) (pH6)	"	5-I	5-I	(a) (pH8)	65	1	1	1	25
Invention	143	"	"	5-I	(b)	"	"	"	" (pH4)	183	4	5	5	62
"	144	"	"	"	(c)	"	"	"	(b)	190	5	4	5	63
"	145	"	5-II	5-II	(a) (pH4)	"	"	"	(c)	189	4	5	5	66
"	146	50	2-I	3-I	" (pH6)	50	2-II	2-I	(a) (pH6)	173	5	5	5	67
"	147	"	"	"	(c)	"	"	"	(c)	177	4	5	4	58
"	148	"	3-II	3-II	(b)	"	"	5-I	(a) (pH4)	183	4	5	5	59
"	149	"	"	"	(c)	"	3-I	3-I	(b)	190	4	5	4	58
"	150	"	"	5-I	(a) (pH6)	"	"	"	(c)	192	4	5	5	60
"	151	"	4-I	3-I	" (pH2)	"	4-I	4-I	(a) (pH6)	155	5	4	4	60
"	152	"	"	"	(c)	"	"	5-I	" (pH6)	135	5	5	5	62
Comparative	153	"	"	5-I	(a) (pH8)	"	"	"	(b)	73	1	1	1	30
Invention	154	"	5-I	"	(b)	"	"	"	(c)	172	4	5	5	63
"	155	"	"	5-II	(a) (pH6)	"	5-I	"	(a) (pH4)	163	5	4	5	64
"	156	"	"	"	(c)	"	"	"	(a) (pH2)	167	4	5	5	65

Table 4 (2/3)

	Sample No.	E-1				E-2				Sensi-tivity	Roller marks		Image quality	
		Blending ratio	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalina-tion method	Blending ratio	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalina-tion method		45"	90"	Graini-ness	MTF
Invention	157	70	3-I	3-I	(b)	30	3-I	2-I	(a) (pH2)	180	5	5	5	60
Invention	158	"	"	"	(c)	"	"	"	(B)	177	5	5	4	55
"	159	"	"	5-I	(a) (pH4)	"	"	"	(c)	163	5	5	5	62
"	160	"	4-I	"	" (pH2)	"	4-I	4-I	(a) (pH6)	159	5	5	5	60
"	161	"	4-II	5-II	(b)	"	4-II	"	(c)	174	5	5	5	60
"	162	"	"	"	(c)	"	"	5-I	(a) (pH6)	138	5	5	5	60
"	163	"	"	5-I	(a))pH6)	"	"	"	(b)	176	5	5	4	55
"	164	"	5-I	"	(b)	"	5-I	"	(c)	167	4	5	5	62
"	165	"	"	"	(c)	"	"	5-II	(b)	159	4	5	4	50
Comparative	166	"	6	6	(a) (pH8)	"	6	6	(a) (pH8)	42	1	1	1	30
"	167	30	"	"	(d)	70	"	"	(a) (pH6)	70	2	1	1	42
"	168	"	"	"	"	"	"	"	(d)	60	2	1	2	38
"	169	"	2-I	2-I	(a) (pH8)	"	2-I	3-I	"	80	2	1	1	20
Invention	170	"	"	"	(b)	"	"	"	" (pH6)	172	5	4	4	62
"	171	"	"	5-II	(d)	"	"	4-I	" (pH6)	160	5	5	5	57
Comparative	172	"	4-I	2-I	(a) (pH8)	"	3-I	2-I	"	70	2	1	1	30
"	173	"	"	"	(d)	"	"	"	(a) (pH8)	62	1	1	2	41
Invention	174	"	"	"	" (pH8)	"	"	"	(d)	152	5	4	4	55
"	175	"	5-I	5-I	" (pH8)	"	5-I	3-I	(b)	163	5	4	4	63
"	176	"	"	"	" (pH8)	"	"	"	(d)	173	5	4	4	62
"	177	"	5-II	5-II	(a) (pH6)	"	"	"	"	180	5	5	5	59
"	178	50	2-I	3-I	(d)	50	2-II	2-I	"	157	5	4	5	56
"	179	"	3-II	5-I	(a) (pH6)	"	"	"	"	162	5	4	5	55
"	180	"	"	"	(d)	"	"	"	(a) (pH6)	173	5	4	4	60

Table 4 (3/3)

	Sample No.	E-1				E-2				Sensi-tivity	Roller marks		Image quality	
		Blending ratio	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalina-tion method	Blending ratio	Process for adding sensitizing dye (A)	Process for adding sensitizing dye (B)	Desalina-tion method		45"	90"	Graini-ness	MTF
Invention	181	50	3-II	5-I	(d)	50	2-II	2-I	(b)	180	5	5	5	67
"	182	"	4-I	3-I	"	"	"	"	"	172	5	5	5	62
"	183	"	5-I	5-II	(c)	"	4-I	3-II	(d)	183	5	5	5	50
Comparative	184	"	"	"	(a) (pH8)	"	"	"	"	78	2	2	2	32
Invention	185	70	3-I	3-I	(d)	30	3-I	2-I	(a) (pH2)	184	5	4	5	53
"	186	"	"	"	"	"	"	"	(d)	185	4	5	4	55
"	187	"	4-I	5-I	(a) (pH4)	"	4-I	4-I	"	187	5	4	5	54
"	188	"	5-I	5-I	" (pH4)	"	5-I	5-I	"	160	5	5	5	56
"	189	"	"	"	(d)	"	"	"	"	152	5	5	4	62
Comparative	190	"	6	6	"	"	6	6	(a) (pH8)	50	1	1	1	30

Table 5 (1/3)

Sample No.		Process for adding sensitizing dye	Hardener		Fog	Sensitivity	Graininess		Sharpness (MTF)
			Type	Amount added (mg/g gelatin)			45" treatment	90" treatment	
191	Comparative	1	Comparative	24	0.04	100	3	2	50
192	"	1	H-3	36	0.04	100	3	3	51
193	"	1	H-5	30	0.04	98	4	3	52
194	Comparative	2-I	Comparative	24	0.04	100	3	2	52
195	Invention	2-I	H-3	36	0.02	133	4	4	52
196	Comparative	2-II	Comparative	24	0.04	100	3	2	52
197	Invention	2-II	H-3	36	0.02	139	5	4	53
198	Comparative	3-I	Comparative	24	0.03	102	3	2	52
199	Invention	3-I	H-3	36	0.02	139	5	4	54
200	Comparative	3-II	Comparative	24	0.03	112	3	3	52
201	Invention	3-II	H-3	36	0.02	143	5	4	54
202	Comparative	4-I	Comparative	24	0.02	116	3	3	52
203	Invention	4-I	H-3	36	0.01	148	5	5	55

Table 5 (2/3)

Sample No.		Process for adding sensitizing dye	Hardener		Fog	Sensitivity	Graininess		Sharpness (MTF)
			Type	Amount added (mg/g gelatin)			45" treatment	90" treatment	
204	Invention	4-I	H-5	30	0.01	150	5	5	55
205	Comparative	4-II	Comparative	24	0.02	118	3	3	52
206	Invention	4-II	H-3	36	0.01	142	5	5	56
207	"	4-II	H-5	30	0.01	138	5	5	57
208	Comparative	5-I	Comparative	24	0.03	120	3	3	52
209	Invention	5-I	H-1	30	0.01	160	5	5	58
210	"	5-I	H-3	36	0.01	161	5	5	59
211	"	5-I	H-5	30	0.01	160	5	5	60
212	"	5-I	H-7	40	0.01	159	5	5	60
213	"	5-I	H-9	34	0.01	162	5	5	59
214	"	5-I	H-1 H-3	15 20	0.01	163	5	5	61
215	"	5-I	H-6 H-7	20 22	0.01	163	5	5	61

Table 5 (3/3)

Sample No.		Process for adding sensitizing dye	Hardener		Fog	Sensitivity	Graininess		Sharpness (MTF)
			Type	Amount added (mg/g gelatin)			45" treatment	90" treatment	
216	Comparative	5-II	Comparative	24	0.03	110	3	3	52
217	Invention	5-II	H-3	36	0.01	155	5	4	59
218	"	5-II	H-5	30	0.01	156	5	5	59
219	Comparative	5-III	Comparative	24	0.03	102	3	3	50
220	Invention	5-III	H-3	36	0.01	152	5	4	59
221	"	5-III	H-5	30	0.01	154	5	4	58
222	Comparative	6	Comparative	24	0.04	85	2	2	48
223	Invention	6	H-3	36	0.04	80	3	2	49
224	"	6	H-5	30	0.04	78	3	2	49
225	Comparative	-	Comparative	24	0.05	65	1	1	47
226	Invention	-	H-3	36	0.05	60	2	1	47
227	Invention	-	H-5	30	0.05	59	2	1	46

Table 6 (1/2)

Sample No.		Process for adding sensitizing dye	Hardener		Fog	Sensitivity
			Type	Amount added (mg/g gelatin)		
228	Comparative	1	Comparative-2	24	0.04	100
229	Invention	1	H-7	40	0.04	100
230	Comparative	2-II	Comparative-2	24	0.04	100
231	Invention	2-II	H-7	40	0.03	131
232	Comparative	3-II	Comparative-2	24	0.03	121
233	Invention	3-II	H-7	40	0.02	140
234	Comparative	4-II	Comparative-2	24	0.02	118
235	Invention	4-II	H-7	40	0.01	143
236	"	4-II	H-9	34	0.01	145
237	Comparative	5-I	Comparative-2	24	0.03	120
238	Invention	5-I	H-7	40	0.01	160
239	"	5-I	H-9	34	0.01	162
240	"	5-I	H-6 H-7	20 22	0.01	161
241	Comparative	5-II	Comparative-2	24	0.03	113

Table 6 (2/2)

Sample No.		Process for adding sensitizing dye	Hardener		Fog	Sensitivity
			Type	Amount added (mg/g gelatin)		
242	Invention	5-II	H-7	40	0.01	155
243	"	5-II	H-9	34	0.01	156
244	Comparative	5-III	Comparative-2	24	0.03	102
245	Invention	5-III	H-7	40	0.01	150
246	"	5-III	H-9	34	0.01	148
247	Comparative	6	Comparative-2	24	0.04	85
248	Invention	6	H-7	40	0.04	80

Claims

1. A silver halide photographic light-sensitive material comprising a support and provided thereon a plurality of hydrophilic colloidal layers including a silver halide emulsion layer, wherein said silver halide emulsion layer comprises a silver halide emulsion prepared by a process which involves desalting at a pH not exceeding 6 after formation of silver halide grains, and which involves adding a sensitising dye to the silver halide emulsion prior to chemical sensitisation of the silver halide grains.

2. A light-sensitive material according to claim 1, wherein at least one of said hydrophilic layers has been hardened with a vinylsulphone hardener.

3. A light-sensitive material according to claim 1 or 2, wherein said pH is 2 to 5.

4. A light-sensitive material according to any one of claims 1 to 3, wherein said sensitising dye is added during the formation of the silver halide grains or in the desalting step.

5. A light-sensitive material according to claim 4, wherein said sensitising dye is added during the formation of the silver halide grains when the addition of water-soluble silver salt is from 70 to 100 mol%.

6. A light-sensitive material according to claim 4 or 5, wherein said sensitising dye is added at a pH of 4 to 10 during the formation of the silver halide grains.

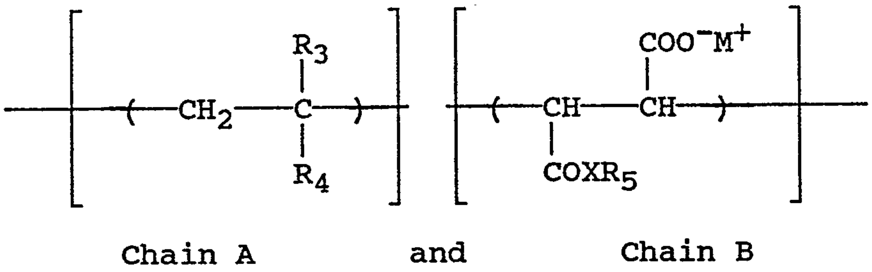
7. A light-sensitive material according to claim 6, wherein said sensitising dye is added at a pH of 6 to 9.

8. A light-sensitive material according to any one of the preceding claims, wherein said sensitising dye is added in an amount from 1 mg to 1 g per mole of silver contained in the silver halide emulsion.

9. A light-sensitive material according to claim 8, wherein said amount is from 5 mg to 500 mg per mole of silver.

10. A light-sensitive material according to any one of the preceding claims, wherein a high-molecular flocculant or a gelatin flocculant is added to the silver halide emulsion in said desalting step.

11. A light-sensitive material according to claim 10, wherein said high-molecular flocculant possesses 10 to 10^4 recurring units represented by Formula (I):



$$\left[-\!\left(CH_2 - \overset{R_3}{\underset{R_4}{C}} \right)\!- \right] \left[-\!\left(\underset{COXR_5}{CH} - \overset{COO^-M^+}{CH} \right)\!- \right]$$

wherein R_3 and R_4 independently represent a hydrogen atom, an aliphatic group or aryl group; R_5 represents a hydrogen atom, an aliphatic group, an aryl group, an aralkyl group, or M; M represents a hydrogen atom, an alkali metal, a quaternary ammonium group, or a quaternary phosphonium group; X represents -O- or -NH-, provided that X may form a nitrogen-containing ring with R_5 when X is -NH-; it being possible for either of the chain linking carbon atoms of chain B to be connected to $C(R_3)(R_4)$.

12. A light-sensitive material according to claim 11, wherein the molecular weight of said high-molecular flocculant is 10^3 to 10^6.

13. A light-sensitive material according to claim 12, wherein said molecular weight is 3×10^3 to 2×10^5.

14. A light-sensitive material according to any one of claims 11 to 13, wherein said high-molecular flocculant is added in an amount from 1/50 to 1/4 by weight of the amount of protective colloid contained in the silver halide emulsion.

15. A light-sensitive material according to claim 14, wherein said amount is 1/40 to 1/10 by weight of the amount of protective colloid.

16. A light-sensitive material according to claim 10, wherein said gelatin flocculant is added in an amount from 3/10 to 10 by weight of the amount of protective colloid contained in the silver halide emulsion.

17. A light-sensitive material according to any one of claims 2 to 16, wherein a protective layer is hardened with said vinylsulphone hardener.