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㊹ Method for producing a silver halide photographic emulsion.

㊼ A method for producing a spectrally sensitized silver halide photographic emulsion comprising the step of forming silver halide grains in the presence of at least one J-aggregated cyanine dye and at least one supersensitizer.

METHOD FOR PRODUCING A SILVER HALIDE PHOTOGRAPHIC EMULSION

FIELD OF THE INVENTION

The present invention relates to a method for producing a spectrally sensitized silver halide emulsion and, more particularly, to a method of making a silver halide emulsion, in which a cyanine dye of the kind which forms a J-aggregate and a supersensitizer are used during the formation of silver halide grains.

BACKGROUND OF THE INVENTION

In making spectrally sensitized silver halide emulsions, sensitizing dyes are usually added to emulsions after formation of silver halide grains. Methods of adding sensitizing dyes to emulsions prior to completion of grain formation of silver halide are disclosed in U.S. Patents 2, 735,766, 3,628,960, 4,183,756 and 4,225,666 and JP-A-196749/85 (U.S. Patent 4,683,193), JP-A-103149/86, JP-A-249053/86, and JP-A-210345/86 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

Particularly in U.S. Patents 4,183,756 and 4,225,666, it is disclosed that advantages such as an increase in sensitivity and a strengthening of adsorption of sensitizing dyes to silver halide grains are obtained by adding sensitizing dyes to emulsions after the stable nucleation, and during the course of the formation of silver halide grains.

However, frequently silver halide emulsions made in accordance with the methods disclosed in the above-cited patents, which involve adding a J-aggregated cyanine dye prior to the grain formation of silver halide, are spectrally sensitized with markedly low efficiency, or cannot provide a high spectral sensitizing effect.

The efficiency of spectral sensitization can be determined by measuring a relative quantum yield Φr in spectral sensitization. The procedures for measuring Φr are well-known to those skilled in the art, and are described in detail, e.g., in J. Spence & B.H. Carroll, Journal of Physical and Colloid Chemistry, vol. 52, p. 1090 (1948), and Tada-aki Tani & Hitoshi Urabe, Nippon Shashin Gakkai-Shi, vol.41, p. 325 (1978).

SUMMARY OF THE INVENTION

A first object of the present invention is to provide an improved method for spectral sensitization, in which adsorption of dyes is strengthened and thereby a high efficiency of spectral sensitization can be obtained.

A second object of the present invention is to provide an improved method for spectral sensitization, in which the desensitization of dyes is depressed and thereby a high efficiency of spectral sensitization can be obtained.

A third object of the present invention is to provide an improved method for spectral sensitization, in which a large amount of dyes are added to provide high efficiency spectral sensitization.

We have found that an improved silver halide photographic emulsion, which has a high spectral sensitizing effect, and in which adsorption of a sensitizing dye is strengthened, can be made by forming silver halide grains in the presence of not only a J-aggregated cyanine dye but also a sensitizing amount of a supersensitizer. Further, we have found that in accordance with the above-described method, the desensitizing effect of dyes can be depressed and the efficiency of spectral sensitization can be heightened, so an improved silver halide photographic emulsion which has spectral sensitization of high efficiency and chemical sensitization can be prepared. Furthermore, we have found that in accordance with this method, the desensitizing effect of dyes can be depressed to enable the preparation of an improved silver halide photographic emulsion with a high spectral sensitizing efficiency by addition of a large amount of spectral sensitizing dye.

Accordingly, the present invention relates to a method for producing a spectrally sensitized silver halide photographic emulsion by the step of forming silver halide grains in the presence of at least one J-aggregated cyanine dye and a supersensitizer.

DETAILED DESCRIPTION OF THE INVENTION

The term "supersensitizer" as used herein means any compound having a supersensitizing effect conventionally used in the field of silver halide photographic emulsions, and includes compounds capable of increasing the spectral sensitivity of an emulsion when a cyanine dye is used in combination therewith, compared with the use of the cyanine dyev alone.

A cyanine dye of the kind which forms the J-aggregate and a supersensitizer can be added to a silver halide emulsion at any time, provided that it preceeds the completion of the formation of silver halide grains. The addition time can be properly chosen depending on the types of sensitizing dyes and emulsion used. Whole amounts of sensitizing dye and supersensitizer may be added to the reaction system simultaneously with or prior to the beginning of grain formation. On the other hand, the sensitizing dye and the supersensitizer each may be divided into several portions, and added intermittently. In the latter case, for instance, one portion is added at the beginning of the grain formation, and the others can be added at regular time intervals during the course of grain formation. On the other hand, the sensitizing dye and the supersensitizer can be continuously added before completion of the grain formation. These ingredients may be added together with a silver nitrate solution, a halide solution or independently of these solutions. In the latter case, the addition may be initiated simultaneously with or prior to the beginning of grain formation, or at a time after the beginning of grain formation. When an emulsion-making method including a step of growing seed crystals is employed, the dye and the supersensitizer may be continuously or intermittently added during the growing step.

Even though the addition of the J-aggregated sensitizing dyes and the supersensitizer is continued after the completion of grain formation of silver halide, some benefit can be obtained, provided that the amounts added after the completion of grain formation are below one-half the respective total amounts added. However, the continued addition departing from the scope of the present invention causes the lowering of absorbance in the spectrally sensitizable region, and further deterioration in keeping qualities of the emulsion prepared and the sensitive material containing the emulsion.

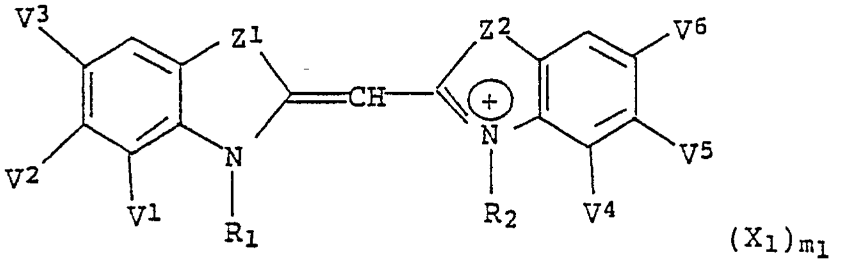
A sensitizing dye and a supersensitizer can be added in various manners as described above, provided that the addition thereof is finished prior to the completion of the grain formation of silver halide. The sensitizing dye and the supersensitizer may be added separately, or as a mixture thereof. They may be added simultaneously or alternately with each other. When both are added simultaneously, each ingredient may be added separately before or afterward. More specifically, it is preferred that the addition of a first ingredient should be started before the quantity of the second ingredient exceeds one-half the total amount to be added, and more than one-half of the total amount of the first ingredient should be finished by the conclusion of the addition of the second ingredient. More preferably, more than two-thirds of the respective total amounts should be added simultaneously. In particular, the simultaneous addition of the respective total amounts is favoured over other manners of addition.

The amounts of each of a sensitizing dye and a supersensitizer to be added to a silver halide photographic emulsion in accordance with the present invention, though depending on the shape and the size of silver halide grains to be supersensitized thereby, preferably range from $1x10^{-6}$ to $5x10^{-3}$ mol, particularly from $1x10^{-5}$ to $2.5x10^{-3}$ mol, per mole of silver halide.

In adding a sensitizing dye to be used in the present invention to a silver halide photographic emulsion in accordance with the method of the present invention, the dye may be directly dispersed into the emulsion, or dissolved in advance in a solvent, such as water, acetone, methanol, ethanol, propanol, methyl cellosolve, 2,2,3,3-tetrafluoropropanol, N,N-dimethylformamide or a mixture of two or more thereof, and then added to the emulsion.

Also, the dissolving a sensitizing dye can be performed with ultrasonic waves. Further, various methods can be employed in adding the sensitizing dyes of the present invention, including a method as described in U.S. Patent 3, 469,987, in which a sensitizing dye is dissolved in a volatile organic solvent, the resulting solution is dispersed into water or a hydrophilic colloid, and then the resulting dispersion is added to an emulsion; a method as described in JP-B-46-24185 (the term "JP-B" as used herein means an "examined published Japanese patent publication"), in which a water-insoluble dye is dispersed into a water-soluble solvent without undergoing any dissolution treatment, and the resulting dispersion is added to an emulsion; a method as described in JP-B-44-23389, JP-B-44-27555, JP-B-57-22091, in which a sensitizing dye dissolved in an acid is added to an emulsion, or a sensitizing dye which is dissolved in the presence of an acid or a base is added to an emulsion; a method as described in U.S. Patents 3,822,135 and 4,006,025, in which a sensitizing dye is made an aqueous or collidal dispersion in the presence of a surface active agent, and then added to an emulsion; a method as described in JP-A-53-102733 and JP-A-58-105141, in which a sensitizing dye is dispersed directly into a hydrophilic colloid, and then added to an emulsion; and a method as described in JP-A-51-74624, in which a sensitizing dye is dissolved by the use of a red-shift compound, and the resulting solution is added to an emulsion.

Cyanine dyes of the kind which form the J-aggregate, which are preferably used in the present invention, are represented by the following general formulae (I), (II) or (III). These dyes can also be employed as compounds referred to as the supersensitizers in the present invention.



(I)

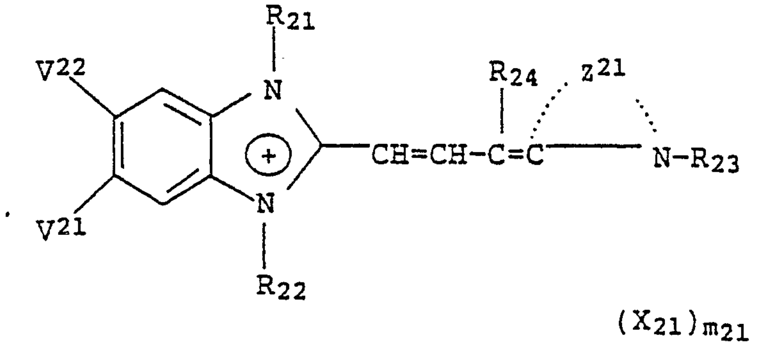
In the foregoing formula (I), Z^1 represents oxygen, sulfur, selenium, or -CH=CH-, and Z^2 represents sulfur, selenium, or -CH=CH-.

R_1 and R_2, which may be the same or different, each represents an unsubstituted or substituted alkyl group.

V^1 and V^4, which may be the same or different, each represents hydrogen or an atomic group necesary for forming a condensed benzene ring with V^2 and V^5, respectively; V^2, V^3, V^5 and V^6, which may be the same or different, each represents a straight- or branched-chain alkyl group containing at most 5 carbon atoms, an alkoxy group containing at most 4 carbon atoms, a hydroxy group, an acylamino group containing at most 4 carbon atoms, an unsubstituted or substituted phenyl group containing at most 8 carbon atoms, a halogen atom, an alkoxycarbonyl group containing at most 5 carbon atoms, a carboxyl group, or a hydrogen atom.

Provided that V^3 may be linked with V^2 and V^6 may be linked with V^5, to form a condensed benzene ring.

m_1 represents 0 or 1; and X_1 represents a counter ion residue necessary for charge balance. Specific examples of a cationic counter ion residue represented by X_1 include Na^+, K^+, a pyridinium cation, and an ammonium cation such as triethylammonium cation, and anionic counter ion residue include Cl^-, Br^-, I^-, SCN^-, p-toluenesulfonium, benzenesulfonium, ClO_4^-, and ethylsulfate.



(II)

In the foregoing formula (II), Z^{21} represents an atomic group necessary for completing a 4-thiazoline, thiazolidine, benzo-4-thiazoline, naphtho[1,2-d]-4-thiazoline, naphtho[2,3-d]-4-thiazoline, selenazolidine, 4-selenazoline, benzo-4-selenazoline, naphtho[1,2-d] 4-selenazoline, naphtho[2,3-d]-4-selenazoline, benzo-4-oxazoline, naphtho[1,2-d]-4-oxazoline, naphtho[2,3-d]-4-oxazoline or benzo-4-imidazoline nucleus, each of which may be unsubstituted or substituted.

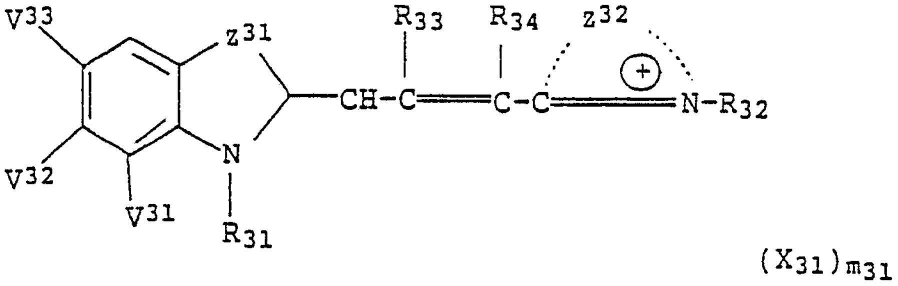
R_{21}, R_{22} and R_{23}, which may be the same or different, each represents an unsubstituted or substituted alkyl group.

R_{24} represents a hydrogen atom or an atomic group necessary for completing a 5- or 6-membered ring in combination with R_{23}.

V^{21} represents an electron attracting group including fluorine, chlorine, a cyano group, an alkoxycarbonyl group containing at most 4 carbon atoms, and an alkylsulfonyl group containing at most 4 carbon atoms.

V^{22} can be a group represented by V^{21}, and further may be hydrogen or an atomic group necessary for completing a condensed benzene ring in combination with V^{21}.

X_{21} has the same meaning as X_1 in formula (I), and m_{21} represents 0 or 1.



(III)

In the foregoing formula (III), Z^{31} represents oxygen, sulfur, or selenium.

Z^{32} represents an atomic group necessary for completing a thiazole, benzothiazole, naphtho[1,2- d]-thiazole, 8,9-dihydro-naphtho[1,2-d]thiazole, naphtho[2,3-d]thiazole, selenazole, benzoselenazole, naphtho-[1,2-d]selenazole, benzoxazole, naphtho[1,2-d]oxazole, or naphtho[2,3-d]oxazole nucleus.

R_{31} and R_{32}, which may be the same or different, each has the same definition as R_1.

R_{33} represents ethyl, propyl, butyl, phenyl or phenetyl and preferably is ethyl.

V^{31}, V^{32} and V^{33} have the same meanings as V^1, V^2 and V_3, respectively, and further, V^{32} and V^{33} may combine with each other to form a 5- or 6-membered ring, which can contain oxygen atoms.

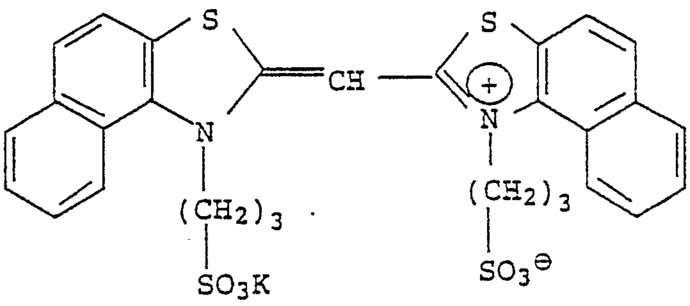
R_{34} represents a hydrogen atom, or an atomic group necessary for completing a 5- or 6-membered ring in combination with R_{32}.

X_{31} has the same meaning as X_1 in (I), and m_{31} represents 0 or 1.

Preferred examples of a substituent group by which alkyl groups represented by R_1, R_2, R_{21}, R_{22}, R_{23}, R_{31} and R_{32} in the foregoing general formulae (I), (II) and (III) can be substituted include a lower alkyl group, a halogen atom, a carbamoyl group, a carboxyl group, an alkoxycarbonyl group, an acylamino group, a hydroxyl group, a sulfo group, and a substituted phenyl group such as a sulfo-substituted phenyl, a carboxy-substituted phenyl. Specific examples of unsubstituted and substituted alkyl groups preferred as R_1, R_2, R_{21}, R_{22}, R_{23}, R_{31} and R_{32} include methyl, ethyl, propyl, pentyl, methoxymethyl, ethoxyethyl, 2,2,2-trifluoroethyl, 2,2,3,3,-tetra-fluoropropyl, carbamoylethyl, hydroxyethyl, carboxymethyl, carboxyethyl, 2-sulfoethyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, p-sulfophenetyl, ethoxycarbonylethyl, 2-hydroxy-3-sulfopropyl, 2-acetylaminoethyl, 2-chloro-3-sulfopropyl and 2 [2-(3-sulfopropoxy)ethoxy]ethyl group.

Specific examples of J-aggregated cyanine dyes which can be used in the present invention are illustrated below. However, the invention is not to be construed as being limited to these examples.

I-1



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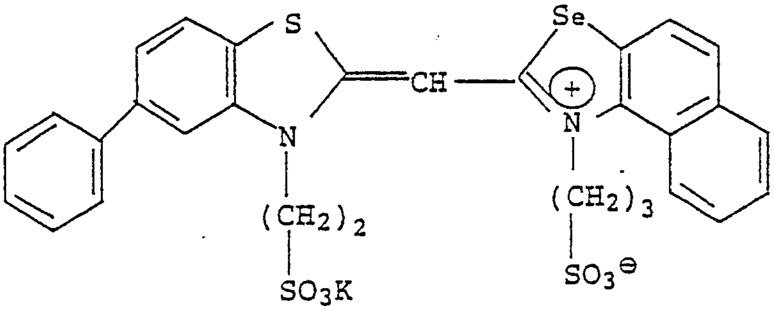

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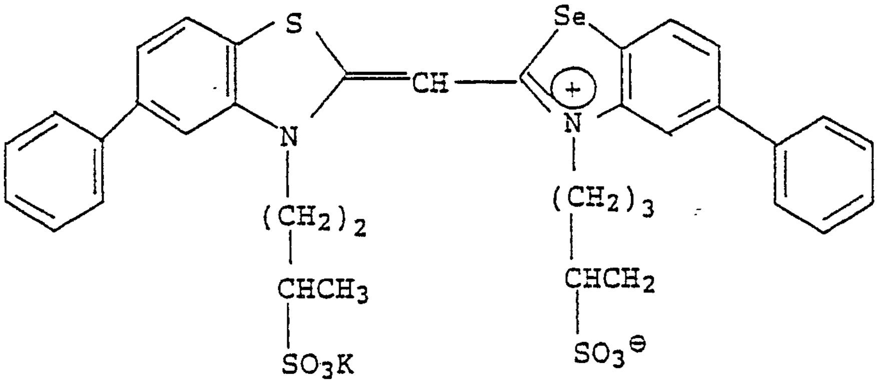

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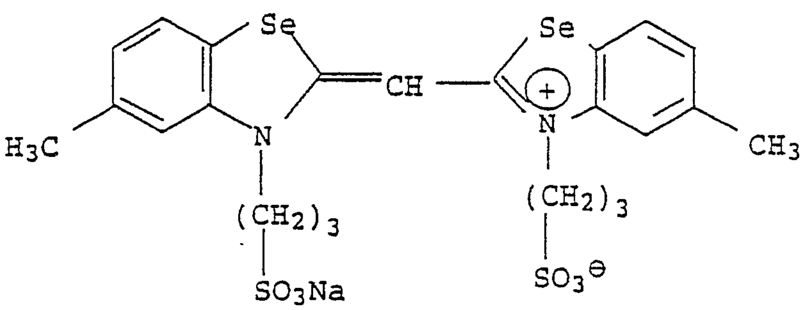

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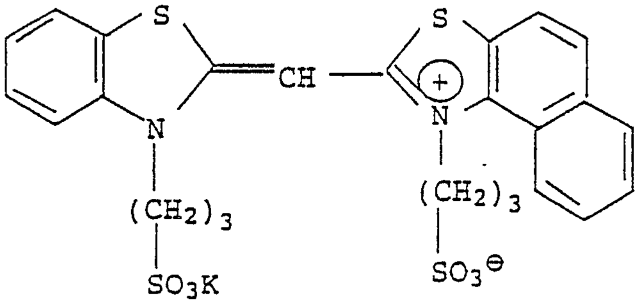

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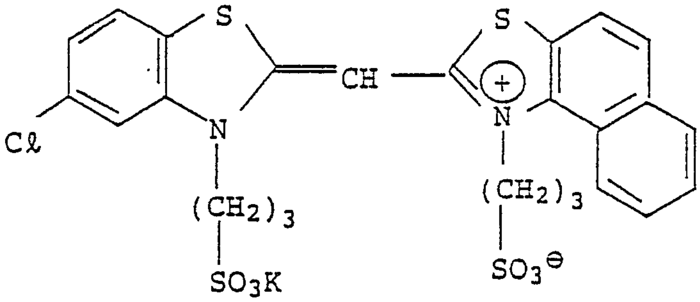

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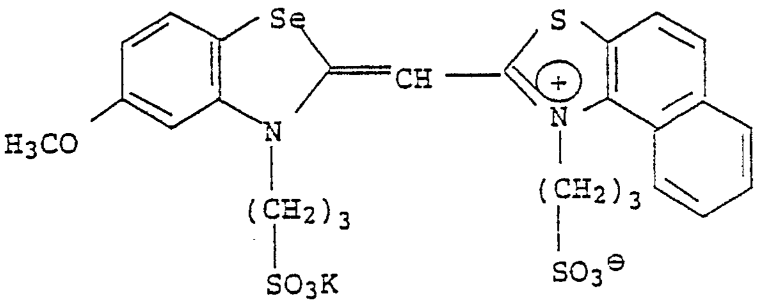

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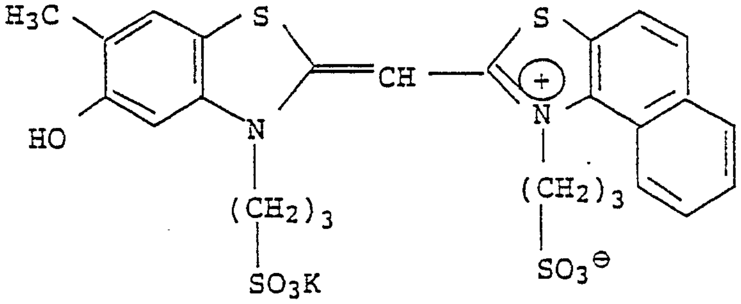

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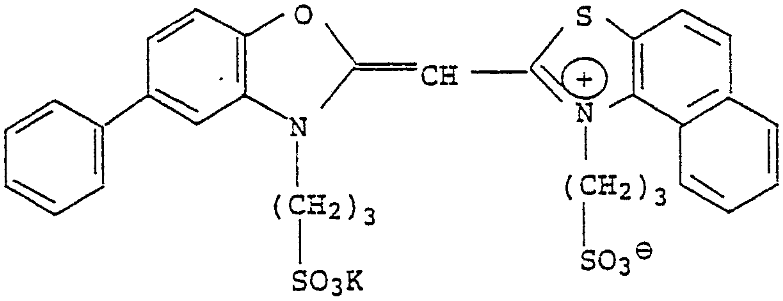

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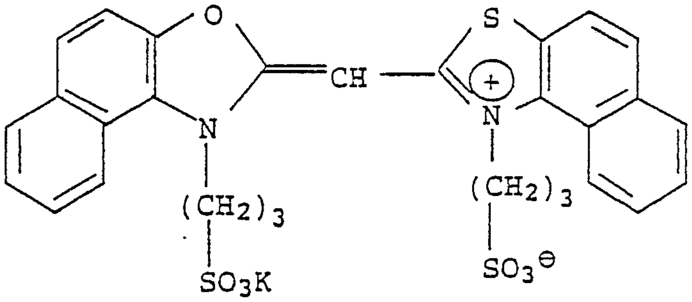
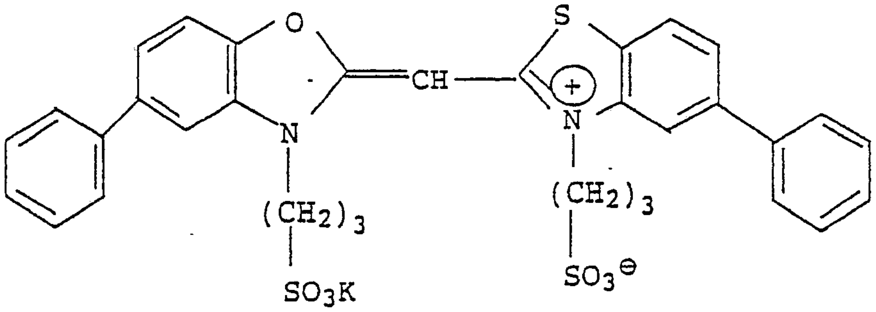
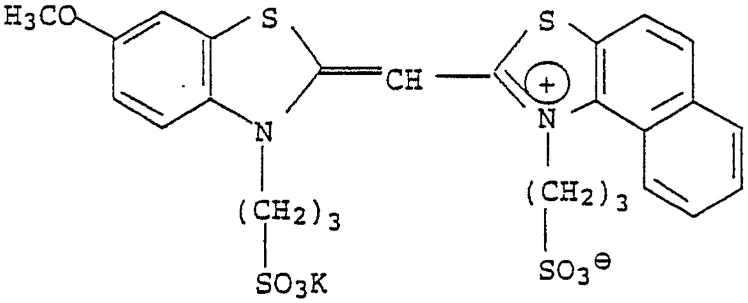

O
CH
S
+
N
N
(CH2)3
(CH2)3
SO3K
SO3⊖

I-11


O
CH
S
+
N
N
(CH2)3
(CH2)3
SO3K
SO3⊖

I-12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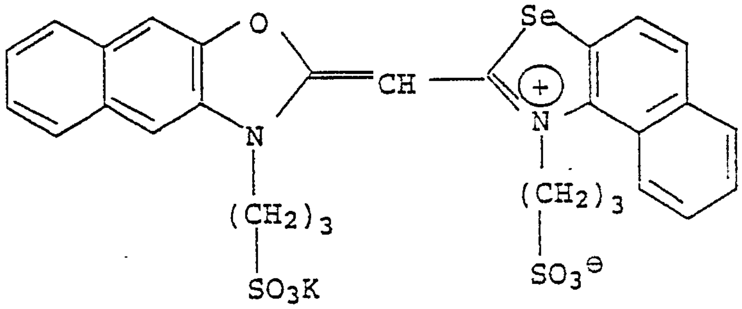
S
CH
S
+
N
N
(CH2)3
(CH2)3
SO3K
SO3⊖

I-13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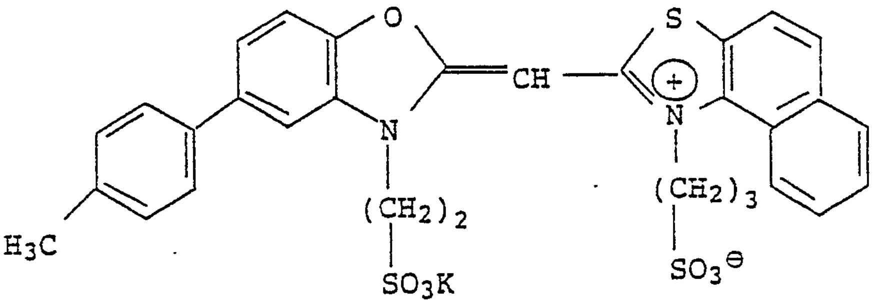
N
$(CH_2)_3$
SO_3K
CH
Se
+
N
$(CH_2)_3$
$SO_3^{\ominus}$

I-14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O
N
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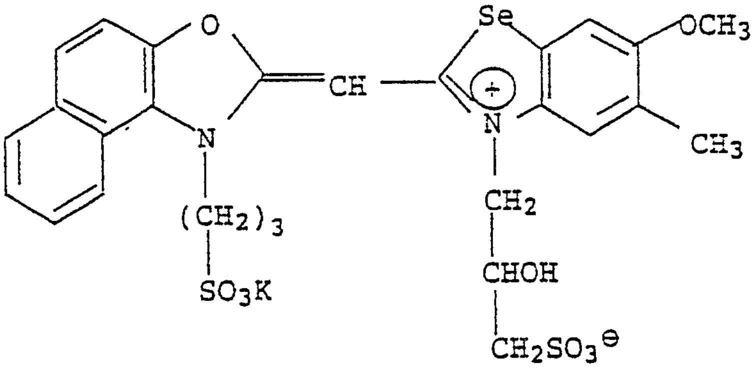
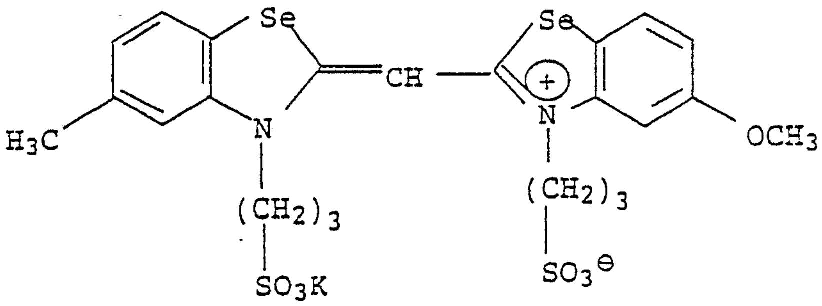
SO_3K
CH
S
+
N
$(CH_2)_3$
$SO_3^{\ominus}$

I-15


O
N
$(CH_2)_3$
SO_3K
CH
Se
+
N
OCH_3
CH_3
CH_2
CHOH
$CH_2SO_3^{\ominus}$

I-16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Se
CH
H3C
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N
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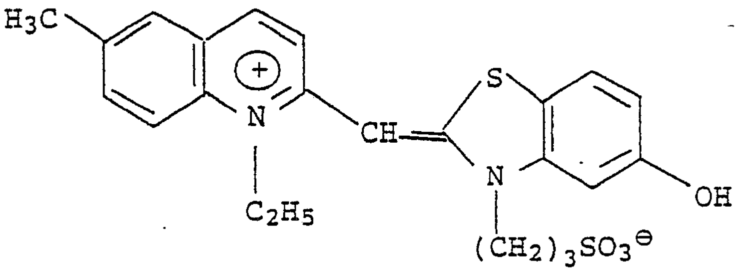
(CH2)3
(CH2)3
SO3K
SO3⊖

I-17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N
OH
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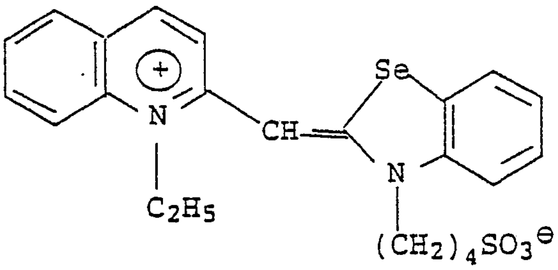
I-18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N
CH
N
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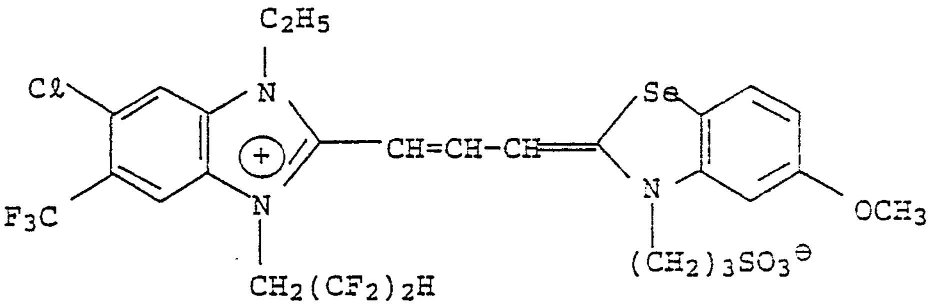
(CH2)4SO3⊖

II-1



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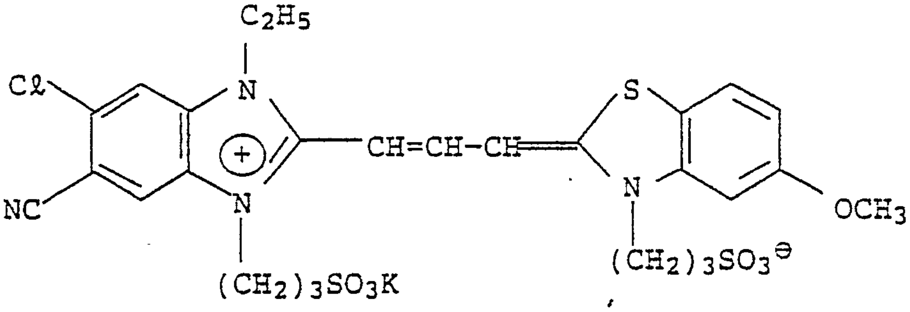

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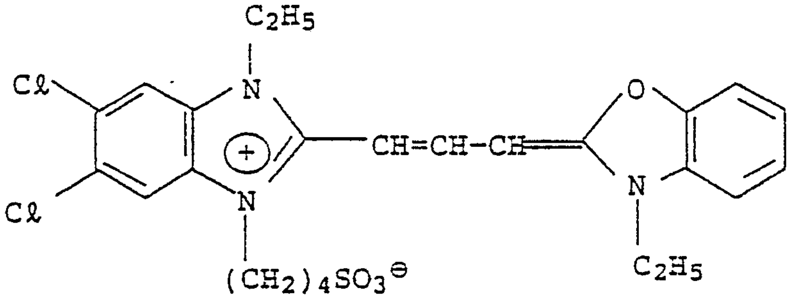
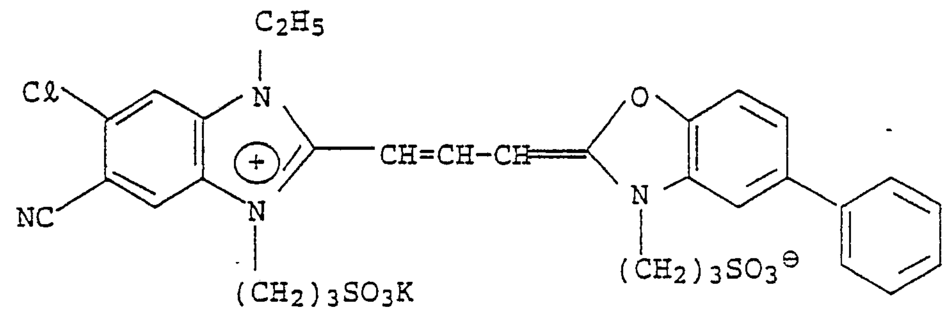


II-4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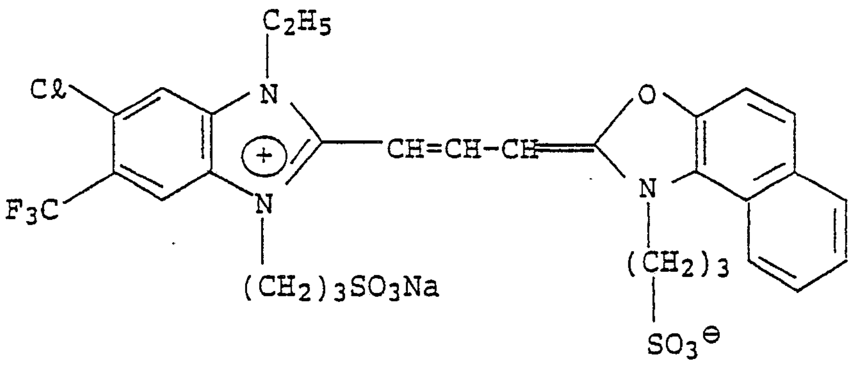
Cℓ
N
CH=CH-CH
O
N
NC
N
(CH₂)₃SO₃K
(CH₂)₃SO₃⊖

II-5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Cℓ
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N
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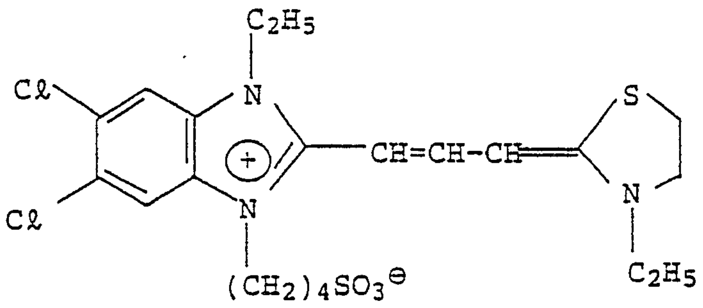
(CH₂)₃
SO₃⊖

II-6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Cℓ
N
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Cℓ
N
N
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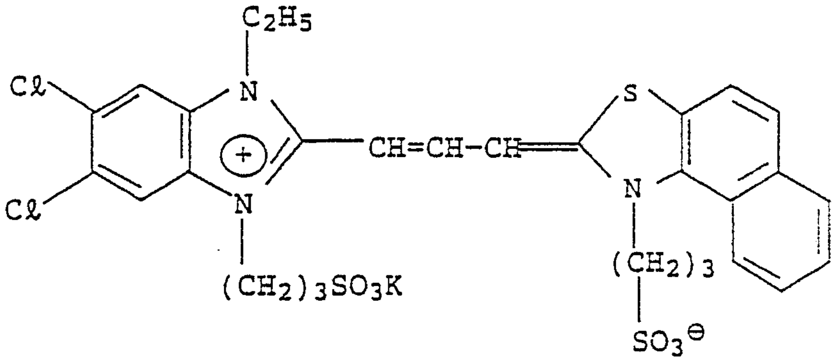
C₂H₅

II-7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Cℓ
Cℓ
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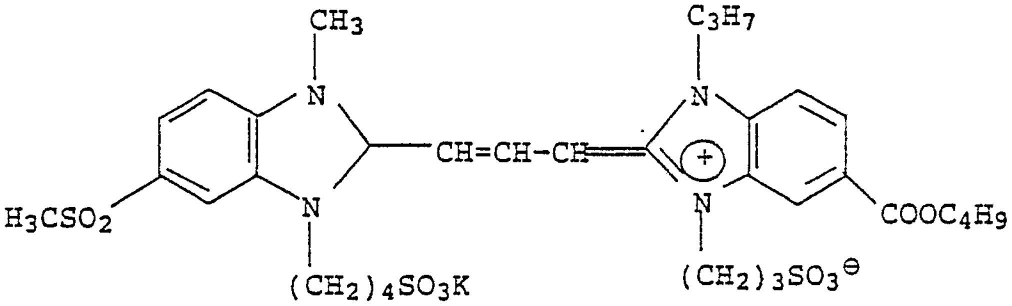
SO₃⊖

II-8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N
+
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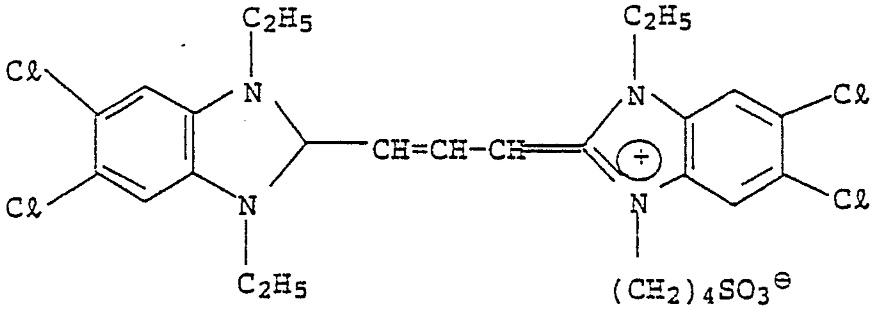
(CH₂)₃SO₃⊖

II-9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C₂H₅
Cℓ
Cℓ
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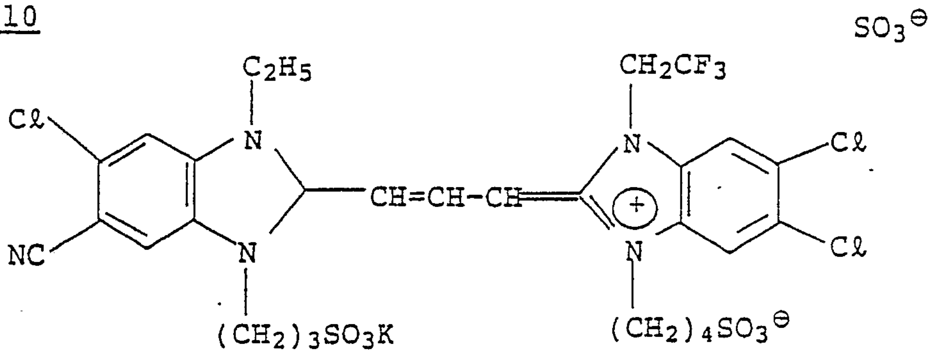
N
+
CH=CH-CH
Cℓ
Cℓ
C₂H₅
(CH₂)₄SO₃⊖

II-10



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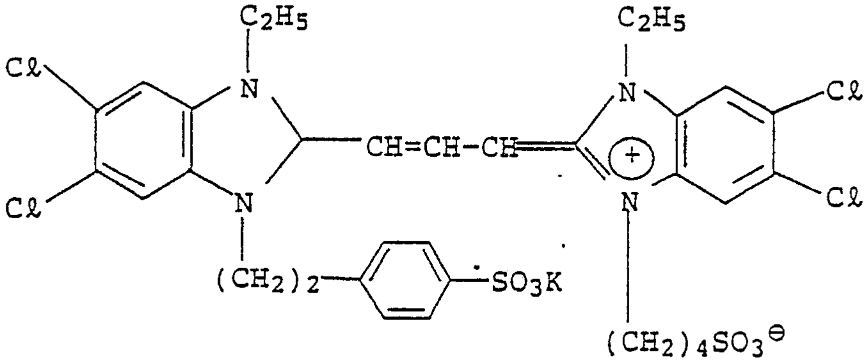

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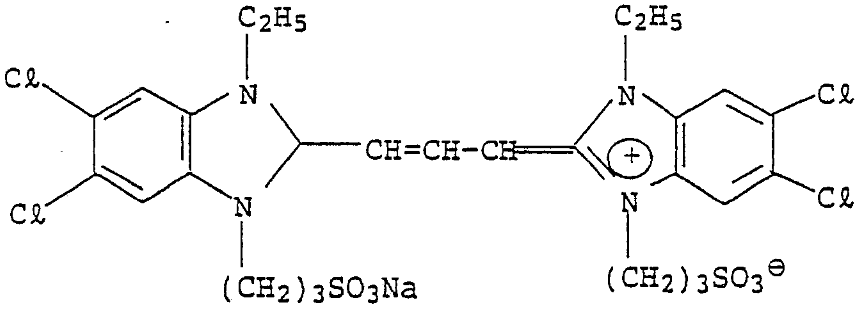

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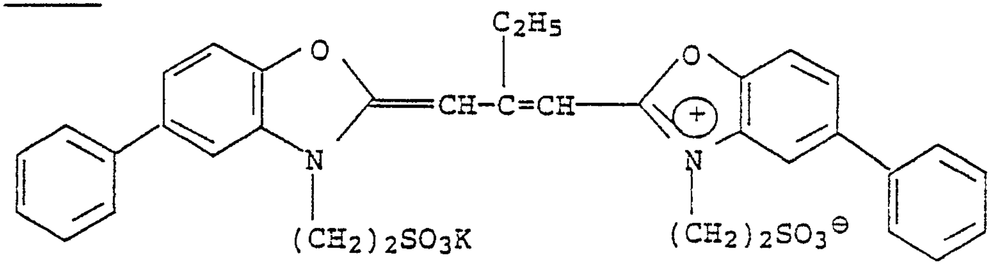

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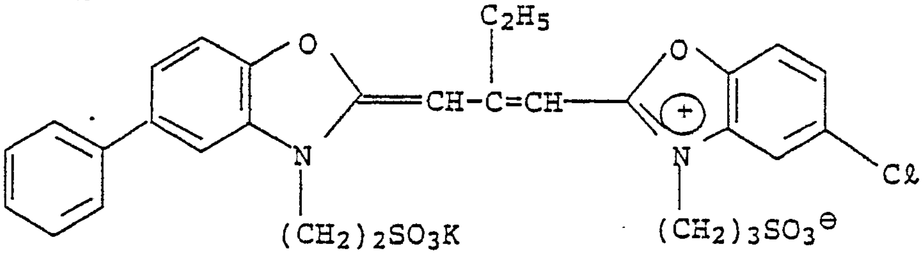

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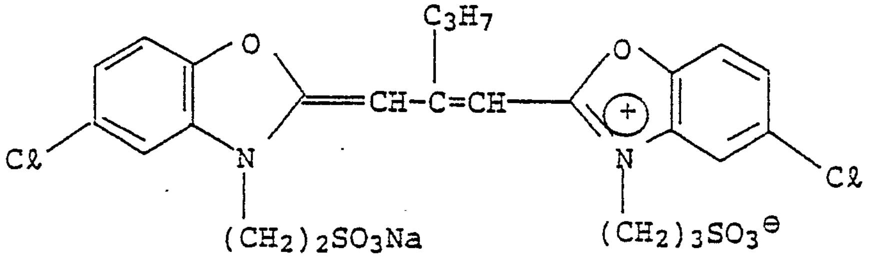

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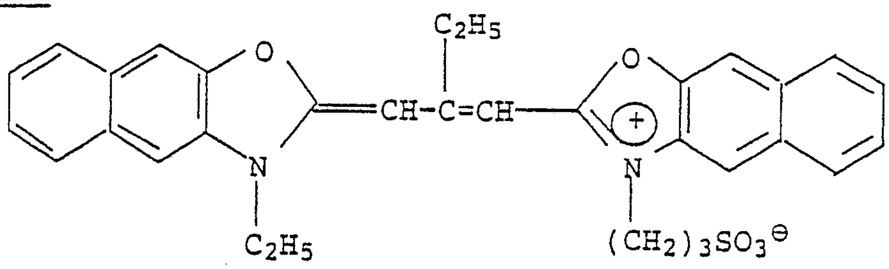

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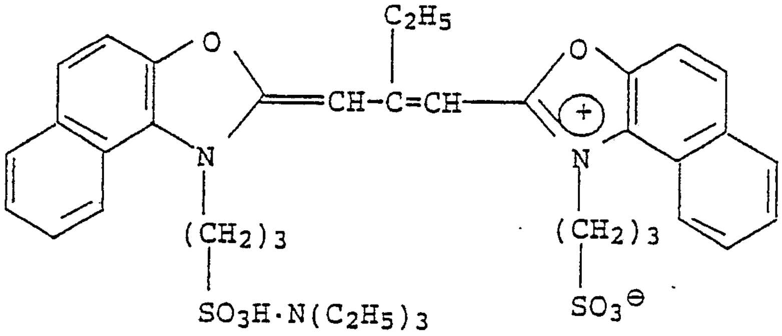

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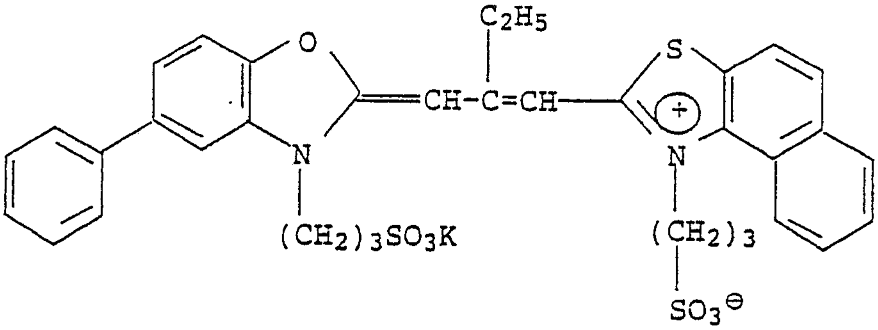

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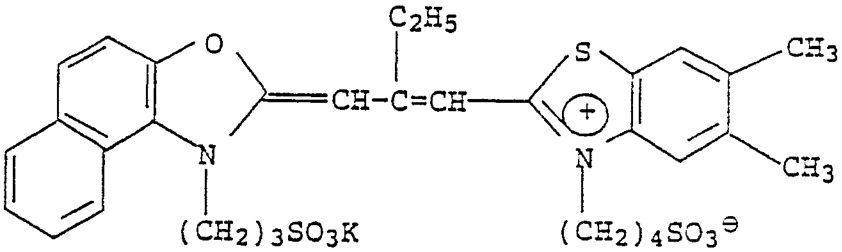

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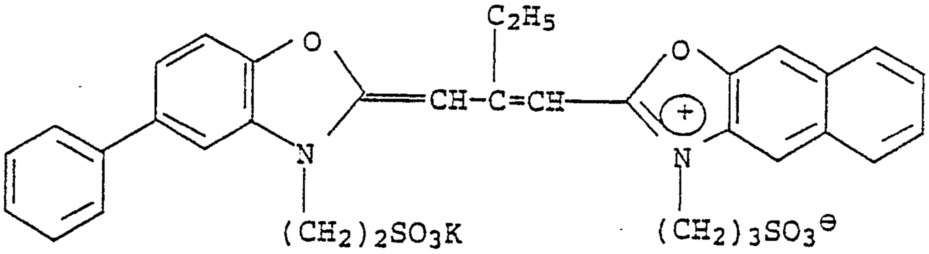

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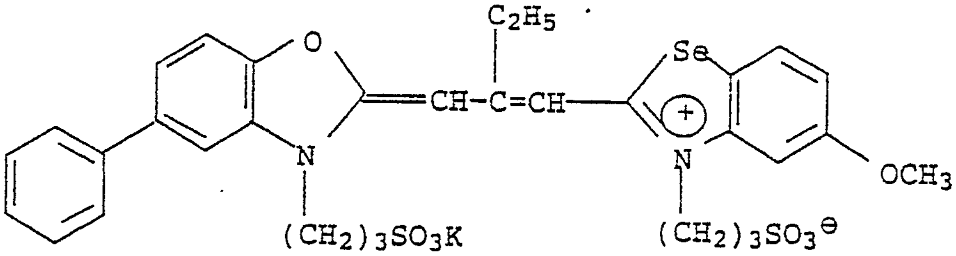

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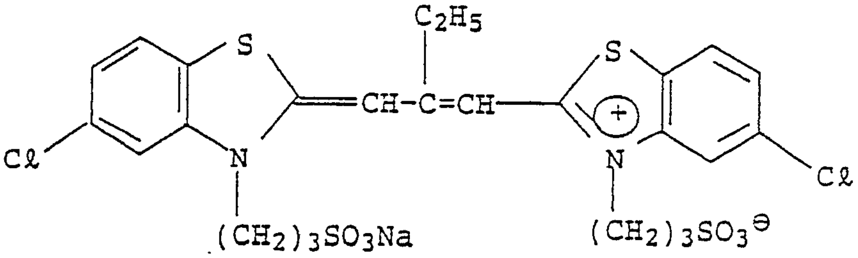

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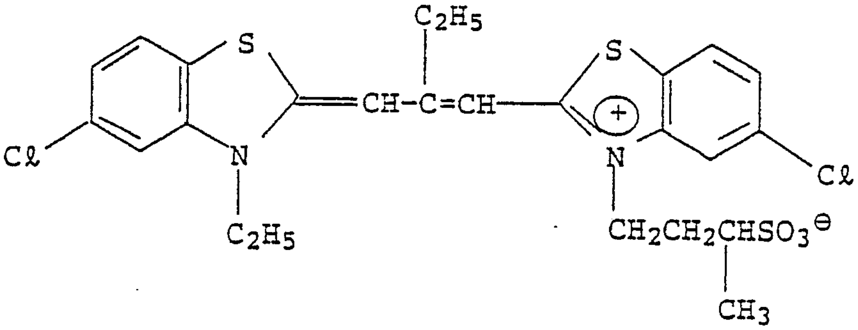

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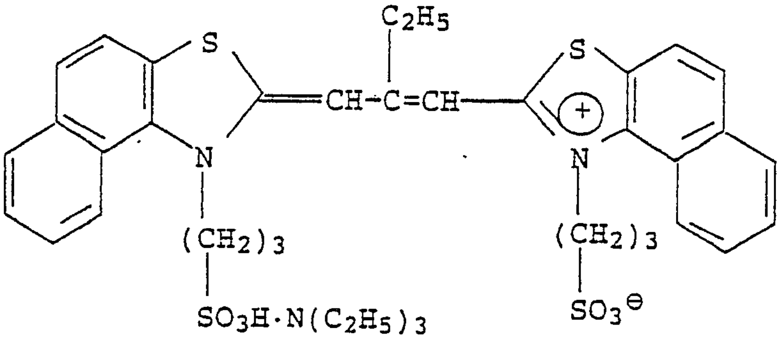

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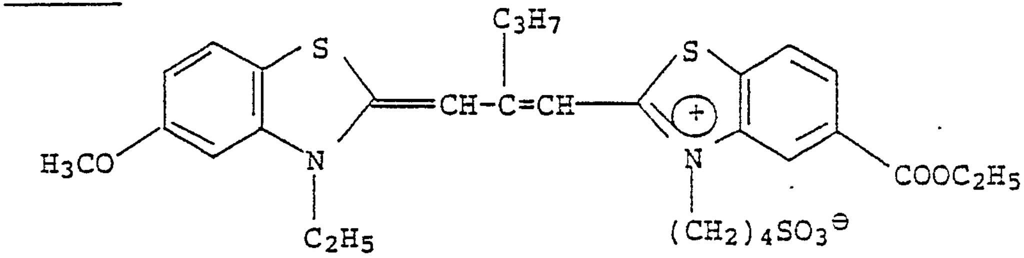

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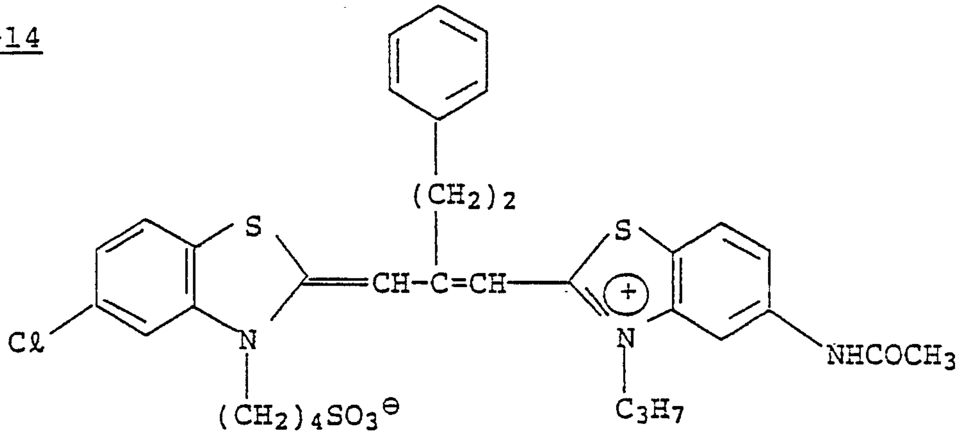

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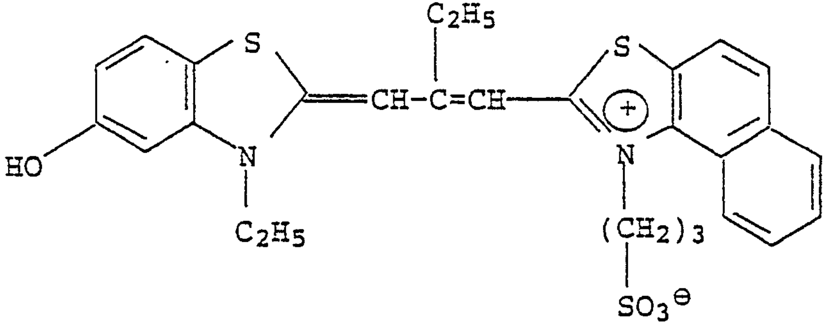

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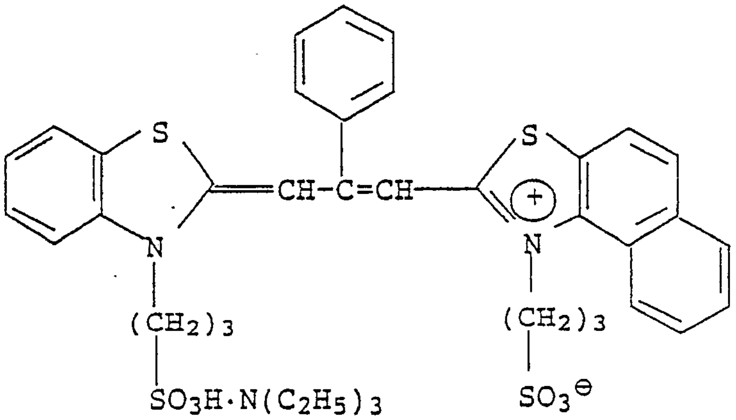

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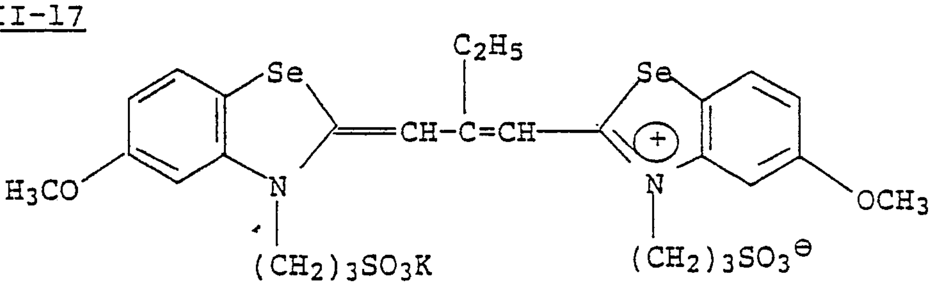

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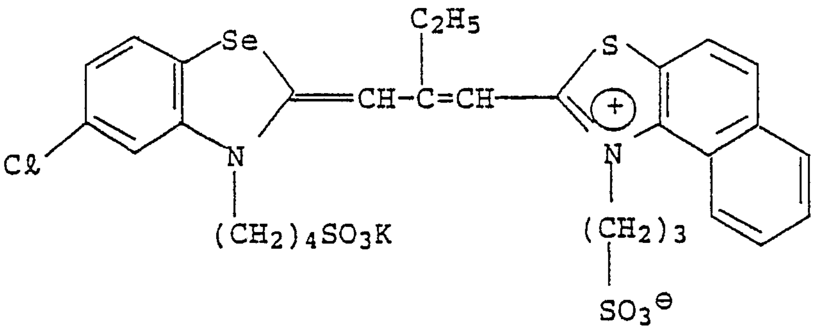

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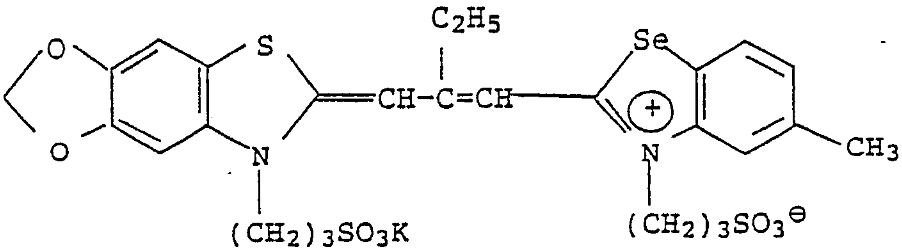
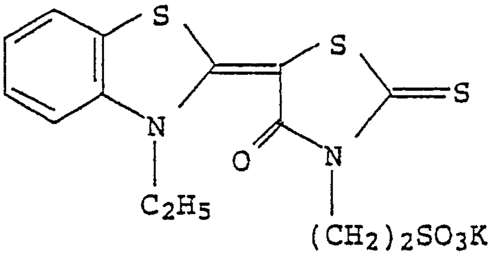
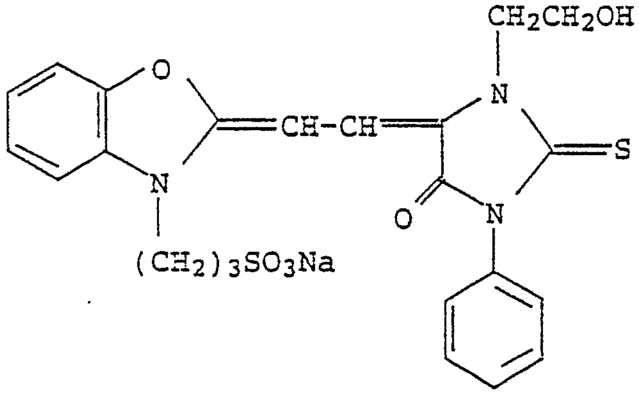
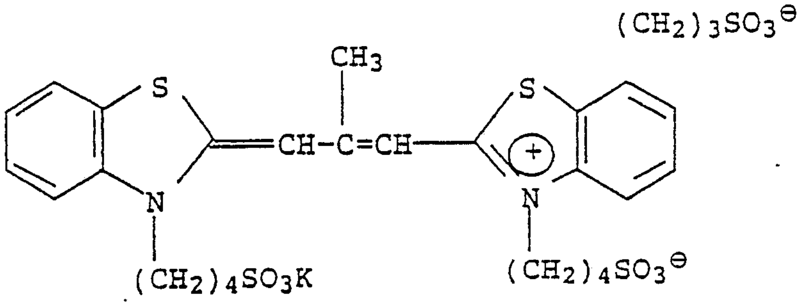


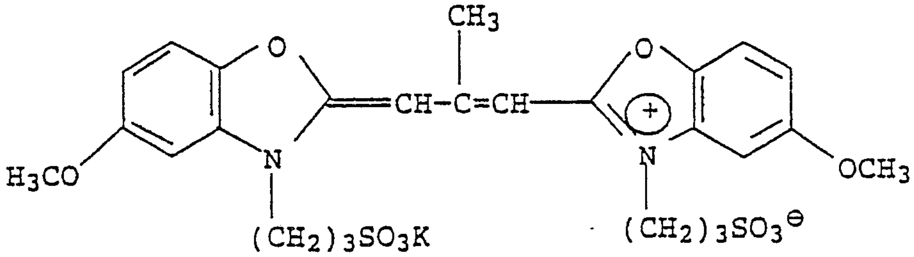
Preferred example of a supensitizer which can be used in the present invention include sensitizing dyes described in U.S. Patents 3,703,377, 2,688,545, 3,397,060, 3,615,635 and 3,628,964, British Patents 1,242,588 and 1,293,862, JP-B-43-4936, JP-B-44-14030 and JP-B_43-10773, U.S. Patent 3,416,927, JP-B-43-4930, U.S. Patents 3,615,613, 3,615, 632, 3,617,295 and 3,635,721; holopolar cyanine dyes described in British Patent 1,153,343, U.S. Patent 4,546,073, JP-A-59-148053; hemicyanines and hemicyanine bases described in U.S.Patent 4,152, 163, JP-B-49-17525 and JP-B-48-38406; and aminostyryl compounds described in British Patents 1,351,149, 1,230,449 and 1,310,994.

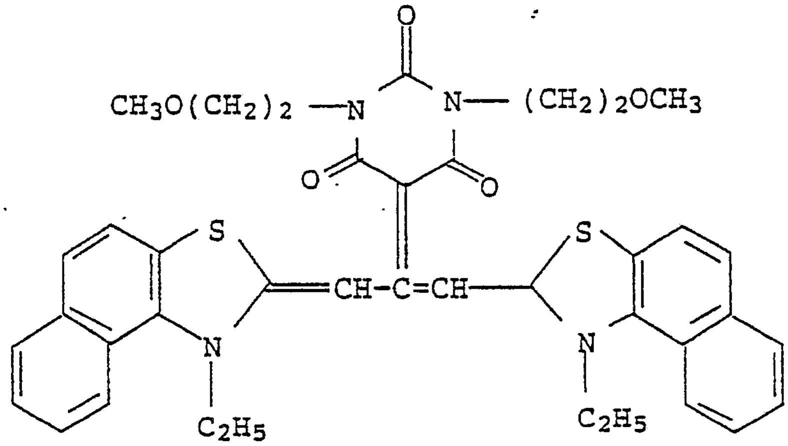
Specific examples of representative supersensitizers which are preferably used in the present invention include cyanine dyes cited above as the compounds forming a J-aggregate, which are represented by the foregoing general formulae (I), (II) or (III), the compounds illustrated below, and azole compounds represented by general formula (IV) described hereinafter, but the present invention is not be construed as being limited thereto.

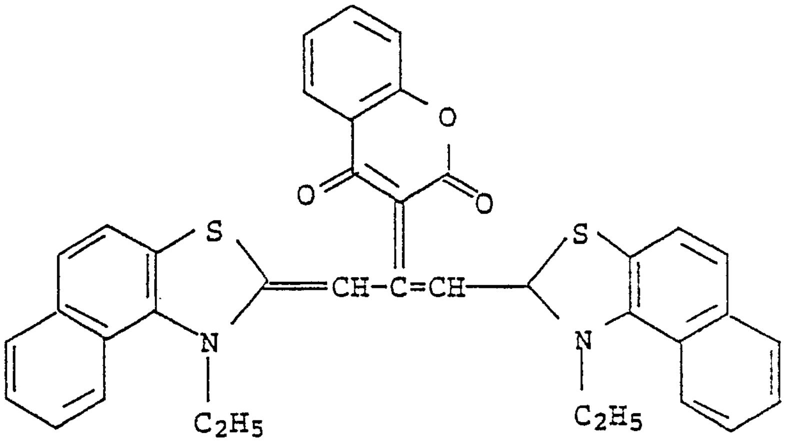


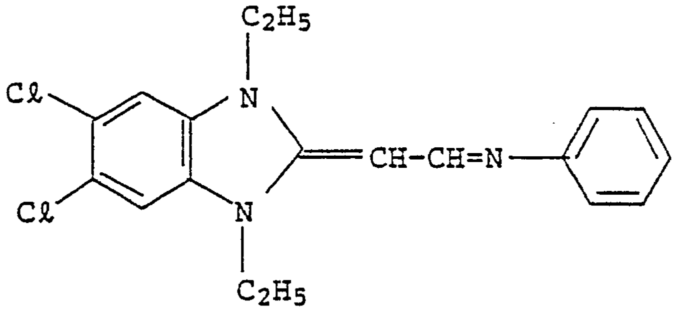


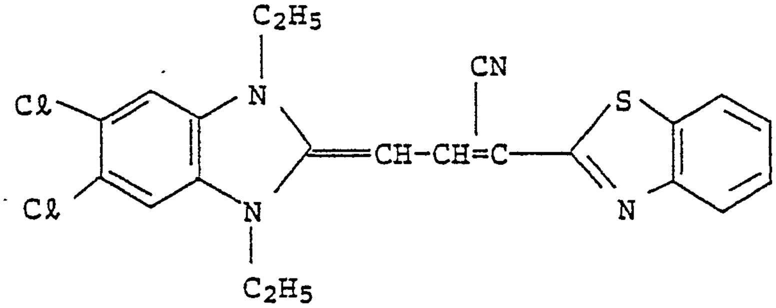

(CH2)3SO3⊖
CH3
S
CH-C=CH
S
+
N
N
(CH2)4SO3K
(CH2)4SO3⊖

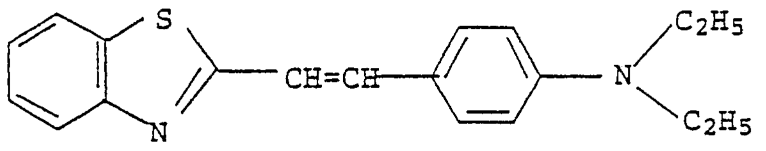

CH3
O
CH-C=CH
O
+
N
H3CO
N
OCH3
(CH2)3SO3K
(CH2)3SO3⊖

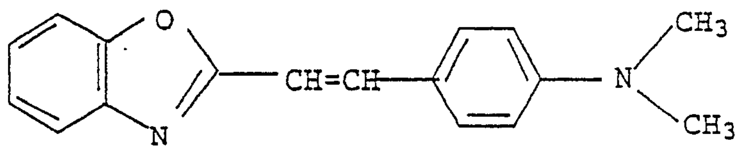

O
CH3O(CH2)2
N
N
(CH2)2OCH3
O
O
S
S
CH-C=CH
N
N
C2H5
C2H5

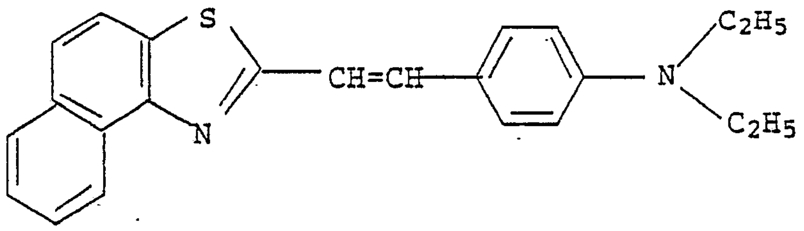


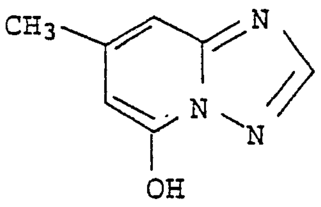


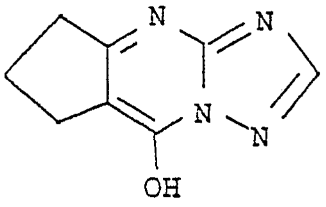


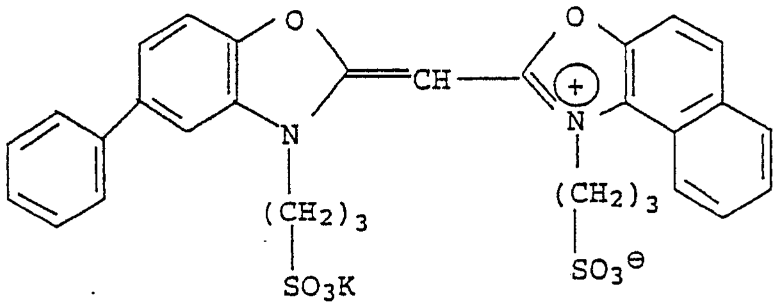












$$Z-SH \qquad (IV)$$

wherein Z represents a nitrogen-containing heterocyclic residue (preferably a 5- or 6-membered ring).

The heterocyclic group for Z may be a condensed ring, and preferably includes imidazole, triazole, tetrazole, thiazole, oxazole, selenazole, benzimidazole, benzoxazole, benzothiazole, thiadiazole, oxadiazole, benzoselenazole, pyrazole, pyrimidine, triazine, pyridine, naphthothiazole, naphthoimidazole, naphthoxazole, azabenzimidazole, purine, azaindene (e.g., triazaindene, tetraazaindene, pentaazaindene, etc.), and the like.

Further, these heterocyclic groups or condensed rings may be substituted with appropriate substituents. Examples of the substituents are an alkyl group (e.g., methyl, ethyl, hydroxyethyl, trifluoromethyl group, sulfopropyl, di-propylaminoehtyl, adamantane), an alkenyl group (e.g., allyl), an aralkyl group (e.g., benzyl, p-chlorophenetyl), an aryl group (e.g., phenyl, naphthyl, p-carboxyphenyl, 3,5-dicarboxyphenyl, m-sulfophenyl, p-acetamidophenyl, 3-capramidophenyl, p-sulfamoylphenyl, m-hydroxyphenyl, p-nitrophenyl, 3,5-dichlorophenyl, 2-methoxyphenyl), a heterocyclic group (e.g., pyridyl), a halogen atom (e.g., chlorine, bromine), a mercapto group, a cyano group, a carboxyl group, a sulfo group, a hydroxyl group, a carbamoyl group, a sulfamoyl group, an amino group, a nitro group, an alkoxy group (e.g., methoxy, ethoxy), an aryloxy group (e.g., phenoxy), an acyl group (e.g., acetyl), an acylamino group (e.g., acetylamino, capramido, methylsulfonylamino), a substituted amino group (e.g., diethylamino, hydroxyamino), an alkylthio or arylthio group (e.g., methylthio, carboxyethylthio, sulfobutylthio), an alkoxycarbonyl group (e.g., methoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), and the like.

The mercapto-containing compounds may be disulfides (Z-S-S-Z) that can be easily cleaved into the form of the formula (IV) in the emulsion.

Specific compounds represented by general formula (IV) include the compounds represented by general formula (1) described in JP-A-222843/85.

In addition, materials which can exhibit a supersensitizing effect in combination with sensitizing dyes although they themselves do not spectrally sensitize silver halide emulsions or do not absorb light in the visible region, for example, aminostilbene compounds substituted with nitrogen-containing heterocyclic groups (e.g., as described in U.S. Patents 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensates (e.g., U.S. Patent 3,743,510), cadmium salts, azaindene compounds and so on, can be employed as the supersensitizer of the present invention.

Sensitizing dyes and supersensitizers which can be used in the present invention can be synthesized according to methods described in F.M. Hamer, Heterocyclic Compounds - Cyanine Dyes and Related Compounds - (John Wiley & Sons, New York-London 1964), D.M. Sturmer, Heterocyclic Compounds - Special Topics in Heterocyclic Chemistry-, chapter 8, paragraph 4, pages 482-515 (John Wiley & Sons, New York-London 1977), and JP-A-60-78445.

The silver halide emulsion which can be used in the present invention is generally made by mixing a solution of a water-soluble silver salt (e.g., silver nitrate) with a solution of a water-soluble halide (e.g., potassium bromide) in the presence of a solution of a water-soluble high polymer, such as gelatin. The silver halide formed therein may be any of silver chloride, silver bromide, and mixed silver halides such as silver chlorobromide, silver iodobromide, silver chloroiodobromide and so on. The mean grain size thereof is preferably less than 4 microns. The term "mean grain size "as used herein refers to the grain diameter in case of grains spherical or approximately spherical in shape, while it refers to the edge length in case of cubic grains. In both cases, it is represented by the mean based on the projected areas of grains. The distribution of grain size may be narrow (monodisperse) or broad.

These silver halide grains may assume any crystal form, such as that of a cube, a tetradecahedron, a rhombic dodecahedron or an octahedron, a composite form of two or more thereof, a sphere, a plate, or so on.

Also, an emulsion in which silver halide grains having a tabular shape such that the grain diameter is 5 or more times the grain thickness are contained in a fraction of 50% or more, based on the total projected area, may be used. The preferred grain size of these grains ranges from 0.5 to 10 μm. (The term "grain size "as used herein refers to the diameter of a circle having the same area as the projected area of a grain, and the term thickness refers to the distance between two parallel faces.) Detailed descriptions are given, e.g., in JP-A 58-127921 and JP-A-58-113927.

The crystal structure of silver halide grains may be uniform throughout, or the silver halide grains may have a multilayer structure in which the interior and the surface of the grains differ in halide composition, or a conversion type structure described in British Patent 635,841, and U.S. Patent 3,622,318. Either silver halide grains of the kind which form latent image predominantly at the surface of the grains, or those of the kind which mainly form latent image inside the grains may be used.

Photographic emulsions which can be used in the present invention can be prepared using methods as described in P. Glafkides, Chimie et Physique Photographique, (Paul Montel 1967), G.F. Duffin, Photographic Emulsion Chemistry, (Focal Press 1966), and V.L. Zelikman et al., Making and Coating Photographic Emulsion, (Focal Press 1964).

More specifically, any of an acid process, a neutral process and an ammonia process can be employed for preparation of photographic emulsions. Suitable methods for reacting a water soluble silver salt with a water-soluble halide may be any of a single jet method, a double jet method and a combination thereof. Also, a method in which silver halide grains are produced in the presence of excess silver ion (the reverse mixing method) can be employed in the present invention. The controlled double jet method, in which the pAg of the liquid phase in which silver halide grains are precipitated is maintained constant, can be also employed. According to this method, a silver halide emulsion having a regular crystal form and grain sizes nearly uniform can be cbtained.

In a process of the formation or physical ripening of silver halide grains, a cadmium salt, a zinc salt, a lead salt, a thallium salt, a iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, an iron salt or a complex salt thereof, and the like may be present.

In order to control the crystal growth of silver halide grains in the step of forming silver halide grains, silver halide solvents, such as ammonia, potassium thiocyanate, ammonium thiocyanate, thioether compounds, thione compounds (e.g., those described in JP-A-53-144319, JP-A-53-82408 and JP-A-55-77737), amine compounds (e.g., those described in JP-A-54-100717) can be used.

While the silver halide emulsion can be employed without being chemically sensitized, that is to say, without being subjected to after-ripening (in the form of a primitive emulsion), it is preferably chemically sensitized. For the chemical sensitization, methods described in. H. Frieser, Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden, pp. 675-734, (Akademische Verlagsgesellschaft 1968) can be employed.

More specifically, sulfur sensitization methods using active gelatin, and compounds containing sulfur capable of reacting with silver ions (e.g., thiosulfates, thioureas, mercapto compounds, rhodanines and so on), reduction sensitization methods using reducing materials (e.g., stannous salts, amines, hydrazine derivatives, formamidine sulfinic acid, silane compounds and so on), noble metal sensitization methods using noble metal compounds (e.g., gold compounds, and complex salts of Group VIII metals such as platinum, iridium, palladium, etc.), and so on can be employed independently or as a combination thereof.

In addition, other sensitizers such as polyoxyethylene derivatives (as described in British Patent 981,470, JP-B-31-6475, U.S. Patent 2,716,062), polyoxypropylene derivatives, derivatives having a quaternary ammonium group, and so on may be employed.

The photographic emulsion employed in the present invention can contain a wide variety of compounds for purposes of preventing fog or stabilizing photographic functions during production, storage, or photographic processing, including azoles, such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, benzotriazoles, aminotriazoles; mercapto compounds, such as mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercapto-thiadiazoles, mercaptotetrazoles (especially 1-phenyl-5-mercaptotetrazole), mercaptopyrimidines, mercapto-triazines; thioketo compounds such as oxazolinethione; azaindenes, such as triazaindenes, tetraazaindenes (especially 4-hydroxy-substituted (1,3,3a,7)-tetraazaindenes), pentaazaindenes; and compounds which have been known as antifoggants or stabilizers, such as benzenethiosulfones, benzenesulfinic acid and benzenesulfonic acid amide.

More specific examples and usages of the above-cited compounds are disclosed in U.S. Patents 3,954,474 and 3,982,947, JP-B-52-28660.

As for the binder or the protective colloid which can be used in applying the silver halide emulsion, which is spectrally sensitized in accordance with the present invention, to a photosensitive material, gelatin can be used. Also, hydrophilic synthetic high polymers and the like can be used. Gelatin which can be used includes lime-processed gelatin, acid-processed gelatin, and derived gelatins. Such gelatins are described in Research Disclosure, Vol, 176, No. 17643, IX (Dec. 1976).

The spectrally sensitized silver halide emulsion of the present invention and the photographic light-sensitive material using the same may contain color image-forming couplers, that is to say, compounds capble of forming colors by color development processing by oxidative coupling with aromatic primary amine developing agents (e.g., phenylenediamine derivatives, aminophenol derivatives, etc.). Nondiffusible couplers which contain a hydrophobic group called a ballast group in a molecule, or polymeric couplers are preferred over others. These couplers may be either four-equivalent or two-equivalent to silver ion. In addition, the emulsion and the light-sensitive material may contain colored couplers having a color compensating effect, couplers capable of releasing a development inhibitor with the progress of development ("DIR couplers"), and couplers capable of releasing a development accelerator or a fogging agent ("DAR couplers" and "FR couplers"). Further, those may contain colorless DIR coupling compounds which can yield a colorless compound by the coupling reaction, that release a development inhibitor.

Suitable examples of magenta couplers include those of 5 pyrazolone type, pyrazolobenzimidazole type, cyanoacetylcumarone type, open-chain acylacetonitrile type, and pyrazoloazole type. Suitable examples of yellow couplers include those of acylacetamide type (such as benzoylacetanilides, pivaloylacetanilides). Suitable examples of cyan couplers include those of naphthol type, phenol type and the like.

In order to provide characteristics required of photosensitive materials, two or more of the above-described couplers can be incorporated in the same layer, or one of them can be added to two or more of different layers.

Compounds which can be additionally used in the silver halide emulsion prepared in accordance with the present invention, and in the photographic light-sensitive material using this emulsion include desensitizers, brightening agents, high boiling organic solvents (coupler solvents), dye-image stabilizers, stain inhibitors, absorbers (dyes, light absorbers and UV absorbers), hardeners, coating aids (surface active agents), plasticizers, lubricants, antistatic agents, matting agents, development accelerators, and so on. As for the additives described hereinbefore and these additives, those described in Research Disclosure, Vol. 176, No. 17643, I to XVI (pages 22 to 28) (Dec. 1978) can be used.

The finished emulsion is coated on an appropriate support such as baryta paper, resin-coated paper, synthetic paper, a triacetate film, a polyethylene tere phthalate film, another plastic base, or a glass plate. Various coating methods, including a dip coating method, an air knife coating method, a curtain coating method and an extrusion coating method utilizing a hopper as described in U.S. Patent 2,681,294, can be employed.

Such a support may be either transparent or opaque depending upon the intended use of the light-sensitive material. When a support used is transparent, it can be colorless or colored by addition of a dye or a pigment.

The exposure for obtaining a photographic image may be carried out in a conventional manner. Any pf various known light sources including natural light (sunlight), a tungsten lamp, a fluorescent lamp, a mercury lamp, a xenon arc lamp, a carbon arc lamp, xenon flash lamp, cathode ray flying spot and so on can be employed for the exposure. Suitable exposure times which can be used include not only exposure times commonly used in cameras ranging from about 1/1000 to about 1 sec., but also exposure times shorter than 1/1000 sec., e.g., about $1/10^4$ to about $1/10^6$, as used with xenon flash lamps and cathode-ray tubes. Exposure times longer than 1 second can also be used. The spectral distribution of the light employed for the exposure can be controlled using color filters, if desired. Laser beams can also be employed for the exposure. Moreover, the emulsion of the present invention may also be exposed to light emitted from phosphors excited by electron beams, X-rays, γ-rays, α-rays and the like.

Photographic light-sensitive materials to which the emulsion of the present invention can be applied include various color and black-and-white photosensitive materials. Specific examples of such materials include color negative films (for amateur use, motion picture use, etc.), color reversal films (for slide use, motion picture use, etc., which may be the coupler-in-emulsion type, or not), color photographic papers, color positive films (for motion picture use, etc.), color reversal photographic papers, heat-developable color photosensitive materials, color photosensitive materials for a silver dye bleach process, photographic light-sensitive materials for a photomechanical process (lith films, scanner films, etc.), X-ray photographic light-sensitive materials (for medical use employing radiography or fluorography, for industrial use, etc.), black and-white negative films, black-and-white photographic papers, microphotographic light-sensitive materials (COM, microfilms, etc.), color diffusion transfer photosensitive materials (DTR), silver salt diffusion transfer photosensitive materials, printout photosensitive materials, and so on.

In the photographic processing of a photosensitive material to which the silver halide emulsion prepared in accordance with the present invention is applied, any known processing method and any known processing solution can be employed. The processing temperature is generally in the range of about 18° C to about 50° C. Of course, temperatures lower than about 18° C or higher than about 50° C may be employed. The photographic processing may include either development processing for forming a silver image (black-and-white photographic processing) or development processing for forming a dye image (color photographic processing).

Specifically, the development processing can be performed using the methods described in Research Disclosure, Vol. 176, No. 17643, pages 28-29, and idi, Vol. 187, No. 18716, page 651, left and right columns.

The present invention is illustrated in greater detail by reference to the following examples. However, the invention is not to be construed as being limited to these examples. Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLE 1

Method 1 (Comparative example)

In a reaction container, 1,000 ml of water, 30 g of deionized bone gelatin, 15 ml of a 50 % NH_4NO_3 aqueous solution and 7.5 ml of a 25 % aqueous ammonia were placed, and kept at 50° C with thoroughly stirring. Thereto, 750 ml of a 1N $AgNO_3$ aqueous solution and a 1N KBr aqueous solution were added over a 40-minute period, and the silver potential relative to a saturated calomel electrode was kept at +50 mV all through the reaction.

The silver bromide grains obtained had a cubic form, and their edge length was 0.62±0.06 µm. The foregoing emulsion was desalted, and thereto were added 140 g of deionized bone gelatin and 700 ml of water. The resulting emulsion was adjusted to pH 6.5 and pAg 8.3 at 50° C (which was called Emulsion (1)-1).

This emulsion was divided into 7 fractions, and each was allowed to stand for 20 minutes at 40° C with thorough stirring in order to effect ripening. During the ripening, the sensitizing dye II-12 was added, in the form of $5x10^{-4}$, $1x10^{-3}$ and $2x10^{-3}$ mol/l of methanol solutions, to three of these fractions in amounts of $8.6x10^{-5}$ mol, $1.72x10^{-4}$ mol and $3.44x10^{-4}$ mol, respectively, per mol of silver, while the sensitizing dye II-12 and the sensitizing dye III-1 to function as a supersensitizer were added to the other four fractions in equimolar amounts of $4.3x10^{-5}$ mol, $8.6x10^{-5}$ mol, $1.72x10^{-4}$ mol and $3.44x10^{-4}$ mol, respectively, per mole of silver. To all of these fractions were further added 0.033 g of sodium 2-(N- methylstearoylamino)-ethylsulfonate, 0.016 g of sodium dodecylbenzenesulfonate and 0.784 g of 1,3-bis(vinylsulfonyl)-2-propanol. Each of the resulting emulsion fractions was coated on a cellulose triacetate film base at a coverage of 7 g/m^2 based on the silver bromide. Each of the coated emulsions was exposed to a tungsten lamp (color temperature: 2,854° K) through interference filters transmitting light of 400 nm, 541 nm and 571 nm, respectively, and a continuous wedge. The exposed emulsion coats were developed at 30° C for 10 minutes using the Developer D19 (comprising 2.2 g of Metol, 96 g of sodium sulfite, 8.8 g of hydroquinone, 48 g of sodium carbonate, and 5 g of potassium bromide in 1 liter of water).

In addition to sensitometric evaluation, the relative quantum yields of the spectral sensitization with the dye II-12 were determined as described in Tada-aki Tani & Hitoshi Urabe, Nippon Shashin Gakkai-Shi, volume 41, page 325 (1978). The results obtained are shown in Table 1.

Method 2 (comparative example)

Silver halide grains were formed in the same manner as in Method 1, except the methanol solution of sensitizing dye II-12 was added continuously at an uniform rate over a period from 4 minutes to 38 minutes after the start of the addition of the aqueous solution of silver nitrate. Therein, the amounts of the sensitizing dye II-12 added were $8.6x10^{-5}$ mol, $1.72x10^{-4}$ mol and $3.44x10^{-4}$ mol, respectively, per mol of silver. The silver bromide grains formed had a cubic form in every case, and edge lengths were 0.62±0.05 µm, 0.61±0.07 µm and 0.60±0.06 µm, respectively (These emulsions were named (2)-1, (2)-2 and (2)-3, respectively).

To each of the foregoing emulsions, 140 g of deionized gelatin and 700 ml of water were added after desalting and washing, and then each was adjusted to pH 6.5 and pAg 8.3. Thereafter, ripening was carried out at 40° C for 20 minutes with thorough stirring. During the ripening, sodium 2-(N-methylstearoylamino)-ethylsulfonate, sodium dodecyl-benzenesulfonate and 1,3-bis(vinylsulfonyl)-2-propanol were added to each emulsion. The resulting emulsions were each coated on a cellulose triacetate base film, exposed and developed in the same manner as used in Method 1.

The results obtained are also shown in Table 1.

Method 3 (Present invention)

The same experiments as in Method 2 were performed, except that the sensitizing dye III-1 to function as a supersensitizer was added at an uniform rate in the form of $2.5x10^{-4}$, $5x10^{-4}$ and $1x10^{-3}$ mol/l methanol solutions simultaneously with addition of the sensitizing dye II-12 in equimolar amounts.

The thus obtained silver bromide grains were also cubic in all cases, and edge lengths were 0.62±0.07 µm, 0.60±0.07 µmand 0.60±0.07 µm, respectively.

The results of the experiments are shown in Table 1.

Table 1

Experiment No.	Emulsion	Addn. Amt. of Dye II-12 mol/mol/ Ag	Addn. Amt. of Dye III-1 mol/mol/ Ag	Absorption Coefficient at 571 nm	Relative Sensitivity at 571 nm	Φr at 571 nm
1 (Comparison)	(1)-1	8.6×10^{-5}	0	0.288	100	0.48
2 (Comparison)	(1)-1	1.72×10^{-4}	0	0.410	96	0.43
3 (Comparison)	(1)-1	3.44×10^{-4}	0	0.547	56	0.49
4 (Comparison)	(1)-1	4.3×10^{-5}	4.3×10^{-5}	0.186	684	0.50
5 (Comparison)	(1)-1	8.6×10^{-5}	8.6×10^{-5}	0.277	703	0.46
6 (Comparison)	(1)-1	1.72×10^{-4}	1.72×10^{-4}	0.382	306	0.53
7 (Comparison)	(1)-1	3.44×10^{-4}	3.44×10^{-4}	0.467	272	0.66
8 (Comparison)	(2)-1	8.6×10^{-5}	0	0.226	22	0.07
9 (Comparison)	(2)-2	1.72×10^{-4}	0	0.345	27	0.11
10 (Comparison)	(2)-3	3.44×10^{-4}	0	0.510	20	0.19
11 (Invention)	(3)-1	4.3×10^{-5}	4.3×10^{-5}	0.211	765	0.50
12 (Invention)	(3)-2	8.6×10^{-5}	8.6×10^{-5}	0.328	1238	0.72
13 (Invention)	(3)-3	1.72×10^{-4}	1.72×10^{-4}	0.477	945	0.68
14 (Invention)	(29)-4	3.44×10^{-4}	3.44×10^{-4}	0.531	754	0.71

(The sensitivity was expressed as a reciprocal of the amount of exposure for the density of fog + 0.2 with the value of the emulsion of Experiment 1 being taken as 100)

As can be seen from the data set forth in Table 1, the values of sensitivity and Φr when where the exposure was carried out with light of 571 nm, at which the sensitizing dye II-12 exhibits its absorption maximum, were extremely low when the sensitizing dye II-12 forming the J-aggregate was added to an emulsion prior to completion of the formation of the silver halide grains (experiments 8 to 10), as compared with the case where the sensitizing dye was added after the completion of the grain formation (experiments 1 to 3). On the other hand, although the simultaneous addition of the sensitizing dye II-12 and the dye III-1 after the grain formation produced a supersensitizing effect (experiments 4 to 7), the simultaneous addition of these dyes prior to the completion of the grain formation in accordance with the present invention (experiments 11 to 14) achieved much higher sensitivities and/or higher Φr values.

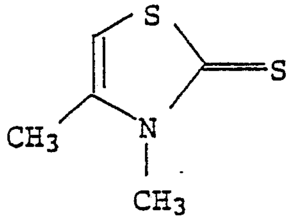
That is, the method of the present invention has proved excellent, since not only was the supersensitizing efficiency higher when the supersensitization was effected prior to the completion of the grain formation than when the supersensitization was carried out after the grain formation, but also very high sensitivity was attained in the former case.

EXAMPLE 2

Method 4 (Comparative example)

To an aqueous 3% gelatin solution which contained 1.6×10^{-4} mol/mol silver of the following compound (compound A);

Compound A



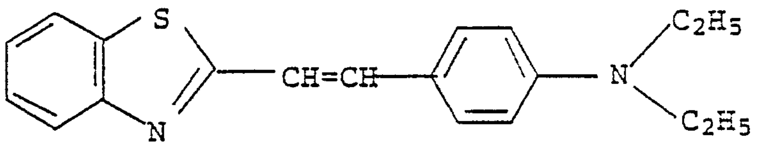
and was kept at 75° C, a 750 ml of 1N aqueous solution of silver nitrate and an aqueous solution containing a mixture of 0.98 mol of potassium bromide and 0.02 mol of potassium iodide in 1 liter of water were simultaneously added with thorough stirring at a constant rate over a period of 60 minutes as the silver potential in the reaction system was maintained constant (-90 mV vs a standard calomel electrode SCE). Thus, octahedral silver iodobromide grains having an iodide content of 2 mol% were formed. The resulting emulsion was desalted according to a conventional flocculation process, to prepare a photographic emulsion.

Therein, a methyl cellosolve 2.5×10^{-3} mol/l solution of the sensitizing dye 1-18 was further added in an amount of 7.2×10^{-4} mol per mol of silver over a period from 10 minutes after the start of the addition of the aqueous solution of silver nitrate to 5 minutes before the conclusion of the addition of the aqueous solution of silver nitrate. The mean grain size of the thus obtained silver halide grains was about 1.03 µm, and the variation coefficient was 8.9 %.

To the above emulsion, a water solution of $Na_3Au(S_2O_3)_3$ was added in an optimal amount, and aged at 50° C for 60 minutes to effect gold-sulfur sensitization. This emulsion was named (4)-1.

Method 5 (Present invention)

Two kinds of silver iodobromide grains were formed in the same manner as in Method 4, except a methyl cellosolve solution containing a mixture of the sensitizing dye I-18 and the following compound B,



B

instead of the sensitizing dye I-18 alone were added at a constant rate so that the total amount of the sensitizing dye I-18 added was 7.2x10^{-4} mol/mol Ag, and those of the compound B 7.2x10^{-5} mol/mol Ag and 2.1x10^{-4} mol/mol Ag, respectively. Then, in the same manner as Method 4, the resulting emulsions were desalted by a flocculation process, and subjected to gold-sulfur sensitization at 50°C by adding an optimal amount of a water solution of $Na_2Au(S_2O_3)_3$. These emulsions were named (5)-1 and (5)-2, respectively.

The mean grain size of each of the two kinds of octahedral silver iodobromide grains formed was about 1.04 μm (and the variation coefficients were 13.5% and 13.9%, respectively).

After addition of 100 g of 10% gelatin gel, the emulsion (4)-1 obtained according to Method 4 was divided into three fractions, and thereto compound B was added at 40°C in amounts of 0, 7.2x10^{-5} mol and 2.1x10^{-4} mol, respectively, per mole of silver. To these emulsions, and to those obtained by further adding 100 g of 10% gelatin gel to the emulsions (5)-1 and (5)-2, respectively, were added successively 4-hydroxy-6-methyl-(1,3,3a,7)-tetraazaindene in an amount of 0.2 g per Kg of emulsion, sodium 2-hydroxy-4,6-dichloro-l,3,5-triazine in an amount of 1.0 g per Kg of emulsion, and sodium dodecylbenzenesulfonate in an amount of 0.1 g per Kg of emulsion. Each of the resulting emulsions was coated in an amount of 3.7 g (as Ag)/m^2 on a polyethylene terephthalate film base to prepare a photographic light-sensitive material.

In coating the above-described emulsion, an aqueous solution containing 5.0 wt% of gelatin as a main component and 0.02 wt% of sodium dodecylbenzenesulfonate (a surface active agent), and 0.057 wt% of sulfostyrene potassium homopolymer (a viscosity-increasing agent) as additives was coated simultaneously on top of the emulsion layer. The gelatin coverage of the thus-formed protective layer was about 1.0 g/m^2.

Each of the coated samples was exposed to a tungsten lamp (color temperature: 2854°K) through interference filters capable of transmitting light of 545 nm and 400 nm, respectively, which corresponded to the absorption maxima of main absorption peaks in the distribution of spectral sensitization, and a continuous wedge. The exposed samples were developed at 20°C for 7 minutes using a developer prepared by diluting the following concentrated liquid developer with an equal volume of water.

Composition of Concentrated Liquid Developer

Water	700 ml
Metol (p-methylaminophenol sulfate)	3.1 g
Anhydrous Sodium Sulfite	45 g
Hydroquinone	12 g
Sodium carbonate (monohydrate)	79 g
Potassium Bromide	1.9 g
Water to make	1 ℓ

The results obtained are shown in Table 2 together with relative quantum yields, Φr, of the spectral sensitization with the dye I-18. The relative quantum yields Φr were determined by the same method in Example 1.

Table 2

Experiment Number	Emulsion	Addition Amount of Compound B mol/mol Ag	Absorption Coefficient at 545 nm	Relative Sensitivity at 545 nm	at Φr 545 nm
1 (Comparison)	(4)-1	-	0.573	100	0.32
2 (Comparison)	(4)-1	7.2×10^{-5}	0.565	214	0.68
3 (Comparison)	(4)-1	2.1×10^{-4}	0.462	151	0.72
4 (Invention)	(5)-1	7.2×10^{-5}	0.608	265	0.80
5 (Invention)	(5)-2	2.1×10^{-4}	0.532	201	0.85

Though compound B had a supersensitizing effect on the sensitizing dye I-18 in all the experiments, the spectrally sensitizing effect was enhanced to a greater extent by adding both compounds before the completion of the grain formation of silver halide in accordance with the present invention.

In another experiment where the emulsion was prepared in the same manner as in Method-4, except the sensitizing dye I-18 was not added during the grain formation of silver halide, but it was added in the same amount during a period after the gold-sulfur sensitization and before the coating, was employed, Φr was 0.36 and the relative sensitivity to light of 545 nm was 112.

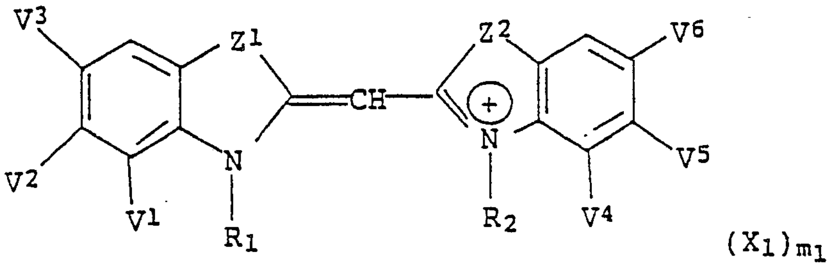
According to the method of the present invention, not only can the relative quantum yield of spectral sensitization Φr be heightened, but also high spectral sensitivities can be achieved over the main portion of the spectral sensitization range, which is important in practical use. The present method is unexpectedly superior to a spectral sensitization method in which a sensitizing dye is added to an emulsion during a period after the grain formation and before the coating, or a spectral sensitization method in which a sensitizing dye forming the J-aggregate is added during the grain formation, while another supersensitizing sensitizing dye is added after the grain formation and before the coating.

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.

Claims

1. A method for producing a spectrally sensitized silver halide photographic emulsion comprising the step of forming silver halide grains in the presence of at least one J-aggregated cyanine dye and at least one supersensitizer

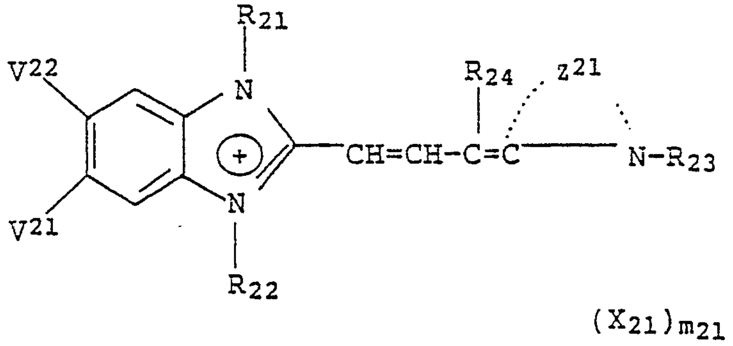
2. The method as claimed in claim 1, wherein said J-aggregated cyanine is represented by formula (I):



(I)

wherein Z^1 represents oxygen, sulfur, selenium, or -CH=CH-; Z^2 represents sulfur, selenium, or -CH=CH-; R_1 and R_2, which may be the same or different, each represents an unsubstituted or substituted alkyl group; V^1 represents hydrogen or an atomic group necessary for forming a condensed benzene ring with V^2; V^4 represents hydrogen or an atomic group necessary for forming a condensed benzene ring with V^5; V^2, V^3, V^5 and V^6, which may be the same or different, each represents a straight-chain or branched chain alkyl group containing at most 5 carbon atoms, an alkoxy group containing at most 4 carbon atoms, a hydroxyl group, an acylamino group containing at most 4 carbon atoms, an unsubstituted or substituted phenyl group containing at most 8 carbon atoms, a halogen atom, an alkoxycarbonyl group containing at most 5 carbon atoms, a carboxyl group or hydrogen, provided that V^3 may be linked with V^2 to form a condensed benzene ring and V^5 may be linked with V^5 to form a condensed benzene ring; m· is 0 or 1: and X· represents a counter ion necessary for charge balance.

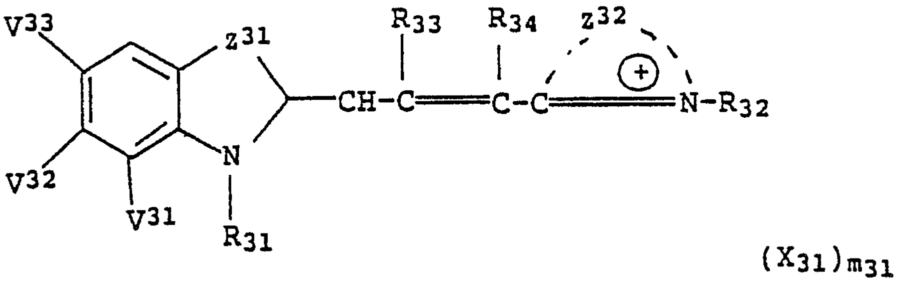
3. The method as claimed in claim 1, wherein said J-aggregated cyanine dye is represented by formula (II):



(II)

wherein Z^{21} represents an atomic group necessary for forming an unsubstituted nucleus selected from 4-thiazoline, thiazolidine, benzo-4-thiazoline, naphtho[1,2-d]-4-thiazoline, naphtho[2,3-d]-4-thiazoline, selenazolidine, 4-selenazoline, benzo-4-selenazoline, naphtho[1,2,-d]-4-selenazoline, naphtho[2,3-d]-4-selenazoline, benzo-4-oxazoline, naphtho[1,2-d]-4-oxazoline, naphtho[2,3-d]-4- oxazoline and benzo-4-imidazoline nucleus; R_{21}, R_{22} and R_{23}, which may be the same or different, each represents an unsubstituted or substituted alkyl group; R_{24} represents hydrogen or atomic group necessary for forming a 5-membered or 6-membered ring in combination with R_{23}; V^{21} represents an electron attracting group; V^{22} represents an electron attracting group, hydrogen or an atomic group necessary for forming a condensed benzene ring in combination with V^{21}; m_{21} is 0 or 1: X_{21} is a counter ion necessary for charge balance.

4. The method as claimed in claim 1, wherein said J-aggregated cyanine dye is represented by formula (III):



(III)

wherein Z^{31} represents oxygen, sulfur or selenium ; Z^{32} represents an atomic group necessary for forming a nucleus selected from thiazole, benzothiazole, naphtho[1,2-d]thiazole, 8,9-dihydronaphtho[1,2-d]thiazole, naphtho[2,3-d]-thiazole, selenazole, benzoselenazole, naphtho[1,2-d]-selenazole, benzoxazole, naphtho[1,2-d]oxazole, or naphtho[2,3-d]oxazole; R_{31} and R_{32}, which may be the same or different, each represents ethyl, propyl, butyl, phenyl or phenetyl;' R_{33} represents ethyl, propyl, butyl, phenyl, or phenetyl; V^{31} represents a hydrogen atom or an atomic group necessary for forming a condensed benzene ring with V^{32}; V^{32} and V^{33}, which may be the same of different, each represents a straight-chain or branched-chain alkyl group containing at most 5 carbon atoms, an alkoxy group containing at most 4 carbon atoms, a hydroxyl group, an acylamino group containing at most 4 carbon atoms, an unsubstituted or substituted phenyl group containing at most 8 carbon atoms, a halogen atom, an alkoxycarbonyl group containing at most 5 carbon atoms, a carboxyl group or hydrogen; provided that V^{32} and V^{33} may be linked to form a 5-membered or 6 membered ring; R_{34} represents a hydrogen atom, or an atomic group necessary for completing a 5- or 6-membered ring in combination with R_{32}; m_{31} is 0 or 1 and X_{31} represents a counter ion necessary for charge balance.

5. The method as claimed in claim 3, wherein said electron attracting group represented by V^{21} and V^{22} is selected from fluorine, chlorine, a cyano group, an alkoxycarbonyl group containing at most 4 carbon atoms and an alkylsulfonyl group containing at most 4 carbon atoms.

6. The method as claimed in claim 4, wherein R_{33} represents ethyl.

7. The method as claimed in claim 2, wherein said substituted alkyl group represented by R_1, and R_2 is substituted with a substituent selected from a lower alkyl group, a halogen atom, a carbamoyl group, a carboxyl group, an alkoxycarbonyl group, an acylamino group, a hydroxyl group, a sulfo group and a substituted phenyl group.

8. The method as claimed in claim 3, wherein said substituted alkyl group represented by R_{21}, R_{22} and R_{23} is substituted with a substituent selected from a lower alkyl group, a halogen atom, a carbamoyl group, a carboxyl group, an alkoxycarbonyl group, an acylamino group, a hydroxyl group, a sulfo group and a substituted phenyl group.

9. The method as claimed in claim 4, wherein said substituted alkyl group represented by R_{31}, and R_{32} is substituted with a substituent selected from a lower alkyl group, a halogen atom, a carbamoyl group, a carboxyl group, an alkoxycarbonyl group, an acylamino group, a hydroxyl group, a sulfo group and a substituted phenyl group.

10. The method as claimed in claim 1, wherein said silver halide grains comprise from about $1x10^{-6}$ to $5x10^{-3}$ mol of each of said sensitizing dye and said supersensitizer per mol of said silver halide.

11. The method as claimed in claim 1, wherein said silver halide grains comprise from about $1x10^{-5}$ to $2.5x10^{-3}$ mol of each of said sensitizing dye and said supersensitizer per mol of said silver halide.

12. The method as claimed in claim 1, wherein said J-aggregated cyanine dye and said supersensitizer are present at the beginning of grain formation.

13. The method as claimed in claim 1, wherein said J-aggregated cyanine dye and said supersensitizer are each added to an aqueous solution containing at least one water-soluble silver salt and at least one water-soluble halide salt during grain formation.

14. The method as claimed in claim 13, wherein at least one-half of said J-aggregated cyanine dye and at least one-half of said supersensitizer are simultaneously added during grain formation.

15. The method as claimed in claim 13, wherein at least two-thirds of said J-aggregated cyanine dye and at least two-thirds of said supersensitizer are simultaneously added during grain formation.

16. The method as claimed in claim 15, wherein the total amounts of said J-aggregated cyanine dye and said supersensitizer are simultaneously added during grain formation.