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(54) Color photographic light-sensitive material.

(57) A silver halide color photographic light-sensitive material is disclosed. The material comprises a support, and, coated thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer, each layer containing a sensitizing dye, wherein the maximum sensitivity wavelength λ Rmax, maximum sensitivity SRmax and sensitivity at 610 nm SR_{610} of the red-sensitive emulsion layer and the maximum sensitivity wavelength λ Gmax, maximum sensitivity SGmax, and sensitivity at 545 nm SG_{545} of the green-sensitive emulsion layer satisfy the following requirements:

$$590 \text{ nm} \leq \lambda \text{ Rmax} \leq 625 \text{ nm},\ SR_{610} \geq 0.8SRmax$$
$$520 \text{ nm} \leq \lambda \text{ Gmax} \leq 570 \text{ nm},\ SG_{545} \leq 0.8SGmax$$

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COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic material, more specifically to a silver halide color photographic material capable of forming color photographic images which offers excellent color reproduction even under various conditions with different light sources.

BACKGROUND OF THE INVENTION

In recent years there have been noticeable image quality improvements in silver halide multiple-layered color photographic light-sensitive materials. Specifically, all of the three major factors of image quality, i.e., graininess, sharpness and color reproduction have reached a fair level. For example, prints and slide photographs obtained by users in ordinary color photography do not appear to be significantly unsatisfactory.

However, with respect to one of the three factors, namely color reproduction, there have been no significant improvements in the color reproduction of those colors which have conventionally been said to be difficult to reproduce photographically, though there have been improvements in color purity.

In other words, much remains unsatisfactory as to hue reproducibility. For example, the colors such as purple and bluish purple which reflect light of wavelengths longer than 600 nm and the green colors such as bluish green and yellowish green are sometimes reproduced into colors by far different from the original color, which may disappoint the user. Spectral sensitivity distribution and interlayer effect (interimage effect) have been reported as the major factors associated with color reproduction.

With respect to the interimage effect, it is effective on the improvement in color reproducibility parameters, particularly color purity, in silver halide multiple-layered color photographic light-sensitive materials. To obtain an interimage effect are available the recently commonly used method using a so-called diffusible DIR, which offers high mobility for inhibitor or its precursor, and the method which provides an effect similar to the interimage effect by using a colored coupler in an amount more than the amount to compensate the undesirable absorption in the case of color negative films.

However, when using a large amount of a colored coupler, the minimum film density increases and it becomes very difficult to make a proper judgment for printing color density correction, which may often result in print color quality degradation. In addition, the interimage effect is difficult to control with respect to its orientation, and is faulty in that it causes a hue change, though it offers an increased color purity. Control of interimage effect orientation is described in US Patent No. 4,725,529, for instance.

To solve these problems, there has been proposed a method based on a combination of spectral sensitivity distribution and interimage effect, which is disclosed in Japanese Patent Publication Open to Public Inspection No. 34541/1986, for instance.

In these proposals, an attempt has been made to improve hue reproduction for the above-mentioned colors which are difficult to reproduce using color films, and it appears effective to some extent. In a typical example of this method, it is intended to obtain an interimage effect not only from the major wavelength for each of the blue-, green-and red-sensitive layers as conventional but also from a wavelength other than the major wavelength of each color-sensitive layer.

This method appears to be effective to some extent in the improvement of hue reproduction for some colors. However, to ensure the interimage effect, an interimage effect ensuring layer and another kind of light-sensitive silver halide are needed in addition to the essential blue-, green- and red-sensitive layers. In addition, increases in the coating amount of silver and the number of production processes pose a problem of high production cost, and the obtained effect is not fully satisfactory.

On the other hand, to improve the color reproducibility, consideration must be given to minimization of hue change in color reproduction among light sources used in taking pictures.

With respect to this kind of problems, much attention has been paid to color reproducibility fluctuation due to changes in light source color temperature. As a means of solving this problem, US Patent No. 3,672,898, for instance, discloses an appropriate spectral sensitivity distribution to mitigate color reproducibility fluctuation among light sources used in taking pictures.

These approaches are based on the reduction in sensitivity fluctuation in each layer in relation to light source color temperature changes in taking pictures by approximating the spectral sensitivity distribution of the blue- and red-sensitive layers to that of the green-sensitive layer. In this case, however, color purity degradation occurs because the spectral sensitivity distributions overlap each other due to approximation of the three color-sensitive layers. In this regard, color purity degradation can be prevented to some extent by enhancing the interimage effect using a so-called diffusible DIR or another appropriate means as commonly known.

It was found, however, that even any combination of the methods described above offers nothing more than extremely unsatisfactory color reproduction in the case of picture taking under fluorescent lamp or under mixed light of strobe light and fluorescent lamp. Specifically, when using a fluorescent lamp light source alone or even when using strobe light under the influence of a fluorescent lamp, the reproduced colors tend to be greenish, particularly the reproduced skin color lacks liveliness.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a color photographic light-sensitive material with high sensitivity which offers exact color reproduction not only under daylight picture taking conditions but also under fluorescent lamp picture taking conditions.

DETAILED DESCRIPTION OF THE INVENTION

The present inventors made intensive investigations and found that the object of the invention described above can be accomplished by a silver halide color photographic light-sensitive material having at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer on the support, wherein the maximum sensitivity wavelength λR_{max}, maximum sensitivity SR_{max} and sensitivity at 610 nm SR_{610} of the red-sensitive emulsion layer and the maximum sensitivity wavelength λG_{max}, maximum sensitivity SG_{max} and sensitivity at 545 nm SG_{545} of the green-sensitive emulsion layer satisfy the following requirements:

$$590\text{nm} \leqq \lambda R_{max} \leqq 625\text{nm} \quad SR_{610} \geqq 0.8\ SR_{max}$$

$$520\text{nm} \leqq \lambda G_{max} \leqq 570\text{nm} \quad SG_{545} \leqq 0.8\ SG_{max}$$

The present invention is hereinafter described in more detail.

With respect to color reproduction in picture taking under different kinds of light sources, focus of discussion has been placed on light source color temperature, and a large number of proposals have been made for technical improvements. In recent years, however, there have been frequent occurrence of troubles in picture taking under fluorescent lamp lighting as fluorescent lamps have become commonly used lighting equipment in daily life.

A typical claim is that pictures taken in the presence of fluorescent lamp light are so greenish that the face of a person photographed lacks liveliness. This was found to be due to the spectral distribution of fluorescent lamp light consists of two components, one having a continuous smooth curve in the visible region and the other having a bright line (characteristic curve) in a particular wavelength region, and is sensed as strongly greenish, less reddish by color films while being felt white by human eyes. On a related note, there are numerous kinds of fluorescent lamps, and the so-called three-wavelength fluorescent lamp, which has recently gained wide popularity as ordinary household appliance, was found to expand the color shift described above in color photography because of the great contribution of the bright line.

The present inventors found that the problem described above can be well overcome by setting the spectral sensitivity distribution at a minimum density (D_{min}) + 0.3 so that the green- and red-sensitive layers fall in the relationship described in the claim of the invention.

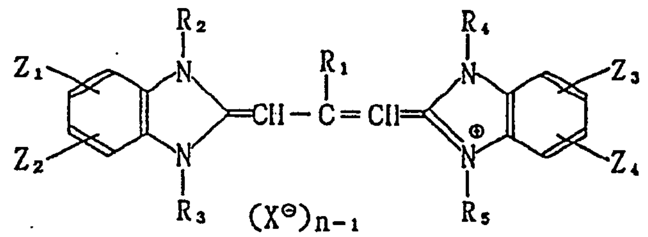
In a preferred mode of the present invention, it is more preferable that the sensitivity at 610 nm, SR_{610} exceed 90% of the maximum spectral sensitivity, SR_{max} in the spectral sensitivity distribution $SR(\lambda)$ of the red-sensitive layer at a density of D_{min} + 0.3.

Also, to efficiently obtain the desired spectral sensitivity, it is preferable to adsorb the sensitizing dyes of the present invention contained in the green- and red-sensitive layers upon the chemical sensitization of the silver halide.

To obtain the spectral sensitivity distribution in the red-sensitive layer of the present invention, various means can be used, including the use of a spectral sensitizing dye. This constituent can be obtained by a combination of at least one sensitizing dye represented by the formula I and at least one sensitizing dye represented by the formula III, and the sensitizing dye represented by the formula I is used in an amount of 10 to 90 mol%, preferably 60 to 90 mol%, based on the total amount of dyes used. It is also possible to combine at least one of the formula I, at least one of the formula II and at least one of the formula III.

The sensitizing dyes represented by formulas I, II and III are described below.

Formula I



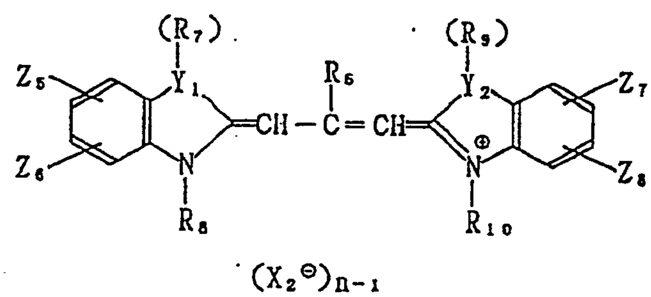
wherein R_1 represents a hydrogen atom, an alkyl group or an aryl group; R_2, R_3, R_4 and R_5 independently represent an alkyl group or an aryl group.

Z_1, Z_2, Z_3 and Z_4 independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group or a sulfonyl group.

Z_1 and Z_2 and/or Z_3 and Z_4 respectively may link together to form a ring.

X_1^- represents an anion. n represents the integer 1 or 2; when the sensitizing dye forms an intramolecular salt, n represents 1.

Formula II

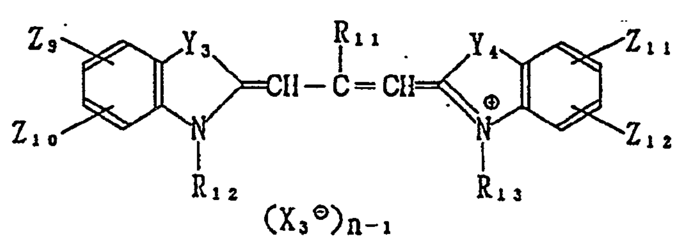


wherein R_6 represents a hydrogen atom, an alkyl group or an aryl group; R_7, R_8, R_9 and R_{10} independently represent an alkyl group or an aryl group.

Y_1 and Y_2 independently represent a nitrogen atom, an oxygen atom, a sulfur atom or a selenium atom; when Y_1 is a sulfur atom, an oxygen atom or a selenium atom, it does not have the above R_7. Also, both Y_1 and Y_2 do not represent a nitrogen atom or a sulfur atom.

Z_5, Z_6, Z_7 and Z_8 independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group, or a sulfonyl group. Z_5 and Z_5 and/or R_7 and R_8 respectively may link together to form a ring. Also, $X_2^{\ominus}$ represents an anion. n represents the integer 1 or 2; when the sensitizing dye forms an intramolecular salt, n represents 1.

Formula III

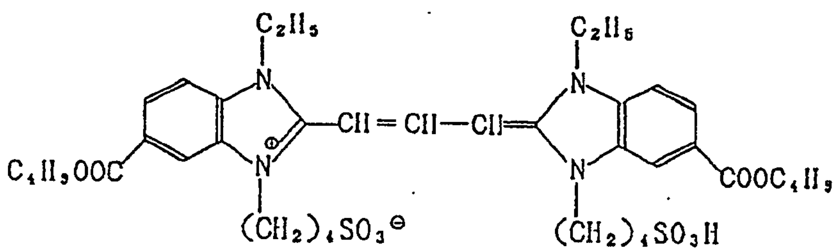


wherein R_{11} represents a hydrogen atom, an alkyl group or an aryl group; R_{12} and R_{13} independently represent an alkyl group or an aryl group. Also, Y_3 and Y_4 independently represent a sulfur atom or a selenium atom.

Z_9, Z_{10}, Z_{11} and Z_{12} independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a sulfonyl group, a carbamoyl group, an aryl group, an alkyl group or a cyano group. Z_9 and Z_{10} and/or Z_{11} and Z_{12} respectively may link together to form a ring. $X_3^{\ominus}$ represents an anion. n represents the integer 1 or 2; when the sensitizing dye forms an intramolecular salt, n represents 1.

Typical examples of the sensitizing dyes represented by formulas I, II and III are given below.

(I－1)



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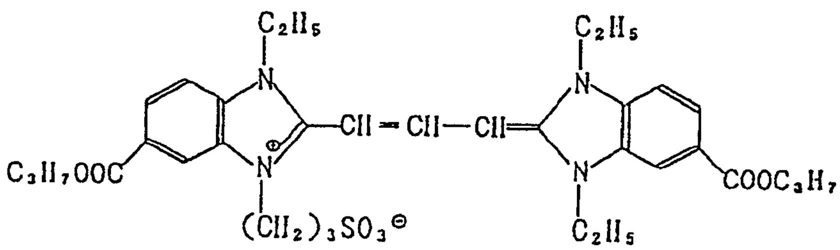

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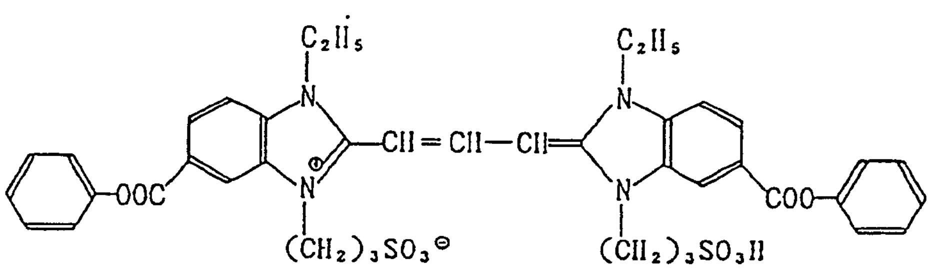

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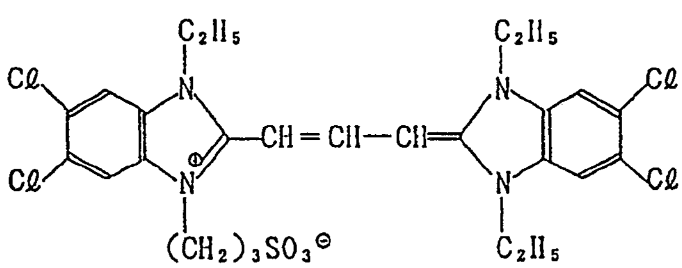

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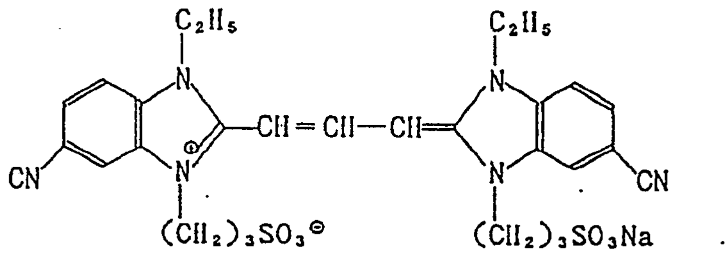

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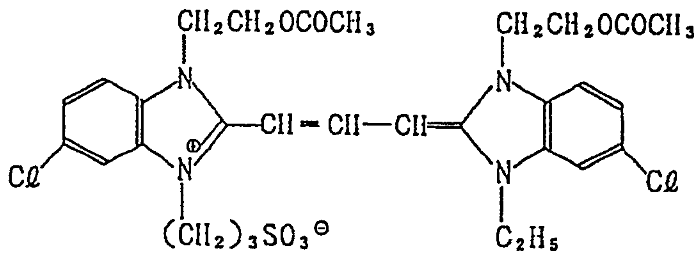

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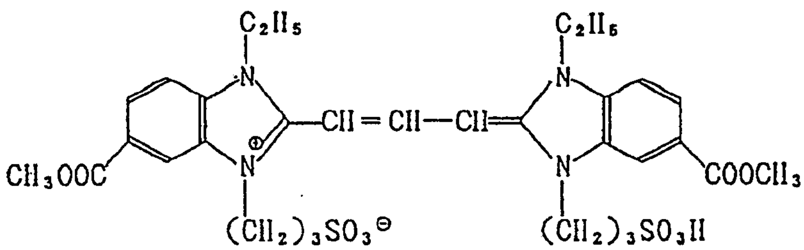

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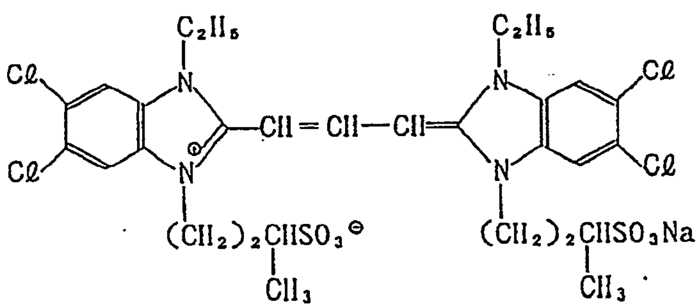

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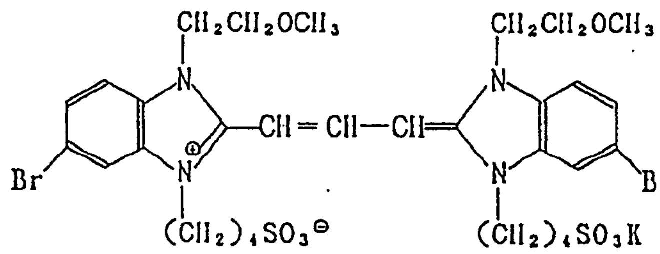

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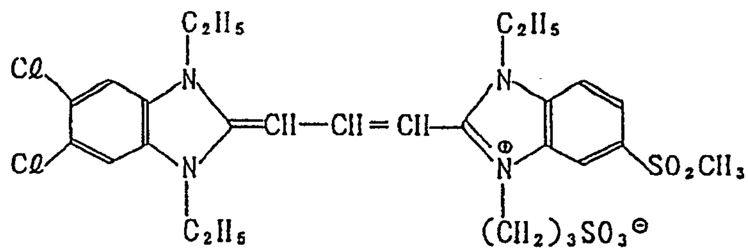

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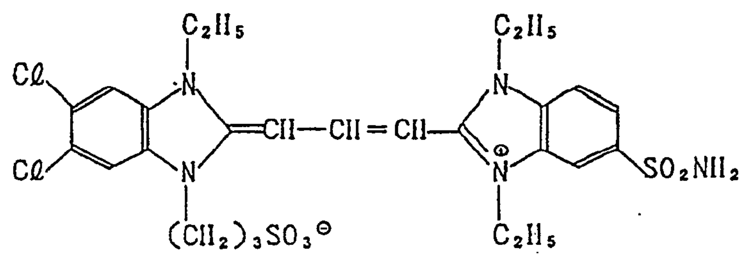

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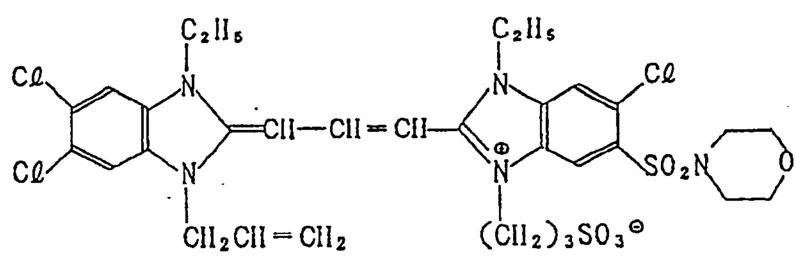

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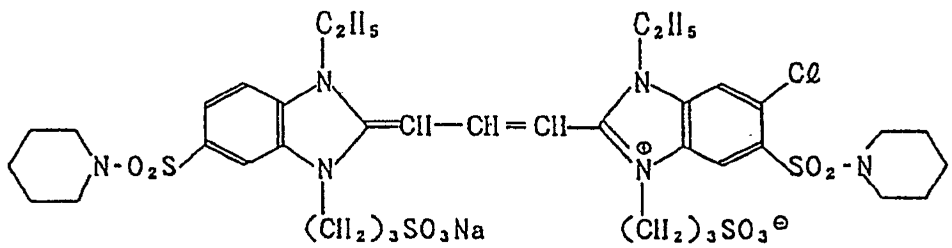

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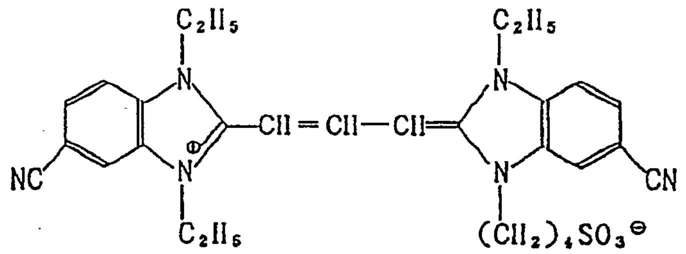

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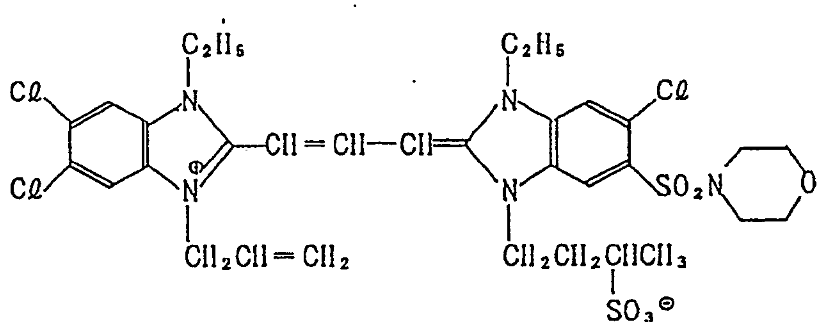

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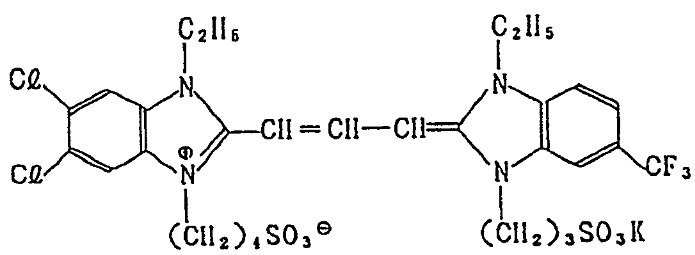

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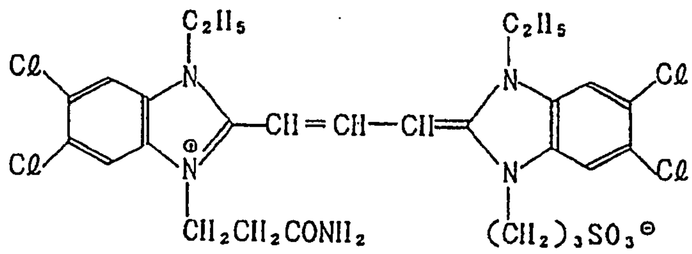

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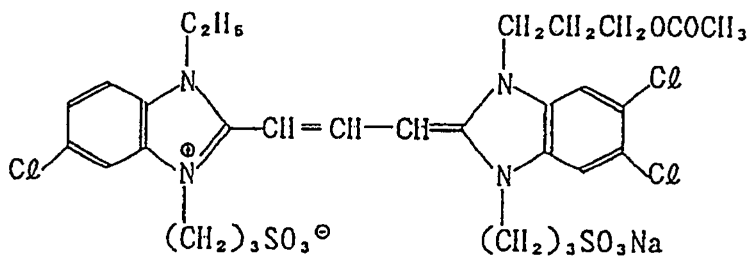

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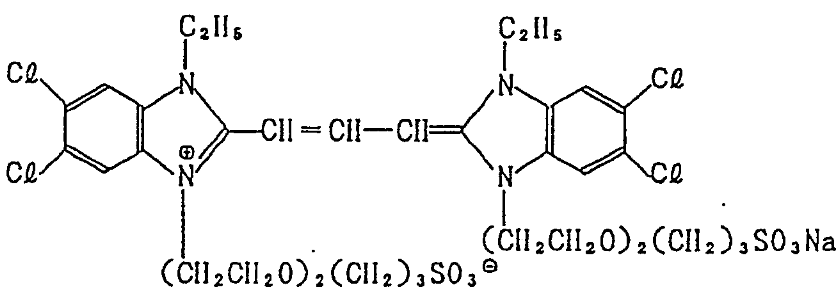

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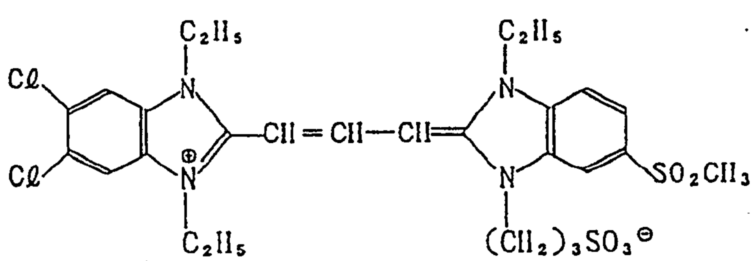

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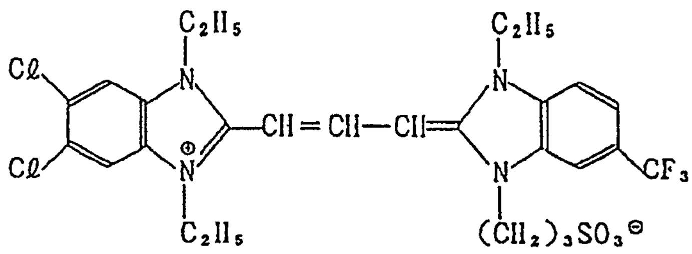

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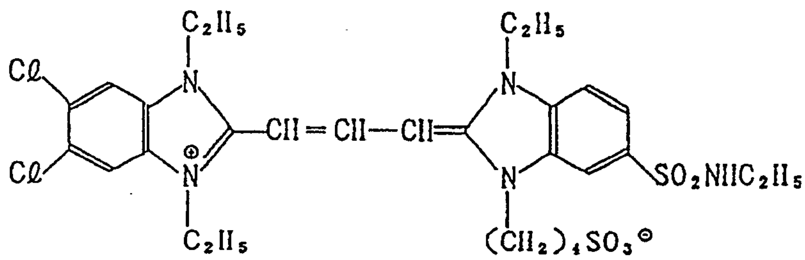

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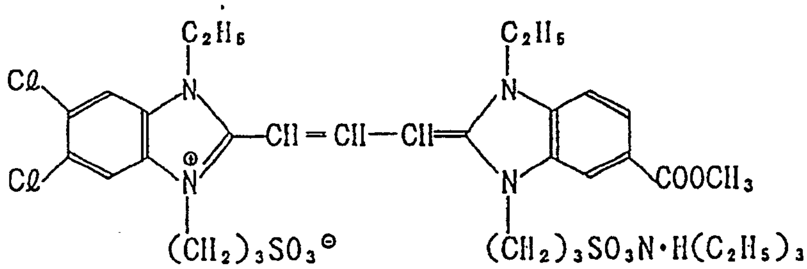

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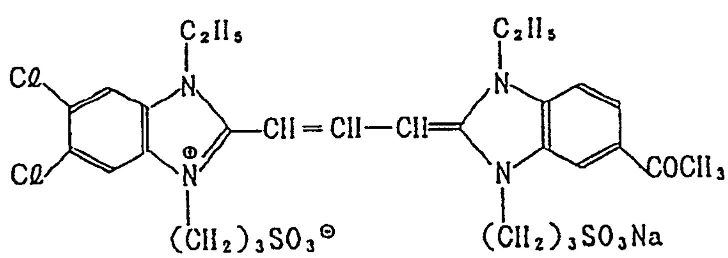

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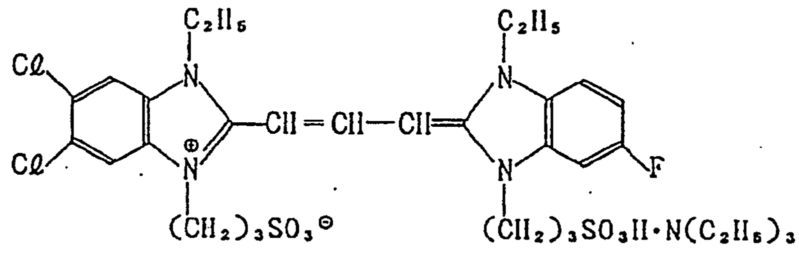

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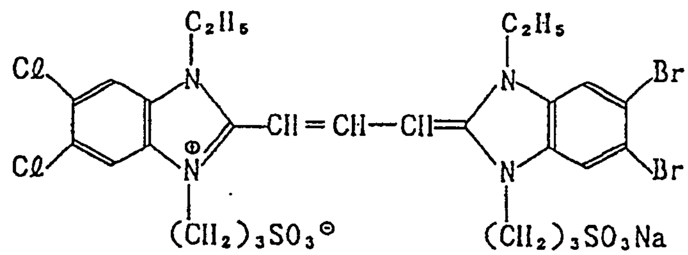

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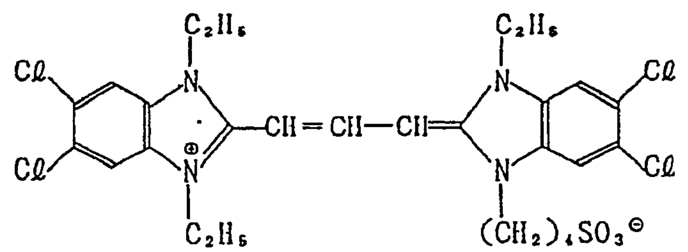

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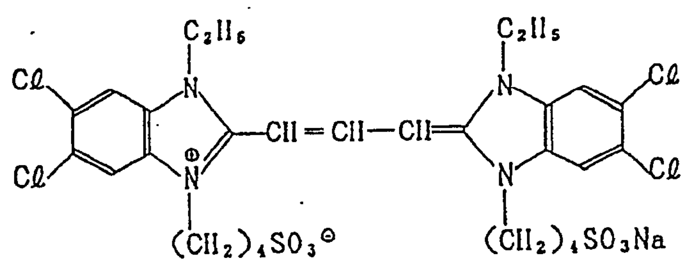

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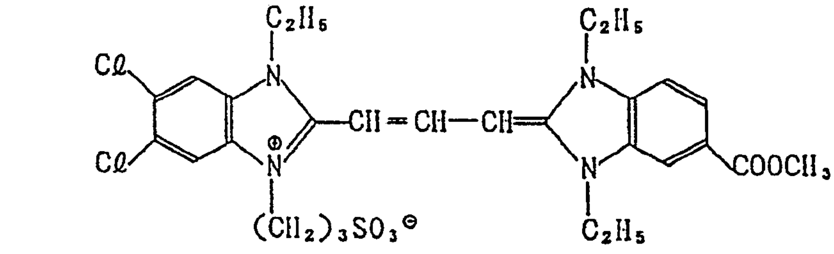

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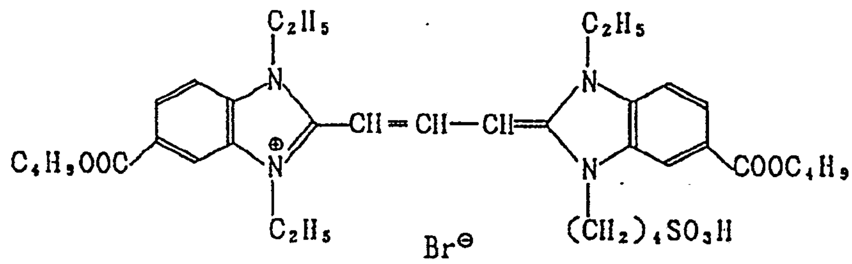

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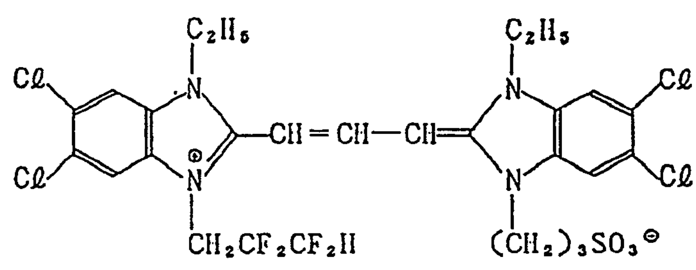

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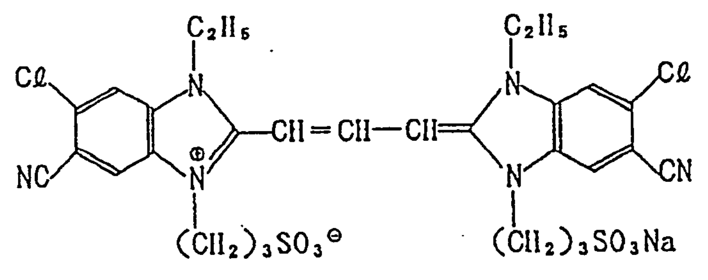

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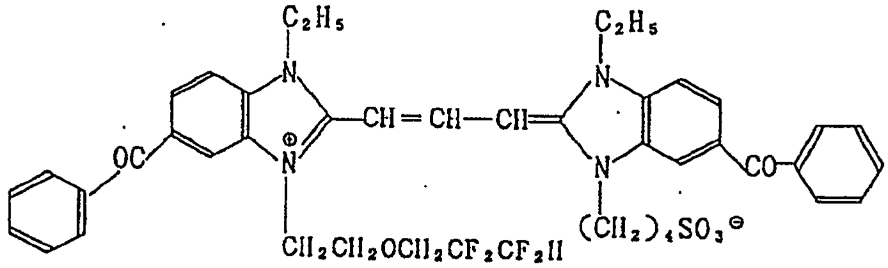

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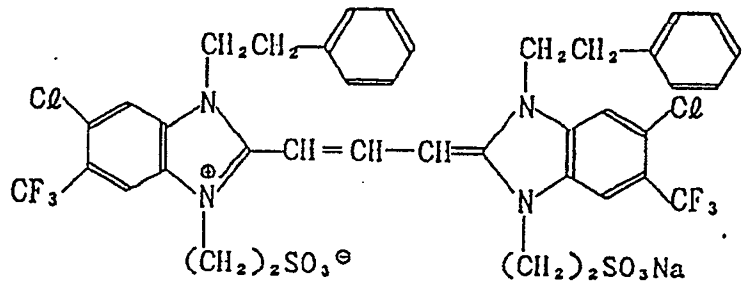

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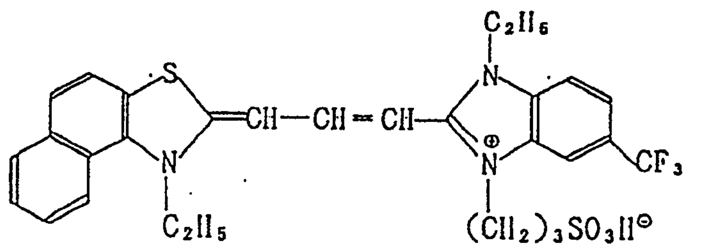

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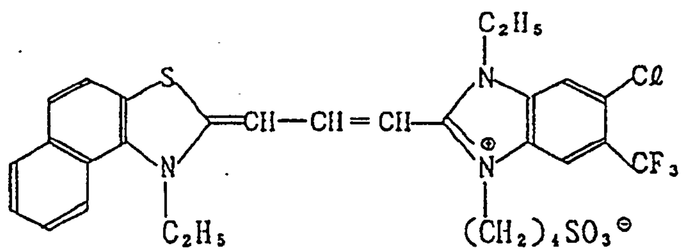

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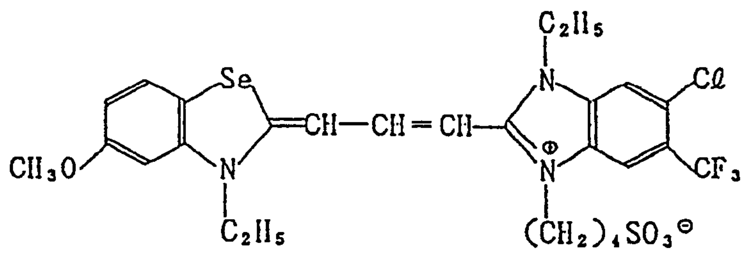

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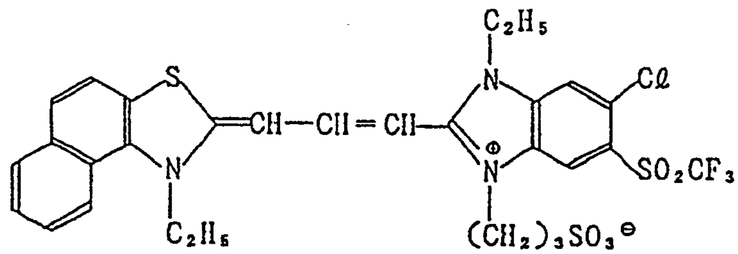

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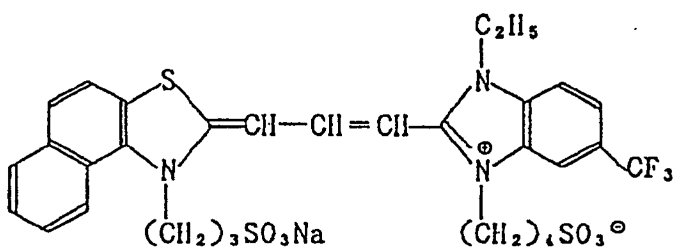

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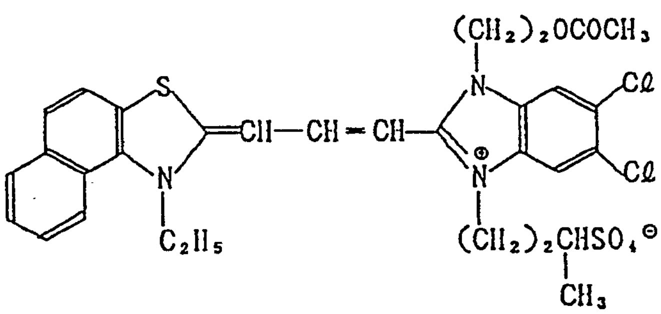

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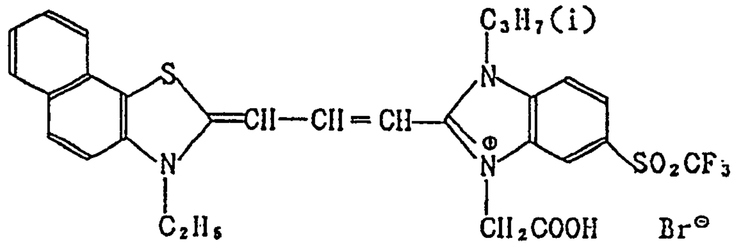

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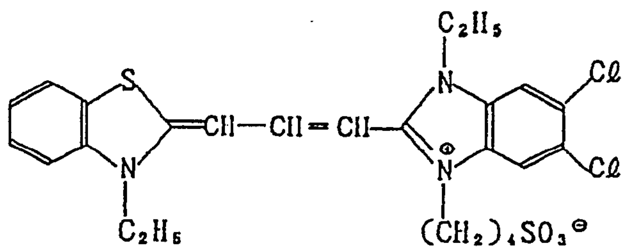

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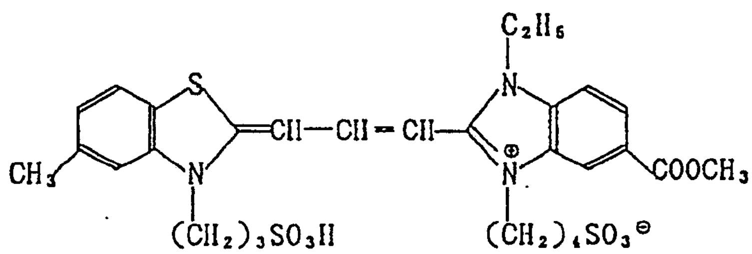

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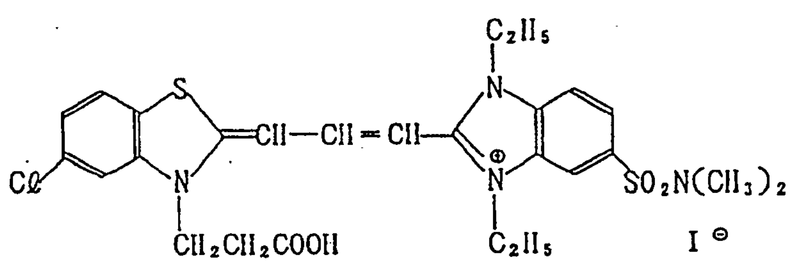

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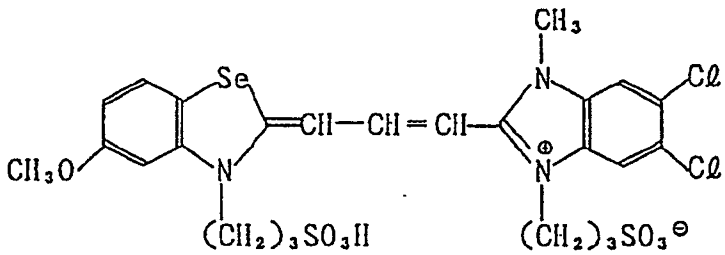

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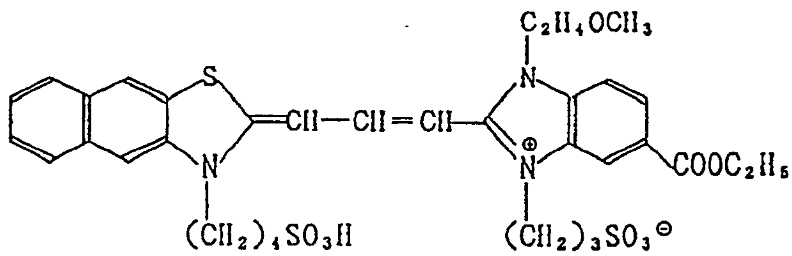

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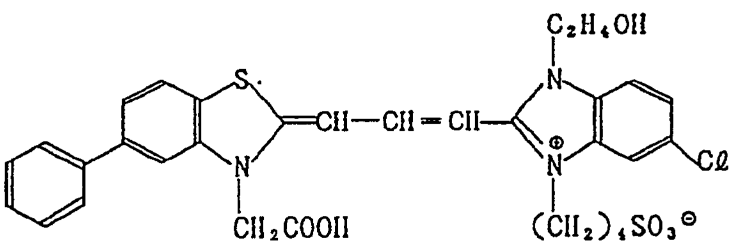

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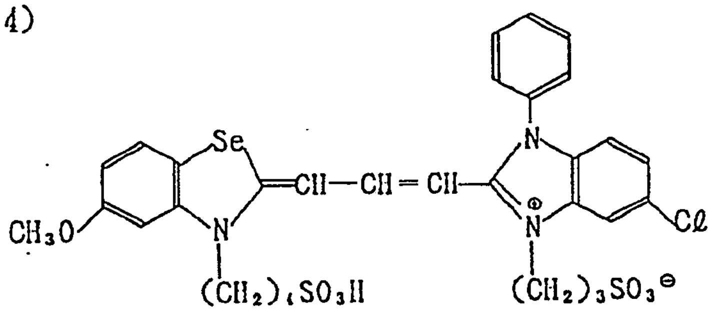

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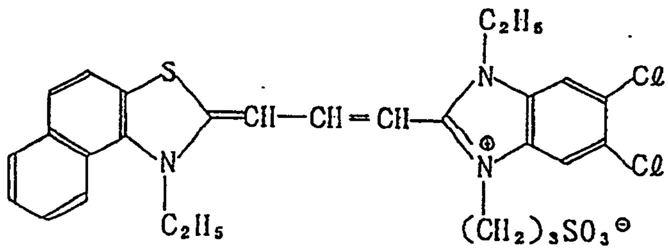

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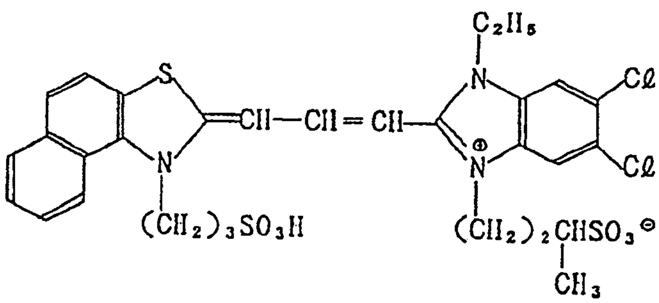

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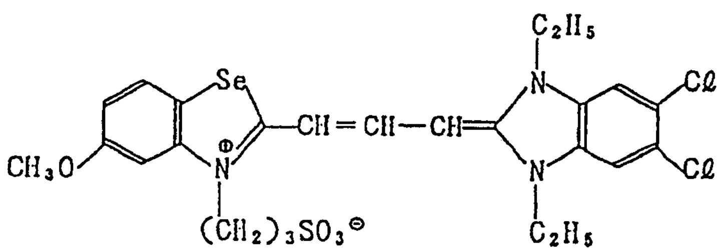

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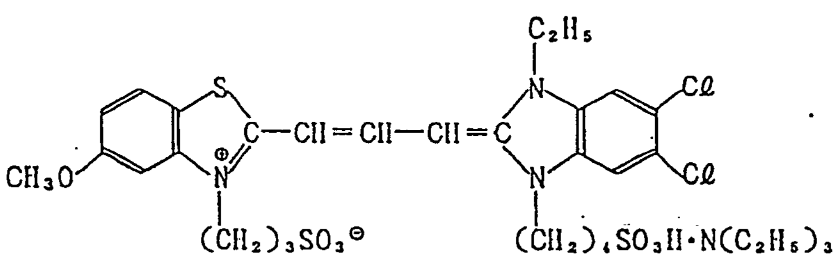

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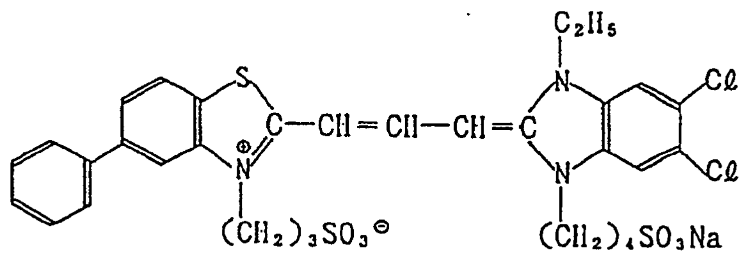

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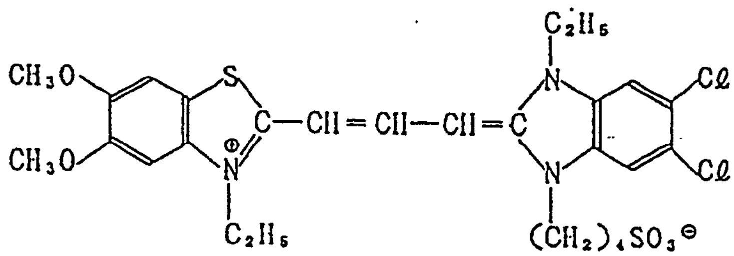

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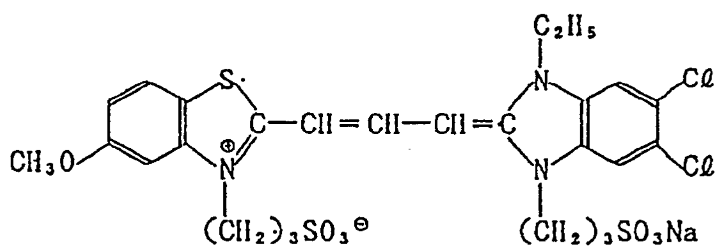

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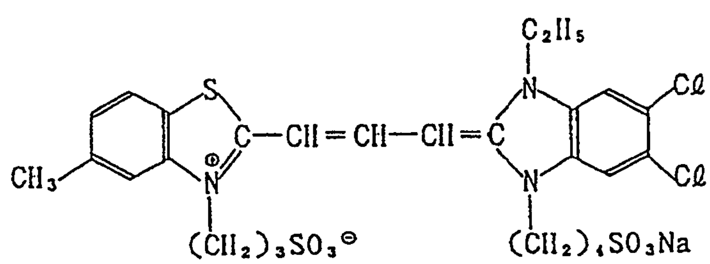

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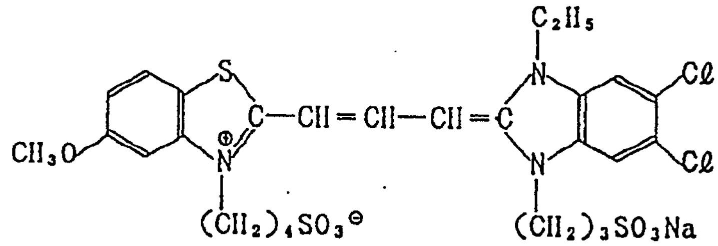

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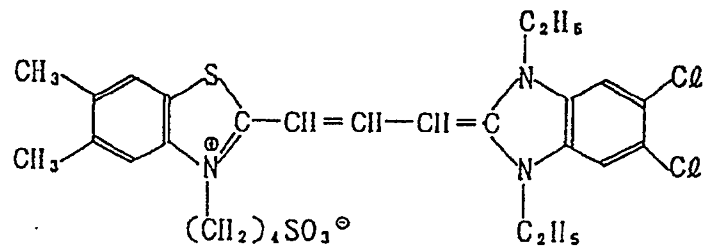

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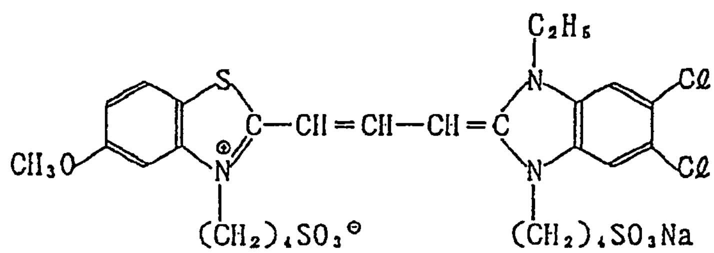

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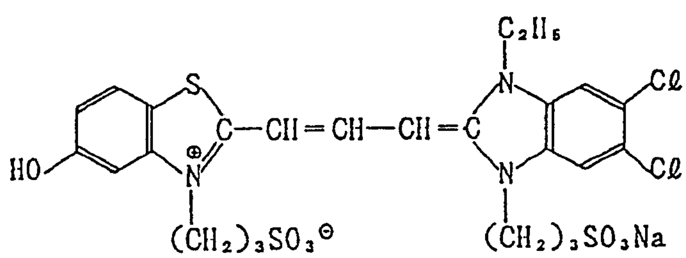

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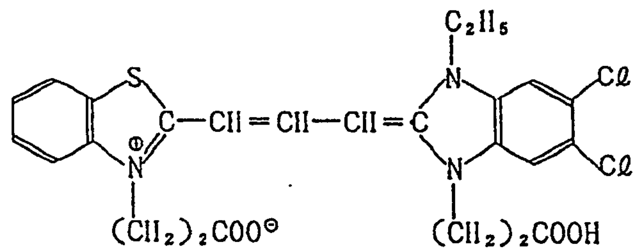

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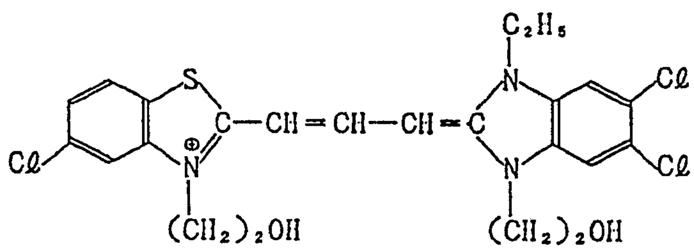

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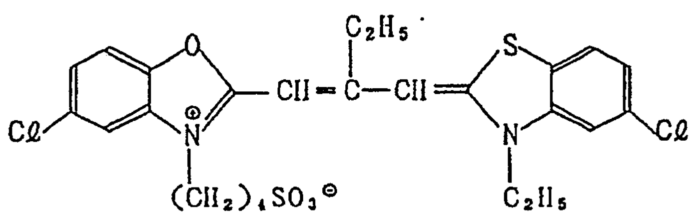

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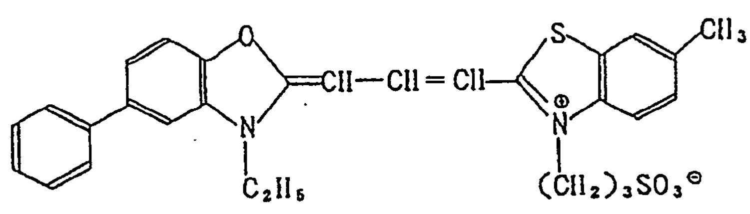

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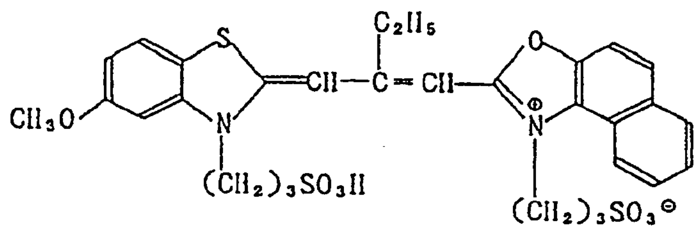

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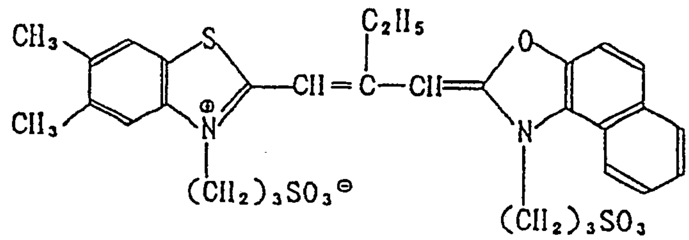

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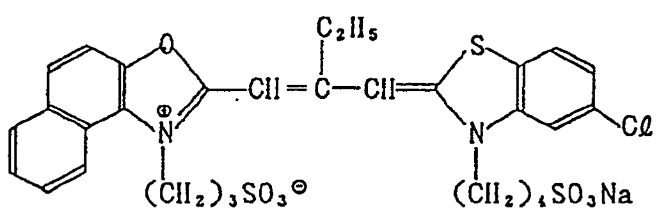

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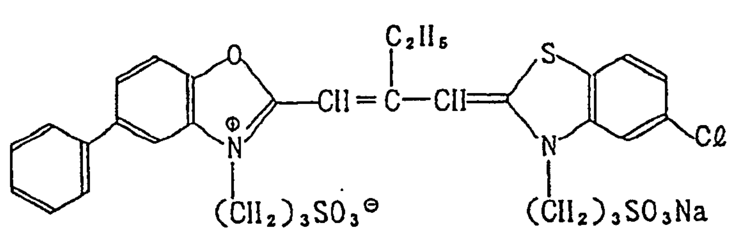

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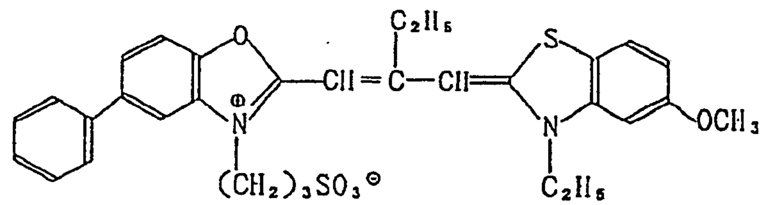

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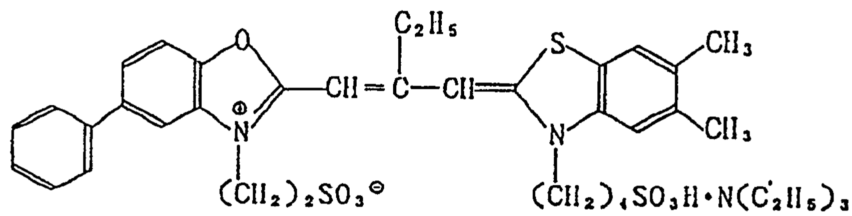

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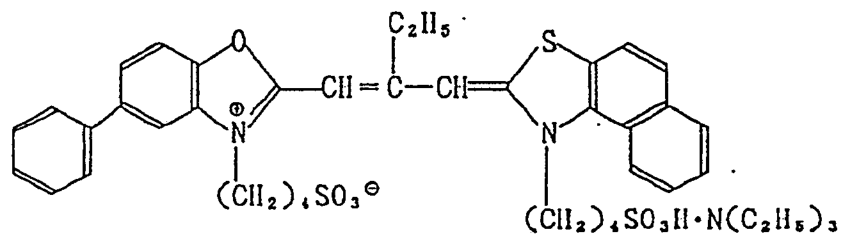

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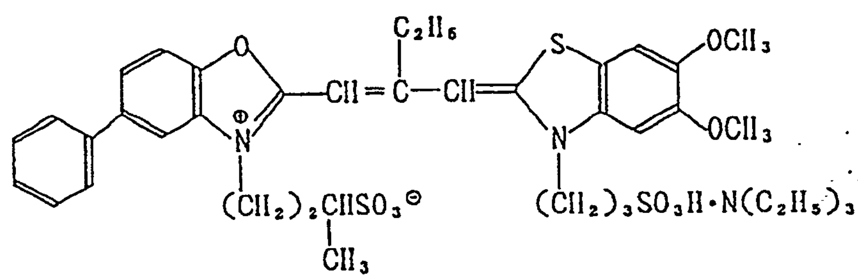

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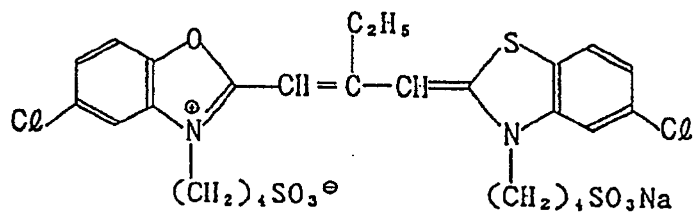

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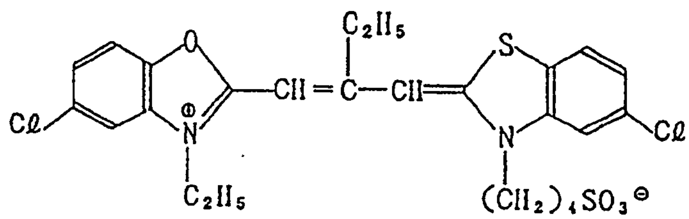

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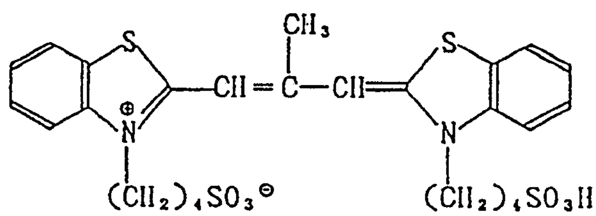

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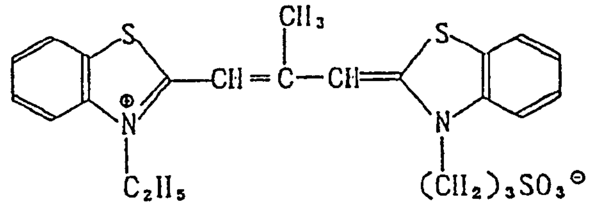

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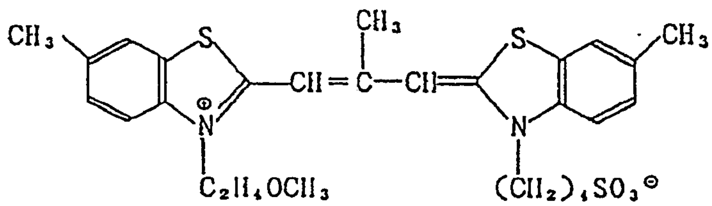

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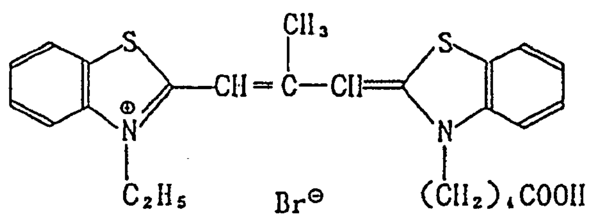

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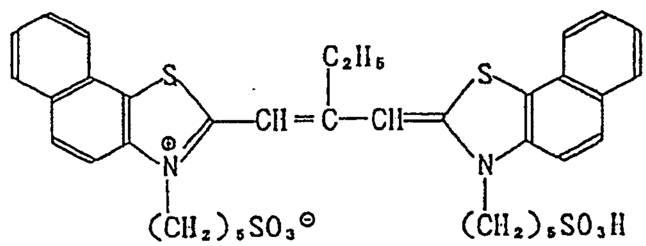

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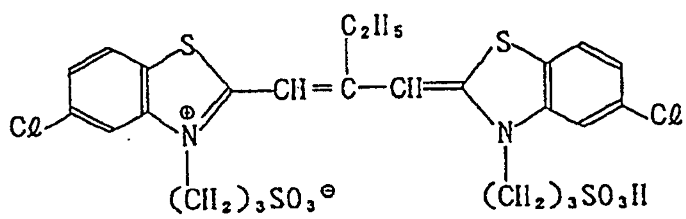

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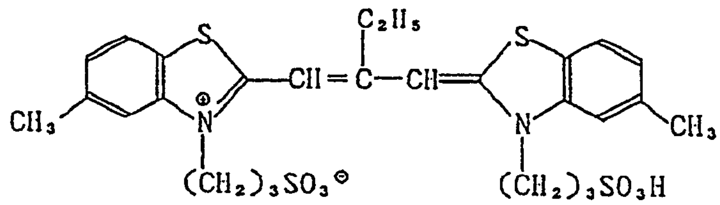

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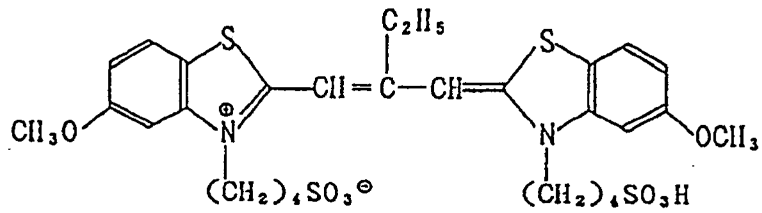

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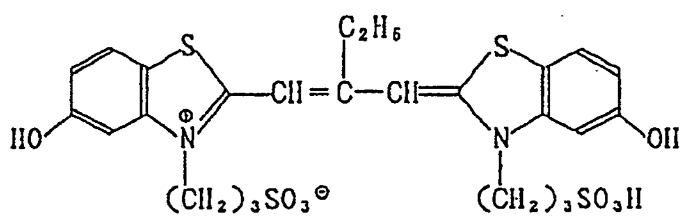

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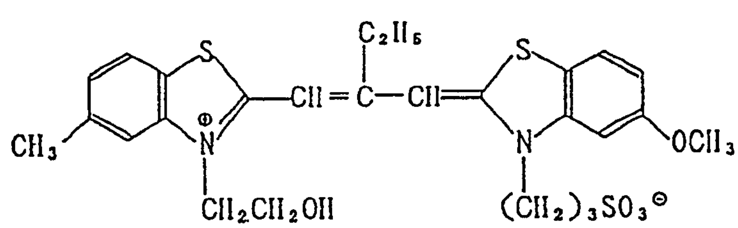

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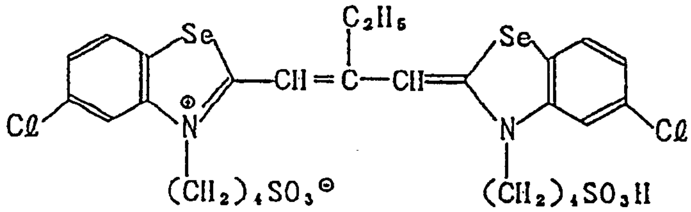

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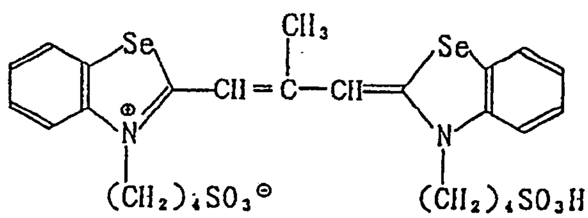

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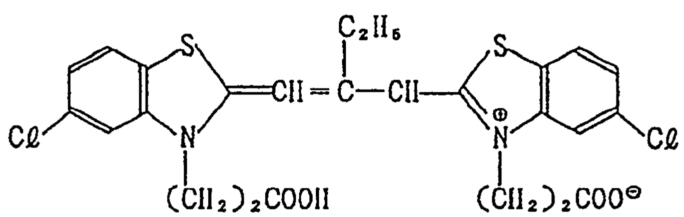

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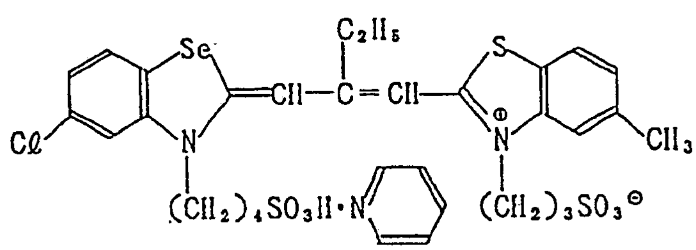

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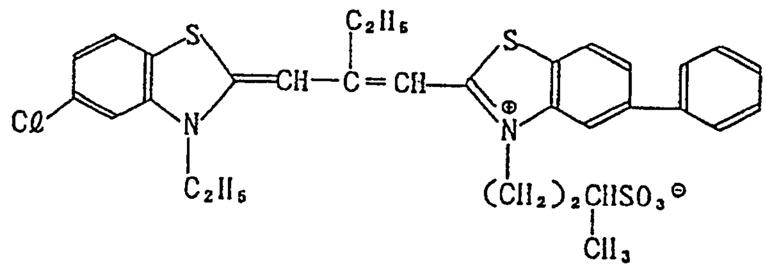

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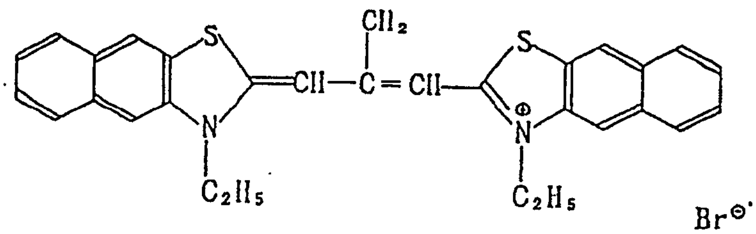

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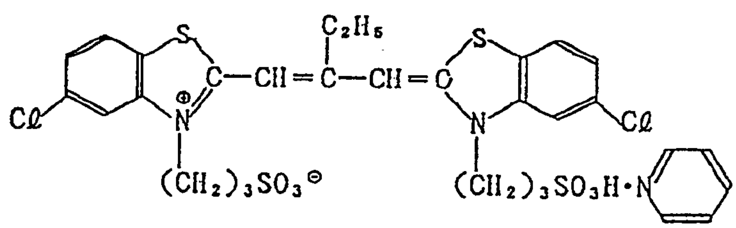

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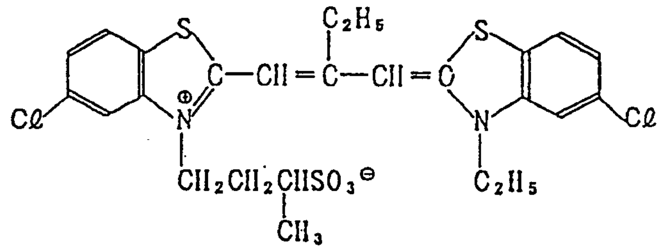

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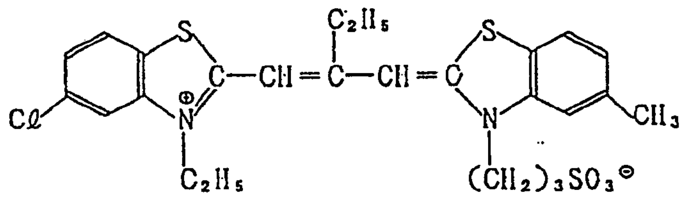

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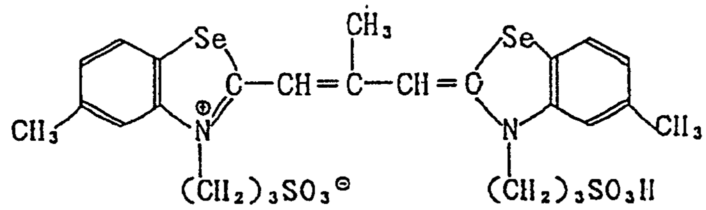

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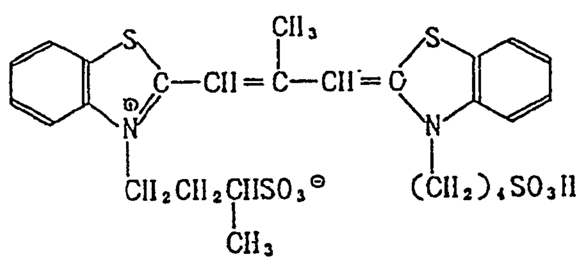

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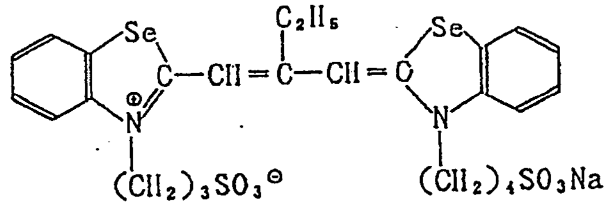

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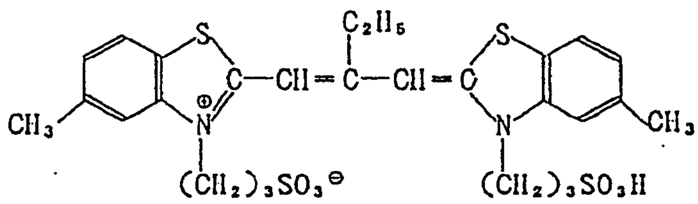

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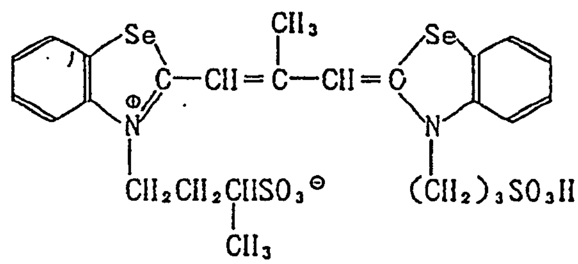

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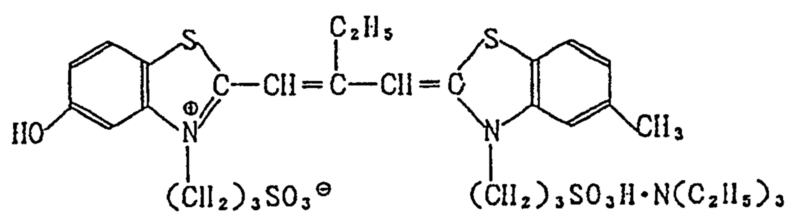

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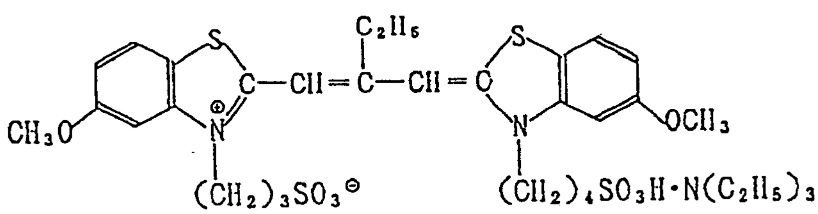

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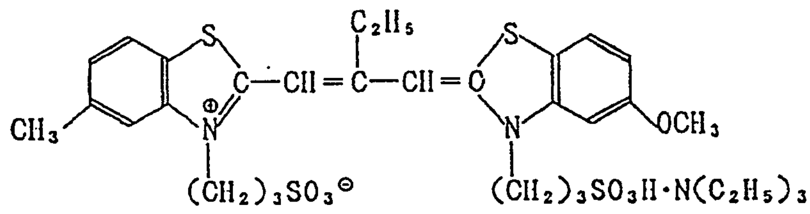

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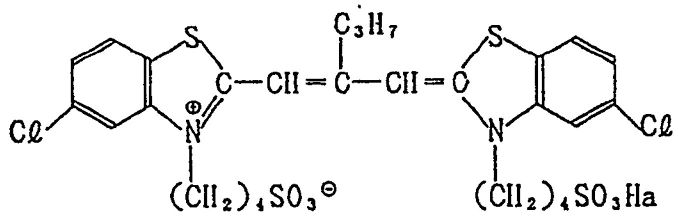

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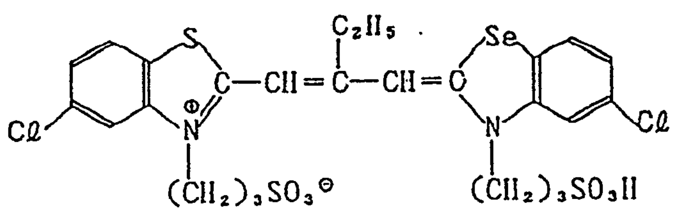

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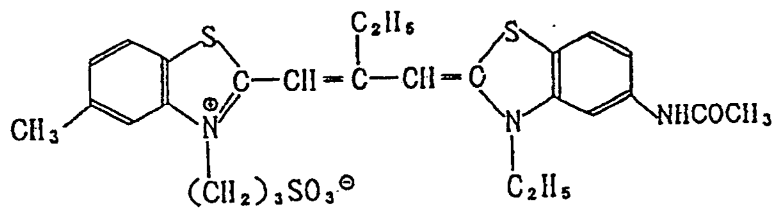

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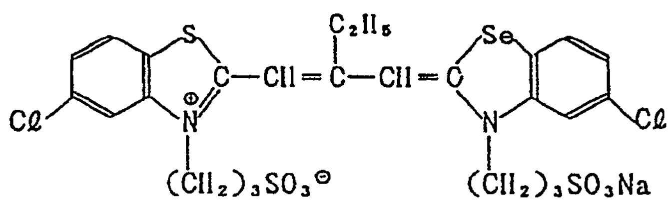

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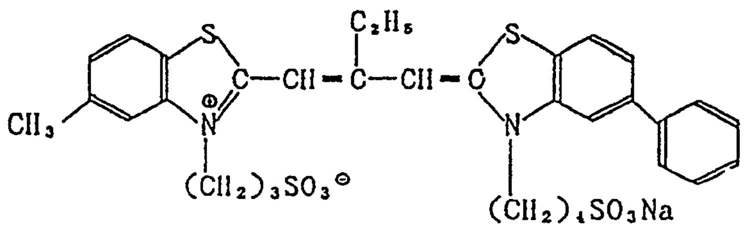

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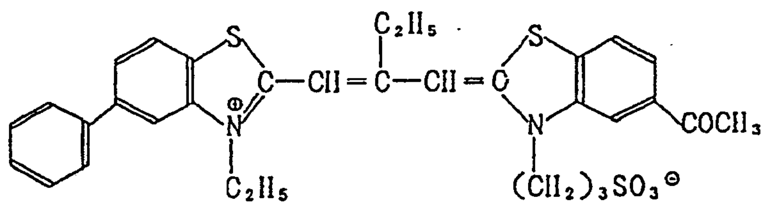

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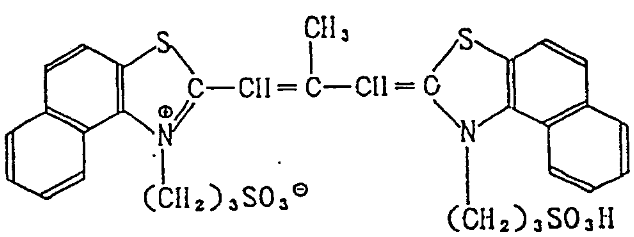

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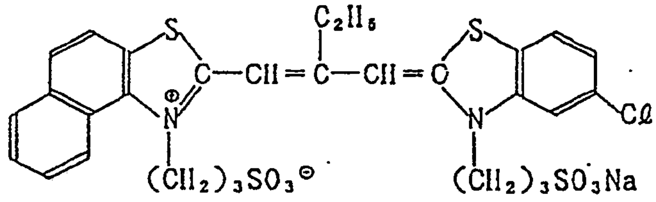

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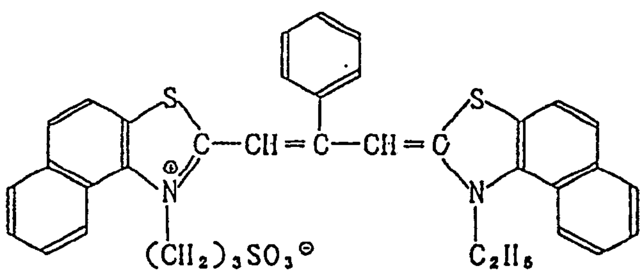

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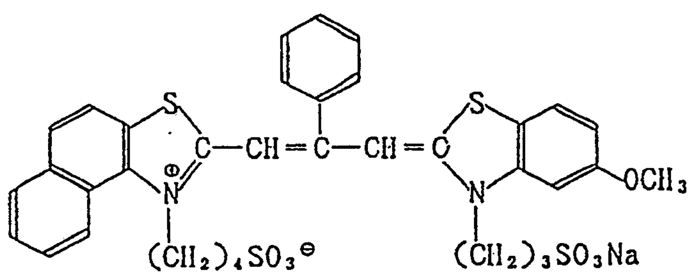

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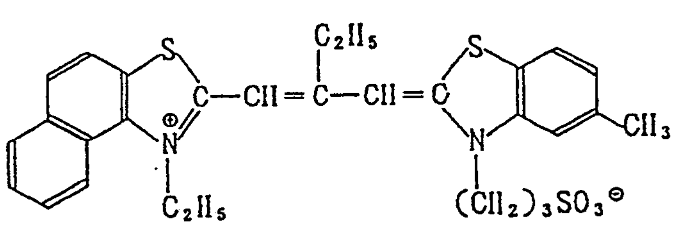

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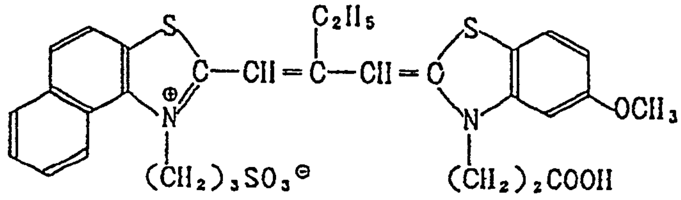

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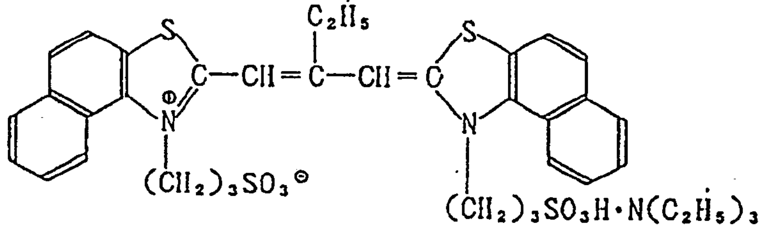

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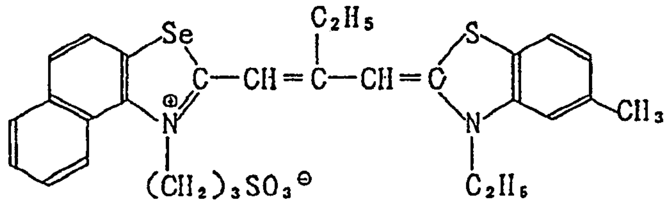

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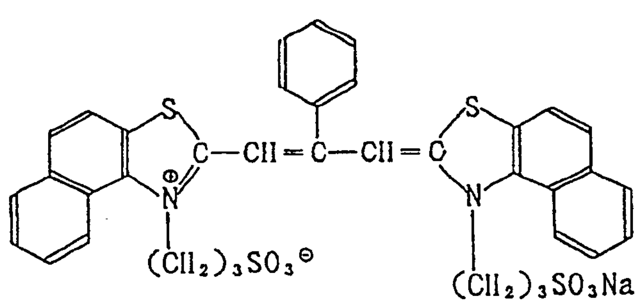

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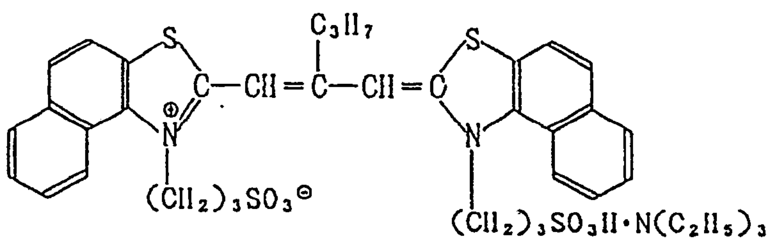

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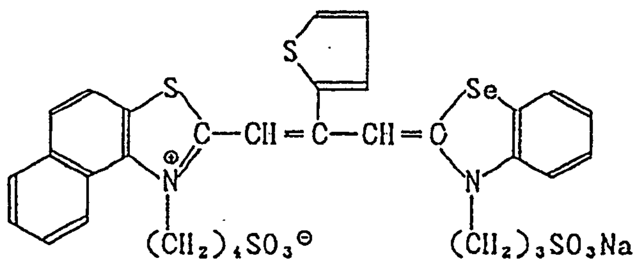

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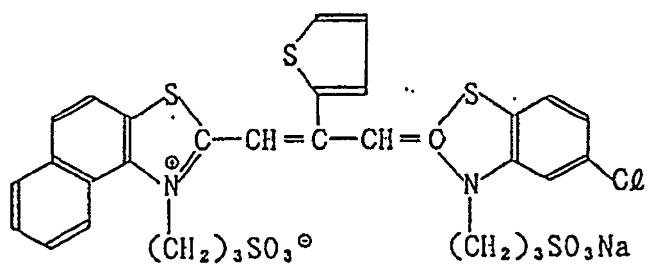

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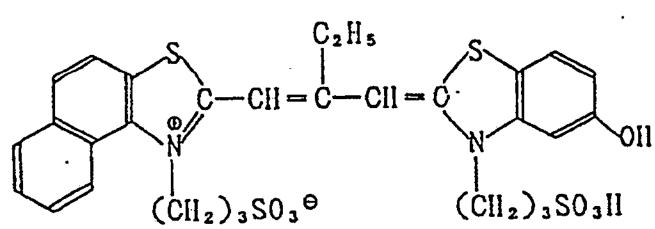


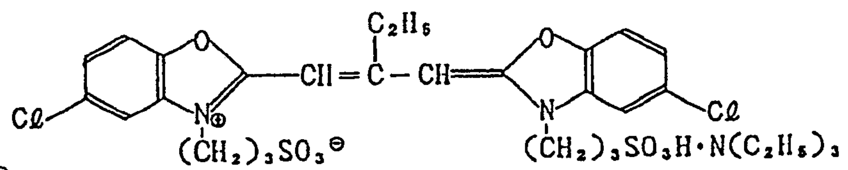
To obtain the constitution of the present invention described above for the spectral sensitivity in the green-sensitive layer, any appropriate means can be used. For example, such a spectral sensitivity distribution can be obtained using a spectral sensitizing dye.

Typical examples of the sensitizing dye oxacabocyanine, oxabenzimidazolecyanine, thia-4′ -cyanine or thia-2′ -cyanine dyes, which can be used for the green-sensitive layer of the present invention is given below, but these are not to be construed as limitative on the invention.

The green-sensitive emulsion layer of the invention contains oxacabocyanine, oxabenzimidazolecyanine, thia-4′ -cyanine or thia-2′ -cyanine dyes in an amount of 50 to 80 mol% based on the total amount of a sedsitezing dye in it.

It is also possible to use the preceding sensitizing dyes represented by formula I or II which can be used to control the spectral sensitization distribution in the red-sensitive layer.

IV − 1



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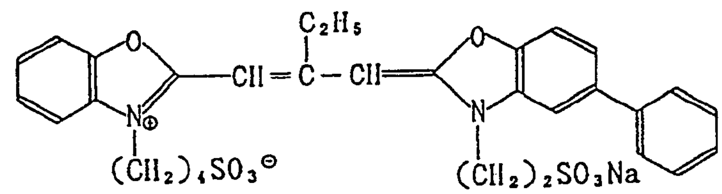

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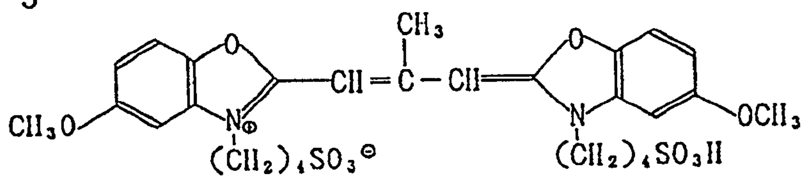

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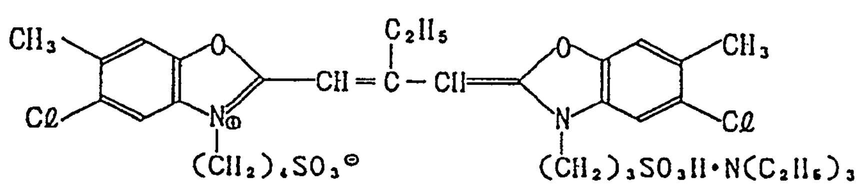

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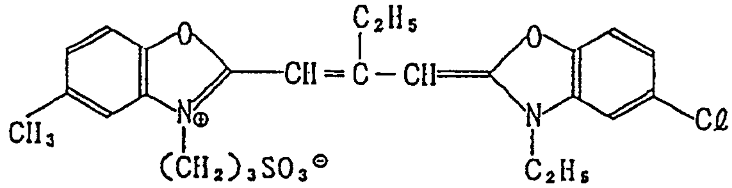

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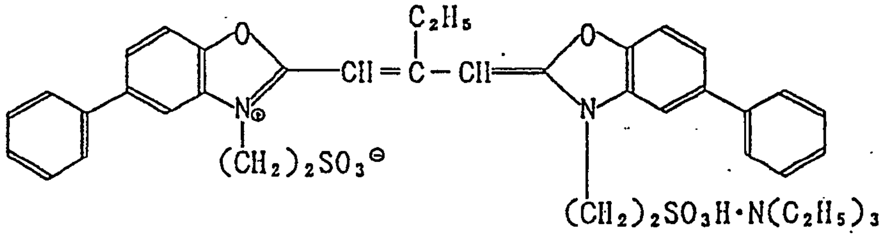

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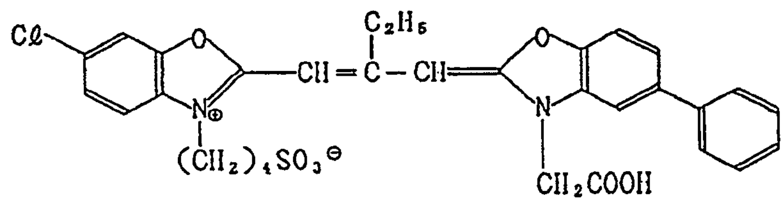

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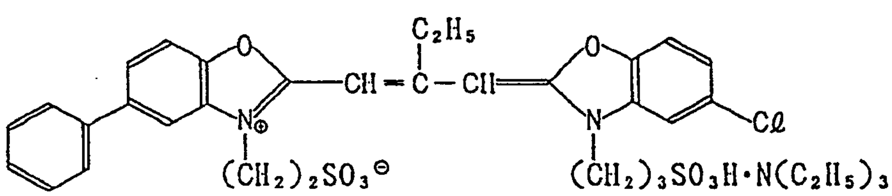

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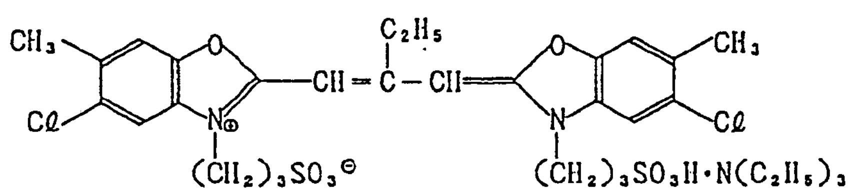

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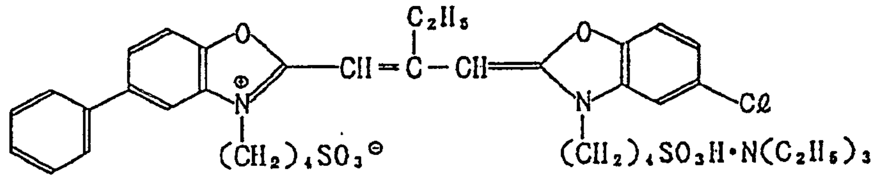

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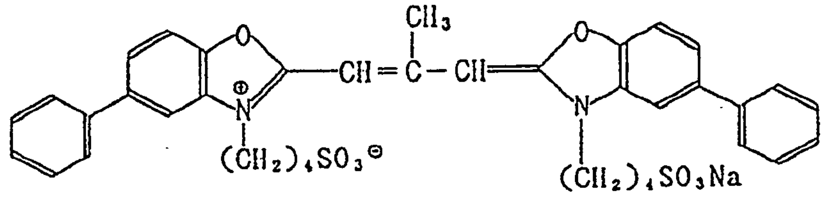

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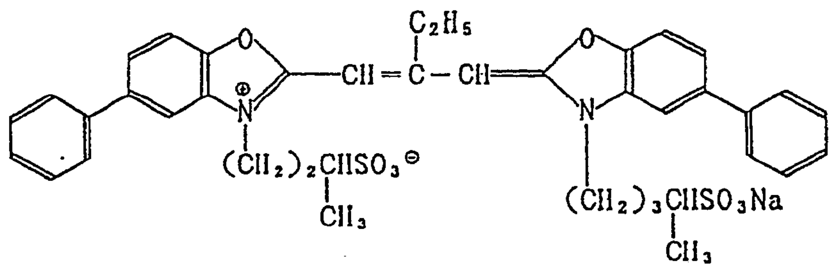

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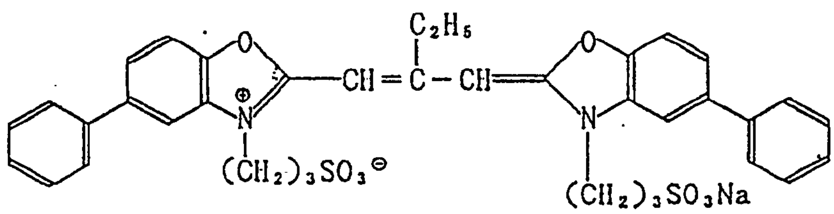

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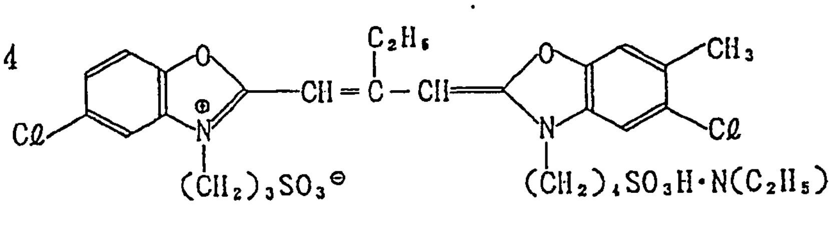

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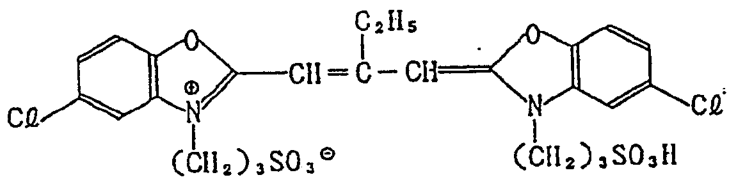

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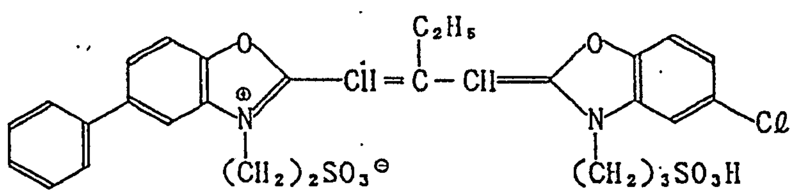

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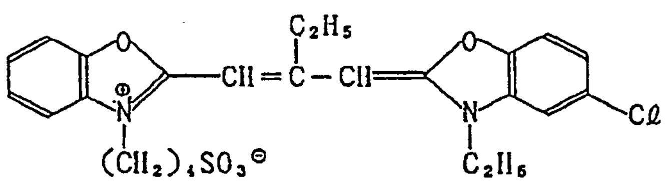

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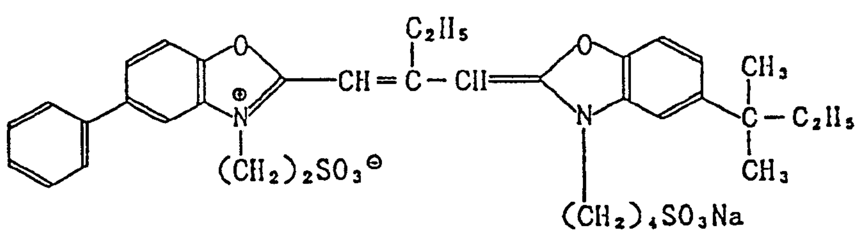

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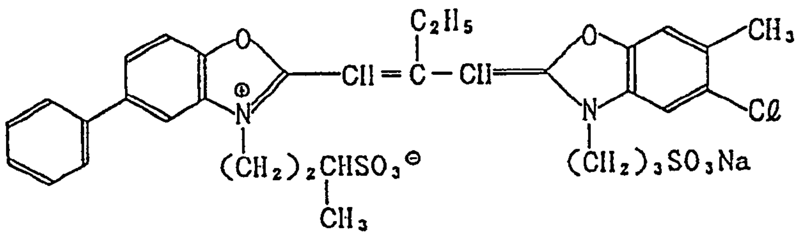

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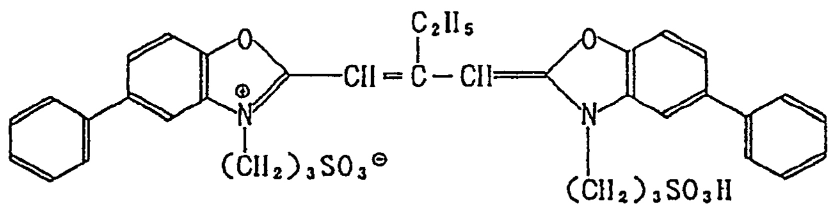

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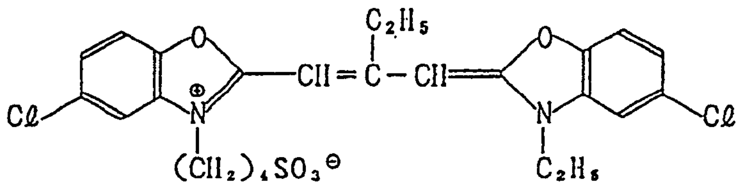

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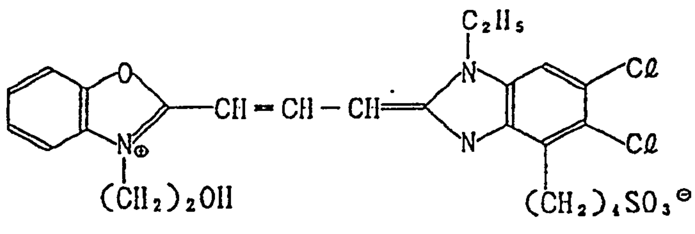

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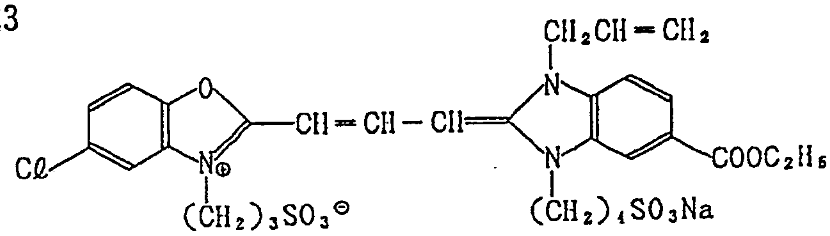

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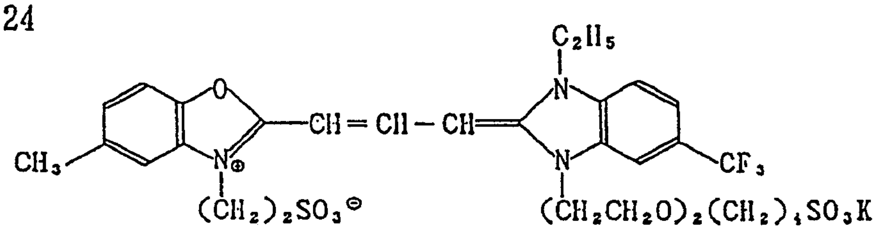

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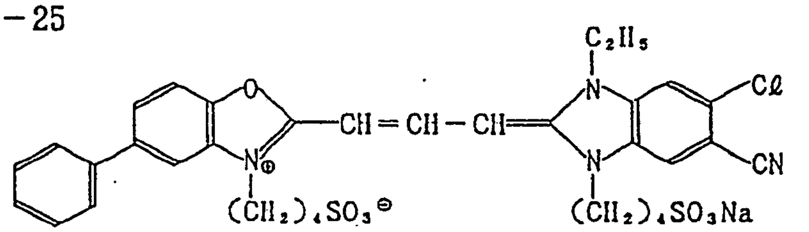

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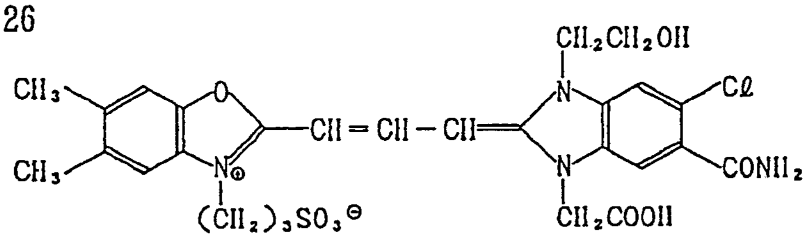

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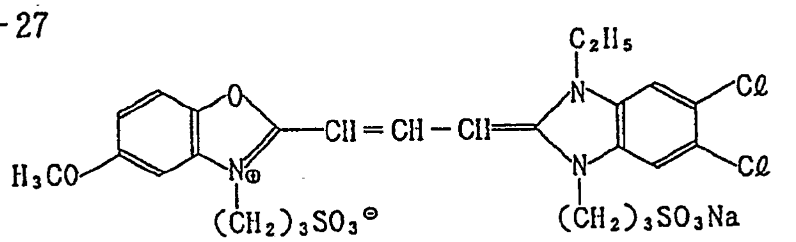

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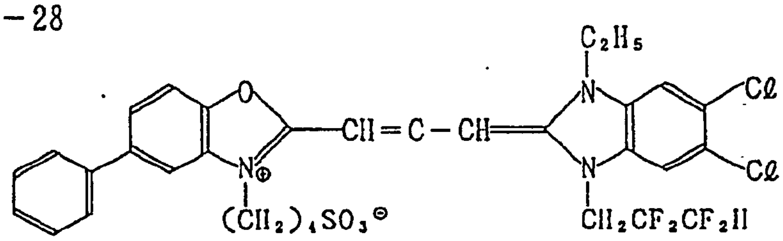

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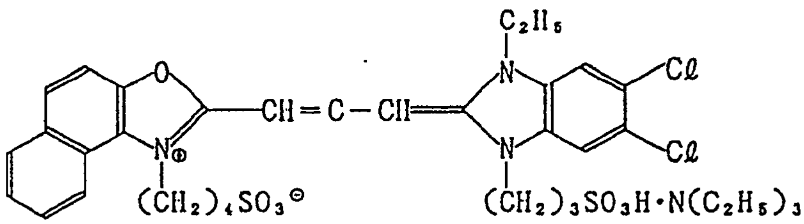

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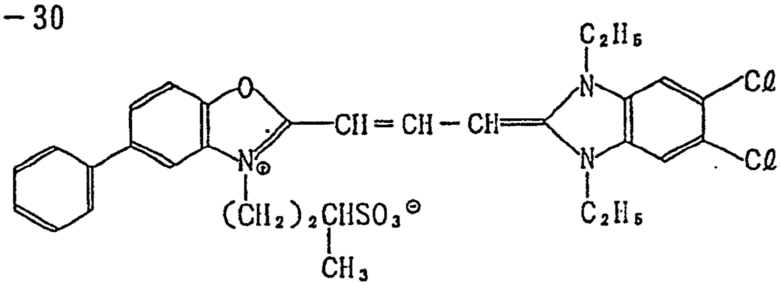

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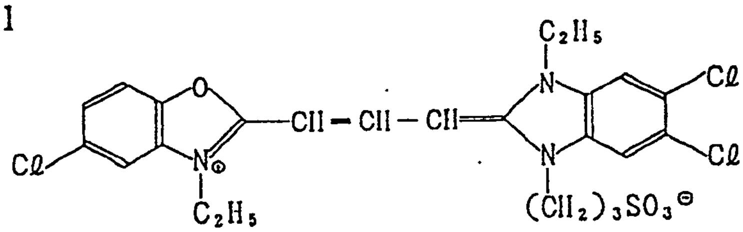

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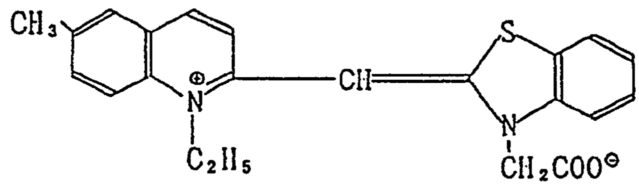

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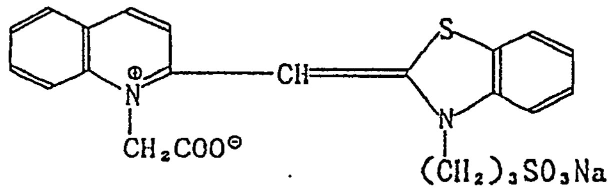

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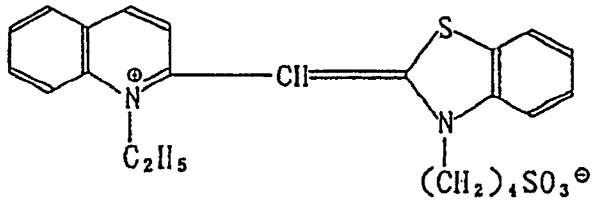

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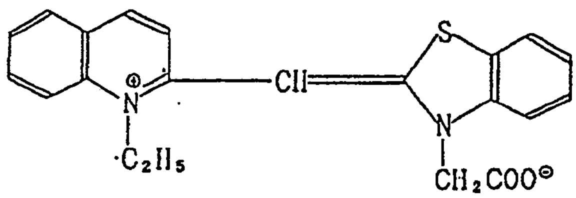

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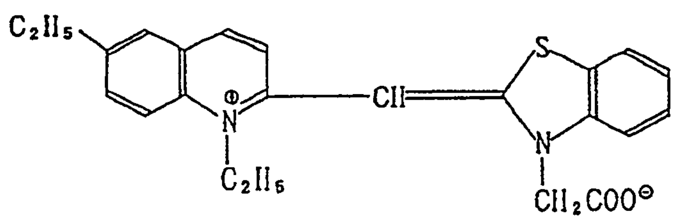

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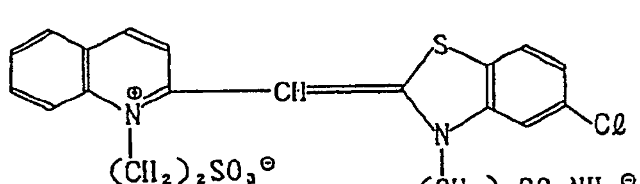

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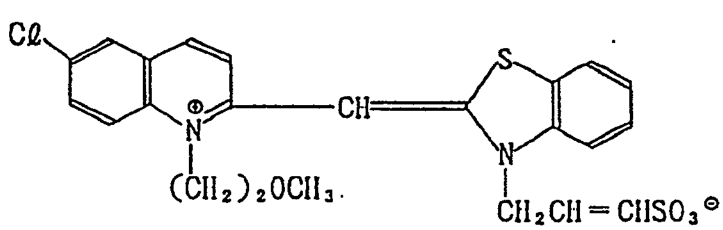

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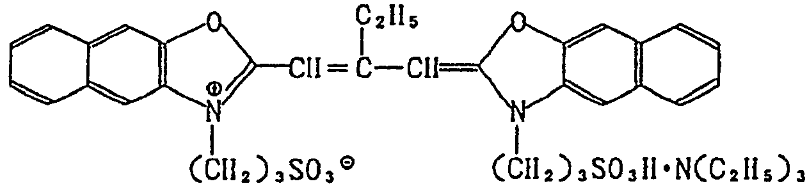

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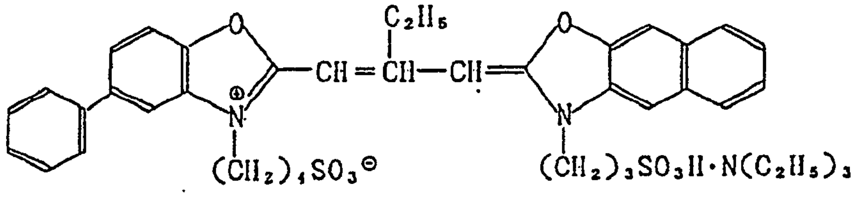

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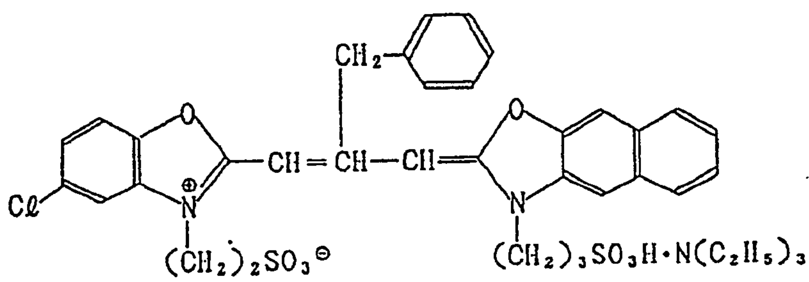

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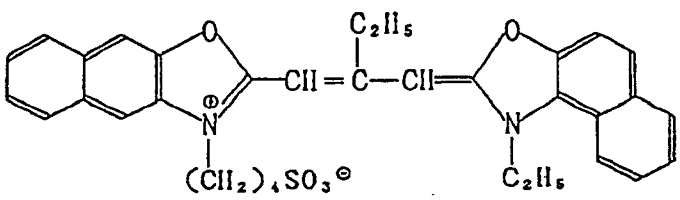

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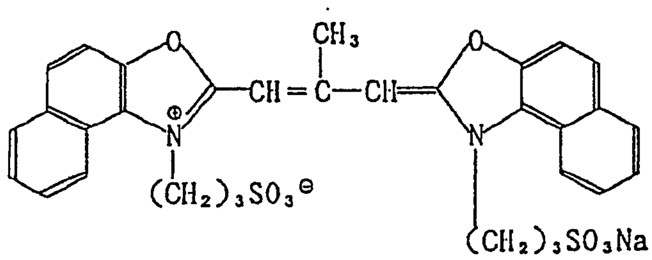

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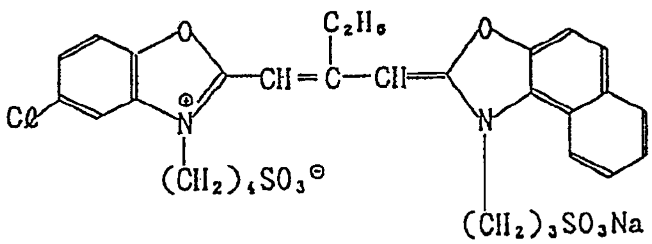

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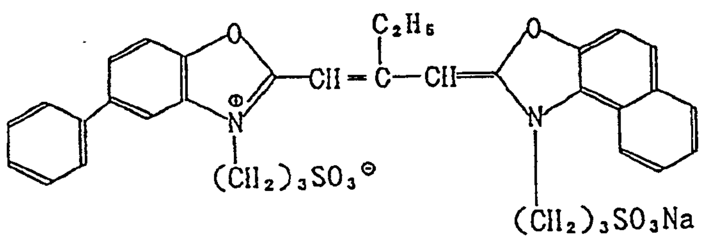


In addition to the sensitizing dyes above described, the benzothiazoles and quinolones described in Japanese Patent Examined Publication No. 24533/1982 and the quinoline derivatives described in Japanese Patent Examined Publication No. 24889/1982 can be added to the red-sensitive emulsion layer or the green-sensitive emulsion layer of the invention as supersensitizers if desired.

Known photographic additives which can be used for the present invention are also described in the following Research Disclosures.

The table below specifies where relevant description appears.

[Item]	[page in RD308119]	[RD17643]	[RD18716]
Antistaining agent	1002 VII-I	25	650
Dye image stabilizer	1001 VII-J	25	
Whitening agent	998 V	24	
UV absorbent	1003 VIII-C, XIII C	25-26	
Optical absorbent	1003 VIII	25-26	
Light scattering agent	1003 VIII		
Filter dye	1003 VIII	25-26	
Binder	1003 IX	26	651
Antistatic agent	1006 XIII	27	650
Hardener	1004 X	26	651
Plasticizer	1006 XII	27	650
Lubricant	1006 XII	27	650
Activator, coating aid	1005 XI	26-27	650
Matting agent	1007 XVI		
Developer (contained in the sensitive material)	1011 XX B		

Various couplers can be used for the present invention. Examples thereof are described in the above Research Disclosures.

The table below specifies where relevant description appears.

[Item]	[page in RD308119]	[RD17643]
Yellow coupler	1001 VII-D	VII C-G
Magenta coupler	1001 VII-D	VII C-G
Cyan coupler	1001 VII-D	VII C-G
Colored coupler	1002 VII-G	VII G
DIR coupler	1001 VII-F	VII-F
BAR coupler	1002 VII-F	
Other couplers which release useful residue	1001 VII-F	
Alkali-soluble coupler	1001 VII-E	

The additives used for the present invention can be added by, for example, the dispersion method described in RD308119 XIV.

In the present invention, the supports described in the above RD17643, p. 28, RD18716 pp. 647-648 and RD308119 XVII.

The light-sensitive material of the present invention may be provided with auxiliary layers such as a filter layer and an interlayer as described in the above RD308119 VII-K.

The light-sensitive material of the present invention can have various layer structures such as ordinary layer structure, reverse layer structure and unit structure as described in the above RD308119 VII-K.

The present invention is applicable to various color light-sensitive materials represented by color negative films for ordinary or movie use, color reversal films for slides or televisions, color papers, color positive films, and color reversal papers.

The light-sensitive material of the present invention can be developed by the ordinary processes described in the above RD17643 pp. 28-29, RD18716 p. 647 and RD308119 XVII.

EXAMPLES

The present invention is hereinafter described in more detail by means of the following examples, but the modes of embodiment of the present invention are not limited to these examples.

In all the following examples, the amount added to the silver halide photographic light-sensitive material is expressed in gram per m^2, unless otherwise specified. Also, the amount of silver halide and colloidal silver is expressed on the basis of the amount of silver.

Example 1

Layers having the following compositions were formed on a triacetyl cellulose film support in this order from the support side to yield a multiple-layered color photographic light-sensitive material sample No. 101. Sample No. 101

Layer 1: Anti-halation layer HC-1

Black colloidal silver	0.2
UV absorbent UV-1	0.15
High boiling solvent Oil-1	0.15
Gelatin	1.4

Layer 2: First interlayer IL-1

Gelatin	1.3
UV absorbent UV-1	0.1
High boiling solvent Oil-1	0.1

Layer 3: Low speed red-sensitive emulsion layer RL

Silver iodobromide emulsion Em-1	0.8
Sensitizing dye III-40	2.4×10^{-5}
Sensitizing dye III-6	1.9×10^{-4}
Sensitizing dye II-40	1.9×10^{-4}
Cyan coupler C-1	0.70
Colored cyan coupler CC-1	0.10
DIR compound D-1	0.03
DIR compound D-3	0.01
High boiling solvent Oil-1	0.64
Gelatin	1.2

Layer 4: Moderate speed red-sensitive emulsion layer RM

Silver iodobromide emulsion Em-2	0.7
Sensitizing dye III-40	1.3×10^{-5}
Sensitizing dye III-6	1.0×10^{-4}
Sensitizing dye II-40	1.0×10^{-4}
Cyan coupler C-1	0.28
Colored cyan coupler CC-1	0.05
DIR compound D-1	0.02
High boiling solvent Oil-1	0.28
Gelatin	0.6

Layer 5: High speed red-sensitive emulsion layer RH

Silver iodobromide emulsion Em-3	0.9
Sensitizing dye III-40	0.8×10^{-5}
Sensitizing dye III-6	0.6×10^{-4}

Sensitizing dye II-40	0.6×10^{-4}
Cyan coupler C-1	0.03
Cyan coupler C-2	0.07
Colored cyan coupler CC-1	0.03
DIR compound D-1	0.04
High boiling solvent Oil-1	0.17
Gelatin	1.2

Layer 6: Second interlayer IL-2

Gelatin 0.8

Layer 7: Low speed green-sensitive emulsion layer GL

Silver iodobromide emulsion Em-1	0.8
Sensitizing dye IV-14	7.2×10^{-4}
Sensitizing dye I-5	8.0×10^{-5}
Magenta coupler M-1	0.30
Magenta coupler M-2	0.19
Colored magenta coupler CM-1	0.10
DIR compound D-2	0.02
DIR compound D-4	0.007
High boiling solvent Oil-2	0.62
Gelatin	1.3

Layer 8: Moderate speed green-sensitive emulsion layer GM

Silver iodobromide emulsion Em-2	0.7
Sensitizing dye IV-14	3.6×10^{-4}
Sensitizing dye I-5	4.0×10^{-5}
Magenta coupler M-1	0.07

Magenta coupler M-2	0.04
Colored magenta coupler CM-1	0.04
DIR compound D-2	0.018
High boiling solvent Oil-2	0.20
Gelatin	0.8

Layer 9: High speed green-sensitive emulsion layer GH

Silver iodobromide emulsion Em-3	0.9
Sensitizing dye IV-14	2.2×10^{-4}
Sensitizing dye I-5	2.4×10^{-5}
Magenta coupler M-2	0.04
Magenta coupler M-3	0.04
Colored magenta coupler CM-2	0.04
DIR compound D-2	0.008
High boiling solvent Oil-2	0.15
Gelatin	0.9

Layer 10: Yellow filter layer YC

Yellow colloidal silver	0.12
Anti-color staining agent SC-1	0.1
High boiling solvent Oil-2	0.13
Gelatin	0.8
Formalin scavenger HS-1	0.09
Formalin scavenger HS-2	0.07

Layer 11: Low speed blue-sensitive emulsion layer BL

Silver iodobromide emulsion Em-1	0.35
Silver iodobromide emulsion Em-2	0.15

Sensitizing dye SD-1	6.1×10^{-4}
Yellow coupler Y-1	0.65
Yellow coupler Y-2	0.12
DIR compound D-1	0.05
High boiling solvent Oil-2	0.16
Gelatin	1.1
Formalin scavenger HS-1	0.08

Layer 12: High speed blue-sensitive emulsion layer BH

Silver iodobromide emulsion Em-4	0.6
Sensitizing dye SD-1	1.8×10^{-4}
Yellow coupler Y-1	0.18
Yellow coupler Y-2	0.02
High boiling solvent Oil-2	0.04
Gelatin	1.1
Formalin scavenger HS-1	0.05
Formalin scavenger HS-2	0.12

Layer 13: First protective layer Pro-1

Fine grains of silver iodobromide emulsion (average grain size 0.08 μm, AgI content 1 mol%)	0.2
UV absorbent UV-1	0.07
UV absorbent UV-2	0.10
High boiling solvent Oil-1	0.06
High boiling solvent Oil-3	0.06
Formalin scavenger HS-1	0.13
Formalin scavenger HS-2	0.37
Gelatin	1.1

Layer 14: Second protective layer Pro-2

Alkali-soluble matting agent (average grain size 2 μm)	0.07
Polymethyl methacrylate (average grain size 3 μm)	0.03
Lubricant WAX-1	0.04
Gelatin	0.6

The emulsions used to prepare the sample described above are as follows:

Em-1

Emulsion containing monodispersed (individual grain silver iodide content relative standard deviation 18%) silver iodobromide grains having an average grain size of 0.35 μm, an average silver iodide content of 6.0 mol% and a core of 35 mol% AgI.

Em-2

Emulsion containing monodispersed (individual grain silver iodide content relative standard deviation 19%) silver iodobromide grains having an average grain size of 0.5 μm, an average silver iodide content of 6.8 mol% and a core of 35 mol% AgI.

Em-3

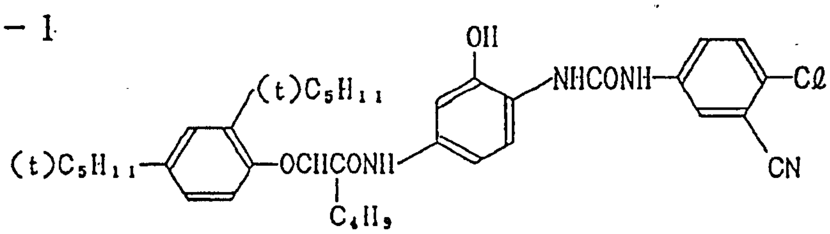
Emulsion containing monodispersed (individual grain silver iodide content relative standard deviation 18%) silver iodobromide grains having an average grain size of 0.65 μm, an average silver iodide content of 8.0 mol% and a core of 35 mol% AgI.

Em-4

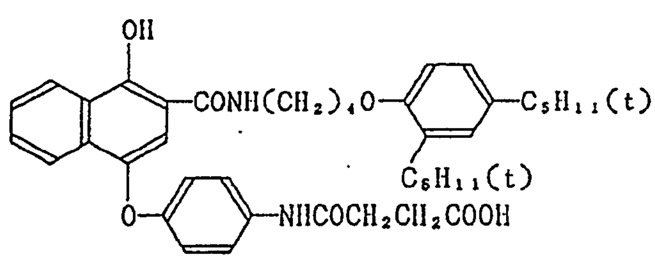
Emulsion containing monodispersed silver iodobromide grains having an average grain size of 0.8 μm, an average silver iodide content of 8.0 mol% and a twin plane of an aspect ratio of 3.5.

The compounds used to prepare the sample described above are as follows:

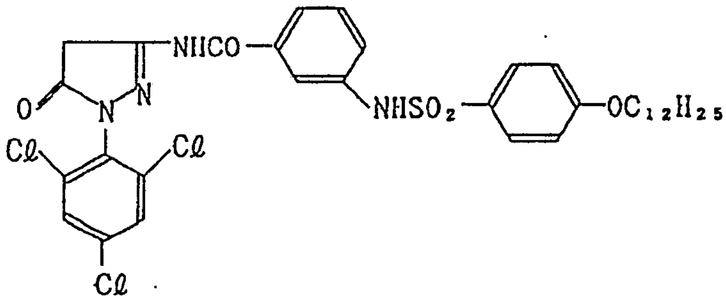
C-1



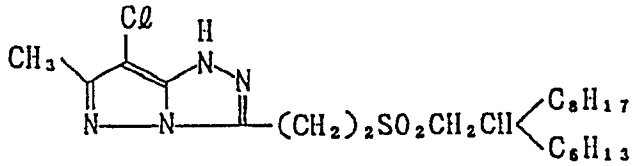
C-2



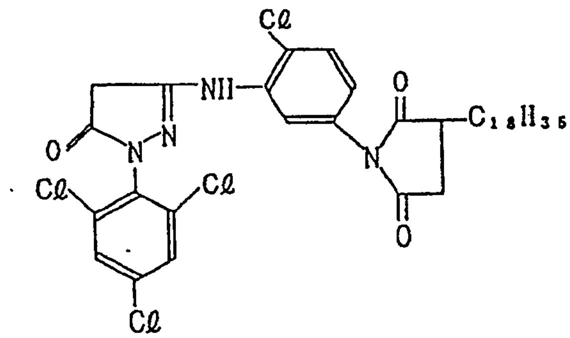
M－1



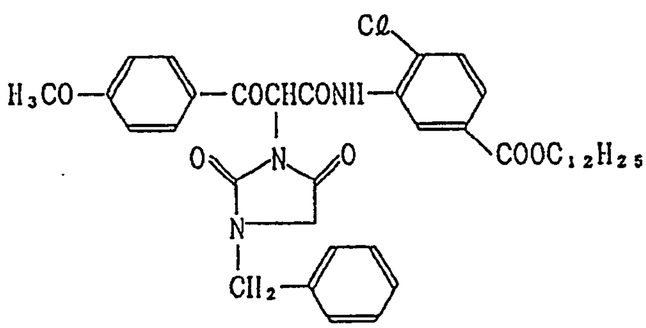
M－2



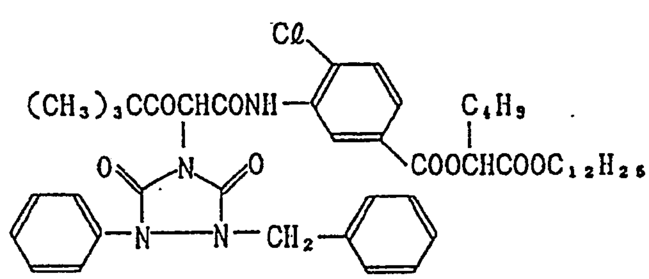
M－3



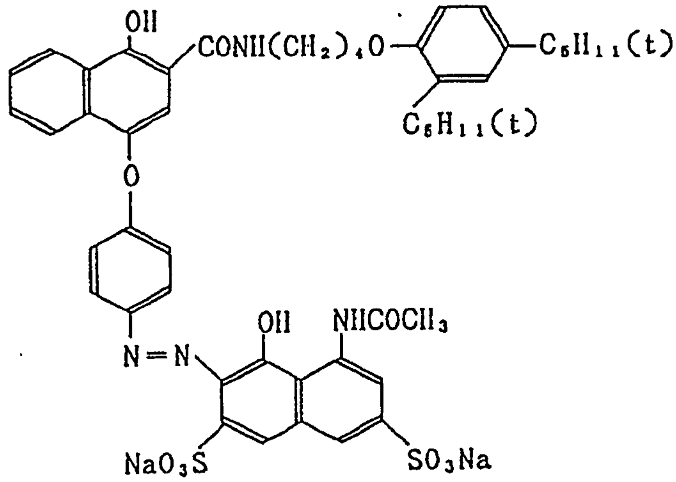
Y－1



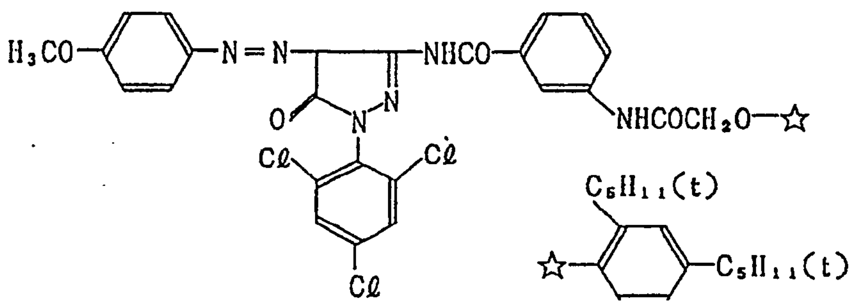
Y－2



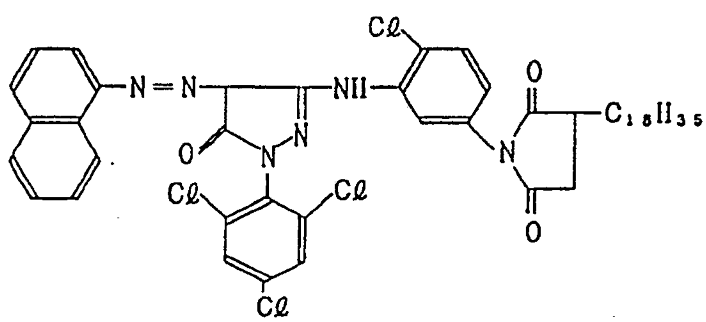
CC-1


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)
O
OH
NHCOCH3
N=N
NaO3S
SO3Na

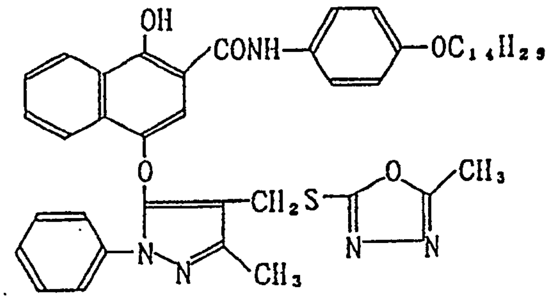
CM-1


H3CO
N=N
NHCO
O
N
N
NHCOCH2O
Cℓ
Cℓ
Cℓ
C5H11(t)
C5H11(t)

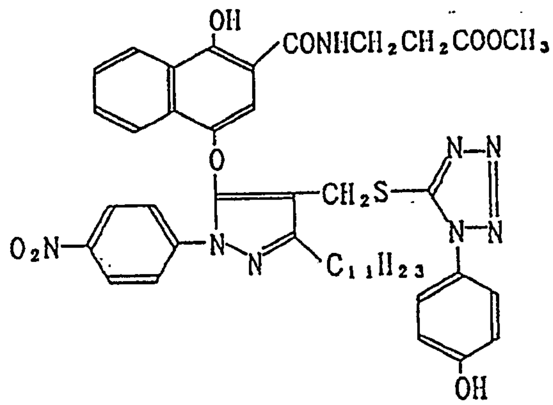
CM-2


Cℓ
N=N
NH
O
O
N
N
N
C18H35
Cℓ
Cℓ
Cℓ
O

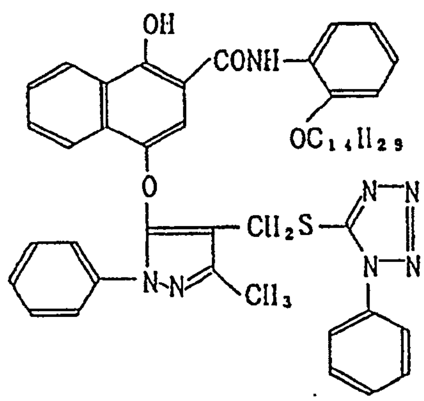
D − 1



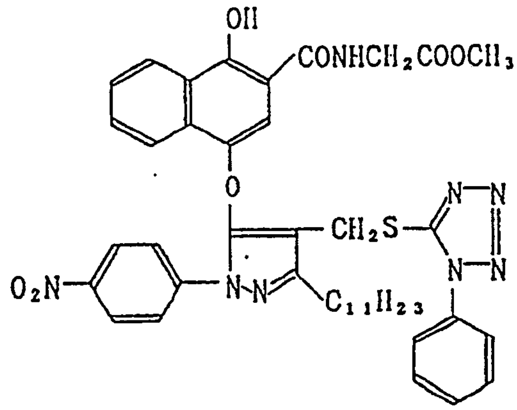
D − 2



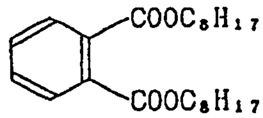
D − 3



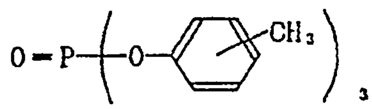
D − 4



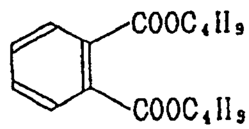
Oil-1



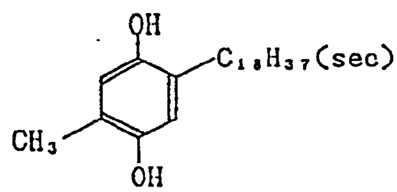
Oil-2



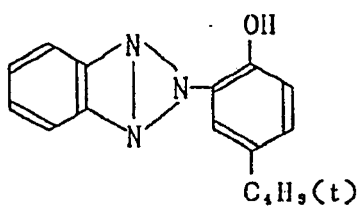
Oil-3



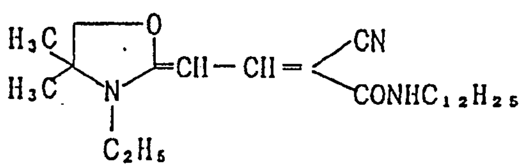
SC-1



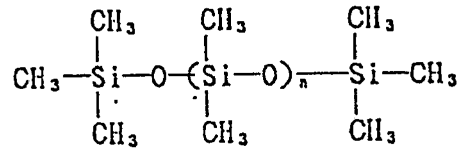
UV-1



UV-2

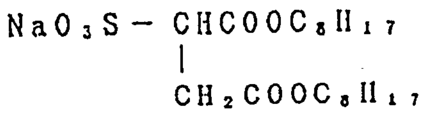


WAX-1

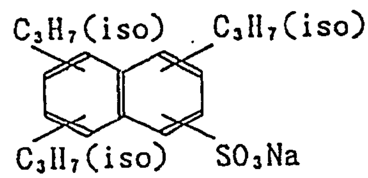


Weight average molecular weight Mw = 3,000

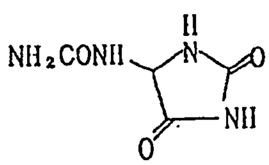
Su-1



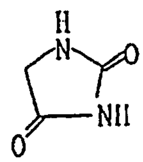
Su-2



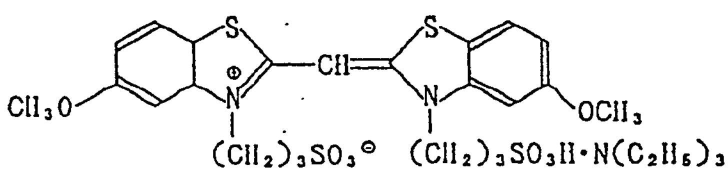
HS-1



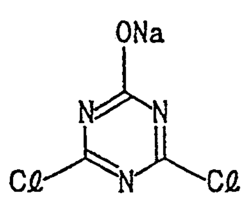
HS-2



SD-1



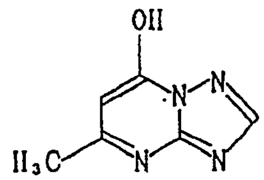
H-1



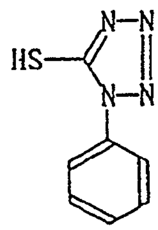
H-2

$(CH_2=CHSO_2CH_2)_2O$

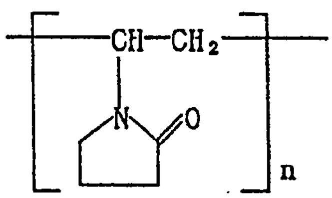
ST−1



AF−1



AF−2



n: Degree of polymerization

In addition to these compositions, a coating aid Su-1, a dispersing agent Su-2, a viscosity regulator, hardeners H-1 and H-2, a stabilizer ST-1, an antifogging agent AF-1 and two kinds of AF-2 having an average molecular weight of 10,000 or 1,100,000, respectively, were added.

The average grain size of silver halide in the emulsions used for the sample described above is expressed as a cube diameter.

Each emulsion was optimally sensitized with gold and sulfur.

Next, sample Nos. 102 through 106 were prepared in exactly the same manner as in sample No. 101 except that the sensitizing dyes for Layers 3, 4, 5, 8 and 9 were altered to those listed in Table 1. The total addition amount of sensitizing dyes listed in Table 1 in each layer is the same in sample Nos. 101 through 106.

Thus, the total amount differences among samples are based on combinations of sensitizing dyes and molar ratios thereof.

Each emulsion contained in sample Nos. 101 through 106 was optimally chemically sensitized with a gold and sulfur sensitizer by an ordinary method.

To determine the spectral sensitivity distribution, color development was conducted by the process described below, followed by spectral exposure, and each parameter of spectral sensitivity distribution was measured at a density of D_{min} + 0.3.

The results are given in Table 1.

In the process, running was carried out until the replenisher was fed in an amount 3 times the capacity of the stabilization tank.

Processing procedure	Processing time	Processing temperature	Amount of replenisher
Color development	3 minutes 15 seconds	38°C	540 mℓ
Bleaching	45 seconds	38°C	155 mℓ
Fixation	1 minute 45 seconds	38°C	500 mℓ
Stabilization	90 seconds	38°C	775 mℓ
Drying	1 minute	40 - 70°C	-

Note: Figures for the amount of replenisher are values per m^2 light-sensitive material.

Stabilization was conducted by the 3-vessel counter current method, wherein the replenisher was fed to the final stabilizer tank and the overflow solution flew into the tank before the final tank.

Also, a part (275 mℓ/m^2) of the overflow solution from the stabilization tank after the fixation tank was returned into the stabilization tank.

The composition of the color developer used is as follows:

Potassium carbonate	30 g
Sodium hydrogen carbonate	2.7 g
Potassium sulfite	2.8 g
Sodium bromide	1.3 g
Hydroxylamine sulfate	3.2 g
Sodium chloride	0.6 g
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	4.6 g
Diethylenetriamine pentaacetate	3.0 g
Potassium hydroxide	1.3 g

Water was added to make a total quantity of 1ℓ, and potassium hydroxide or 20% sulfuric acid was used to obtain a pH of 10.01.

The composition of the color developer replenisher used is as follows:

Potassium carbonate	40 g
Sodium hydrogen carbonate	3 g
Potassium sulfite	7 g
Sodium bromide	0.5 g
Hydroxylamine sulfate	3.2 g
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	6.0 g
Diethylenetriamine pentaacetate	3.0 g
Potassium hydroxide	2 g

Water was added to make a total quantity of 1ℓ, and potassium hydroxide or 20% sulfuric acid was used to obtain a pH of 10.12.

The composition of the bleacher used is as follows:

Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	150 g
Glacial acetic acid	40 mℓ
Ammonium nitrate	40 g

Water was added to make a total quantity of 1ℓ, and aqueous ammonia or glacial acetic acid was used to obtain a pH of 4.5.

The composition of the bleacher replenisher used is as follows:

Ferric ammonium 1,3-diaminopropanetetraacetate	0.40 mol
Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	170 g
Ammonium nitrate	50 g
Glacial acetic acid	61 mℓ

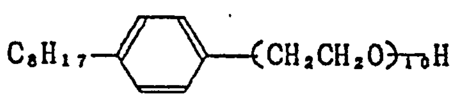
Water was added to make a total quantity of 1ℓ, and aqueous ammonia or glacial acetic acid was used to obtain a pH of 3.5, with proper adjustment made to maintain a given pH level of the bleacher tank solution.

The composition of the fixer and fixer replenisher used is as follows:

Ammonium thiosulfate	100 g
Ammonium thiocyanate	150 g
Anhydrous sodium bisulfite	20 g
Sodium metabisulfite	4.0 g
Disodium ethylenediaminetetraacetate	1.0 g

Water was added to make a total quantity of 700 mℓ, and glacial acetic acid and aqueous ammonia were used to obtain a pH of 6.5.

The composition of the stabilizer and stabilizer replenisher used is as follows:

1,2-benzoisothiazolin-3-one	0.1 g
 (50% solution)	2.0 mℓ
Hexamethylenetetramine	0.2 g
Hexahydro-1,3,5-tris-(2-hydroxyethyl)-5-triazine	0.3 g

Water was added to make a total quantity of 1ℓ, and potassium hydroxide and 50% sulfuric acid were used to obtain a pH of 7.0.

Table 1

Sample No.	Sensitizing dyes for layers 3, 4 and 5 (dye addition amount, mol%)	Sensitizing dyes forlayers 8 and 9 (dye addition amount, mol%)	λ_{Rmax} (nm)	S_{R610}/S_{Rmax} (%)	λ_{Gmax} (nm)	S_{G545}/S_{Gmax} (%)	Grey balance under fluorescent lamp lighting[1)]		Print color features[2)]	Remark
							$\Delta\Delta S_R$	$\Delta\Delta S_G$		
101	III-40 6 III-6 47 II-40 47	IV-14 90 I-5 10	633	75	553	87	-0.20	+0.12	Skin color with marked bluish green.	Comparative
102	III-6 60 I-5 40	IV-14 90 I-5 10	628	82	553	87	-0.12	+0.12	Skin color with bluish green, lacking liveliness.	Comparative
103	III-6 30 I-5 70	IV-14 90 I-5 10	615	97	553	87	-0.02	+0.12	Skin color with green, lacking liveliness.	Comparative
104	III-6 30 I-5 70	IV-14 80 I-5 20	615	97	556	76	-0.02	+0.05	Naturalistic skin color with no significant difference from strobe light print.	Inventive
105	III-6 30 I-5 70	IV-14 70 I-5 30	615	97	563	65	-0.02	+0.01	Naturalistic skin color. Skin color with slight yellow in strobe light print.	Inventive
106	III-6 60 I-5 40	IV-14 80 I-5 20	628	82	556	76	-0.12	+0.05	Skin color with blue, lacking liveliness.	Comparative

1) As the light source, a strobe light or a three-wavelength fluorescent lamp was used. The light-sensitive material was subjected to exposure through an optical wedge and then to the developing procedure described above, and the sensitivity point of D_{min} + 0.3 (logE) was determined. The sensitivity differences ΔS_B, ΔS_G, and ΔS_R between the sensitivity point ($logE_1$) obtained with the strobe light source and the sensitivity point ($logE_2$) obtained with the three-wavelength fluorescent light source were calculated. $\Delta\Delta S_G$ and $\Delta\Delta S_R$ were calculated using the following equations:

$$\Delta\Delta S_G = \Delta S_G - \Delta S_B$$
$$\Delta\Delta S_R = \Delta S_R - \Delta S_B$$

The more approximate to zero both $\Delta\Delta S_G$ and $\Delta\Delta S_R$ are, the more near to the color balance obtained with the strobe light source, which can serve as parameters of the evaluation of color shift in actual prints.

2) Photographs of a Macbeth color checker and a person subject were taken using a strobe light or a fluorescent lamp EX-N as the light source.

A sample was prepared photographing using fluorescent lamp EX-N under such printing conditions that when using the strobe light, the grey portions showed the same grey density as that of the color checker on the print, and then, a print of the sample was prepared. The reproducibility of a skin color chart on the print above obtaind was visually evaluated.

As seen in Table 1, sample Nos. 101 through 103 and 106 were found to offer skin color reproduction with undesirable green and blue tones lacking liveliness.

On the other hand, the inventive sample Nos. 104 and 105 provided a good skin color reproduction and favorable grey reproduction even under fluorescent lamp lighting.

In addition, it was found that even within the constitution of the present invention, the appearance of yellow color is suppressed upon reproduction of skin color under strobe light and thus better skin color reproduction is obtained by keeping the λG_{max} not too high.

Claims

1. A silver halide color photographic light-sensitive material comprising a support, and, coated thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer, each layer containing a sensitizing dye, wherein the maximum sensitivity wavelength λ Rmax, maximum sensitivity SRmax and sensitivity at 610 nm SR_{610} of the red-sensitive emulsion layer and the maximum sensitivity wavelength λ Gmax, maximum sensitivity SGmax, and sensitivity at 545 nm SG_{545} of the green-sensitive emulsion layer satisfy the following requirements:

$$590\text{ nm} \leq \lambda\text{ Rmax} \leq 625\text{ nm},\ SR_{610} \geq 0.8SRmax$$
$$520\text{ nm} \leq \lambda\text{ Gmax} \leq 570\text{ nm},\ SG_{545} \leq 0.8SGmax$$

2. The material of claim 1, wherein said λ Rmax, SRmax, SR_{610}, λ Gmax, SGmax and SG_{545} satisfy the following requirements at a density of Dmin + 0.3:

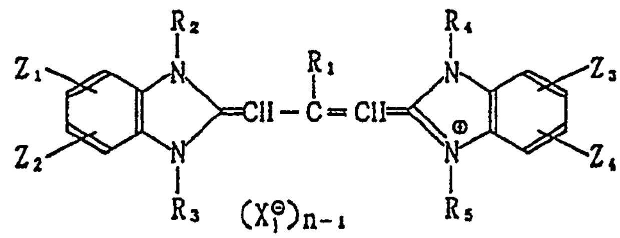
$$590\text{ nm} \leq \lambda\text{ Rmax} \leq 625\text{ nm},\ SR_{610} \geq 0.8SRmax$$
$$520\text{ nm} \leq \lambda\text{ Gmax} \leq 570\text{ nm},\ SG_{545} \leq 0.8SGmax$$

3. The material of claim 1, wherein said λ Rmax, SRmax, SR_{610}, λ Gmax, SGmax and SG_{545} satisfy the following requirements at a density of Dmin + 0.3:

$$590\text{ nm} \leq \lambda\text{ Rmax} \leq 625\text{ nm},\ SR_{610} \geq 0.9SRmax$$
$$520\text{ nm} \leq \lambda\text{ Gmax} \leq 570\text{ nm},\ SG_{545} \leq 0.8SGmax$$

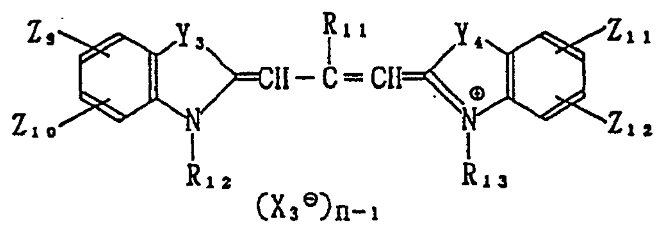
4. The material of claim 1, wherein the red-sensitive emulsion layer comprises a sensitizing dye represented by the following formulae I and III , and the green-sensitive emulsion layer comprises oxacabocyanine, oxabenzimidazolecyanine, thia-4′ -cyanine or thia-2′ -cyanine dyes:

formula I



wherein R_1 represents a hydrogen atom, an alkyl group or an aryl group; R_2, R_3, R_4 and R_5 independently represent an alkyl group or an aryl group; Z_1, Z_2, Z_3, and Z_4 independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group or a sulfonyl group; Z_1 and Z_2 and / or Z_3 and Z_4 may link together to form a ring; X_1 represents an anion; n represents an integer 1 or 2, provided that, when the sensitizing dye forms an intramolecular salt, n represents 1.

formula III



wherein R_{11} represents a hydrogen atom, an alkyl group or an aryl group; R_{12} and R_{13} independently represent an alkyl group or an aryl group; Y_3 and Y_4 independently represent a sulfur atom or a selenium atom; Z_9, Z_{10}, Z_{11}, and Z_{12} independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group or a sulfonyl group; Z_9 and Z_{10} and / or Z_{11} and Z_{12} may link together to form a ring; X_3 represents an anion; n represents an integer 1 or 2, provided that, when the sensitizing dye forms an intramolecular salt, n represents 1.

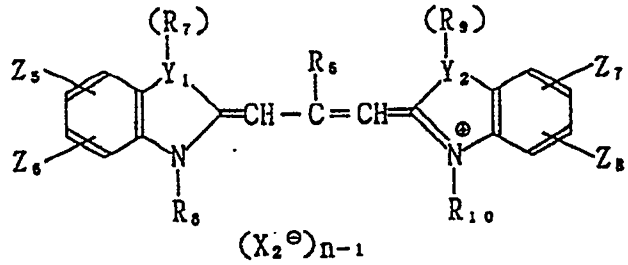
5. The material of claim 4, wherein the red-sensitive emulsion layer contains the sensitizing dye represented by formula I in an amount of 10 to 90 mol% based on the total amount of a sensitizing dye in the red-sensitive emulsion layer.

6. The material of claim 4, wherein the red-sensitive emulsion layer contains the sensitizing dye represented by formula I in an amount of 60 to 90 mol%, based on the total amount of a sensitizing dye in the red-sensitive emulsion layer.

7. The material of claim 4, wherein the green-sensitive emulsion layer contains said oxacabocyanine, oxabenzimidazolecyanine, thia-4′ -cyanine or thia-2′ -cyanine dyes in an amount of 50 to 85 mol% based on the total amount of a sensitizing dye in the green-sensitive emulsion layer.

8. The material of claim 4, wherein the red-sensitive emulsion layer further comprises a sensitizing dye represented by the following formula II :

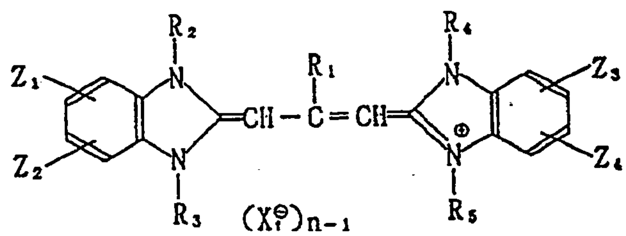
formula II



wherein R_6 represents a hydrogen atom, an alkyl group or an aryl group; R_7, R_8, R_9 and R_{10} independently represent an alkyl group or an aryl group; Y_1 and Y_2 independently represent a nitrogen atom, an oxygen atom, a sulfur atom or a selenium atom, provided that, when Y_1 is an oxygen atom, a sulfur atom or a selenium atom, the sensitizing dye does not contain R_7; Y_1 and Y_2 are not nitrogen atoms or surfur atoms simultaneously; Z_5, Z_5, Z_7, and Z_8 independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group or a sulfonyl group; Z_5 and Z_6 and / or Z_7 and Z_8 may link together to form a ring; X_2 represents an anion; n represents an integer 1 or 2, provided that, when the sensitizing dye forms an intramolecular salt, n represents 1.

9. The material of claim 4, wherein the gree-sensitive emulsion layer further comprises a sensitizing dye represented by the following formula I :

formula I



wherein R_1 represents a hydrogen atom, an alkyl group or an aryl group; R_2, R_3, R_4 and R_5 independently represent an alkyl group or an aryl group; Z_1, Z_2, Z_3, and Z_4 independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group or a sulfonyl group; Z_1 and Z_2 and / or Z_3 and Z_4 may link together to form a ring; X_1 represents an anion; n represents an integer 1 or 2, provided that, when the sensitizing dye forms an intramolecular salt, n represents 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 1960

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y	JP-A-621604499 (FUJI) * the whole document * ---	1-9	G03C7/30
Y	EP-A-0115304 (FUJI) * page 19, line 3 - page 32, line 2 * ---	1-9	
Y	US-A-4028115 (HINATA ET AL.) * column 2, line 24 - column 13, line 37 * -----	1-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 APRIL 1991	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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