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(54) Method for storing infrared-sensitive silver halide photographic material and photographic composite composed of infrared-sensitive silver halide photographic material and packaging material therefor.

(57) A method for storing an infrared-sensitive silver halide photographic material, comprising storing in a deoxidized state the infrared-sensitive silver halide photographic material comprising a support having thereon at least one silver halide light-sensitive emulsion layer spectrally sensitized with at least one sensitizing dye selected from a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, and a heptamethinerhodacyanine sensitizing dye, said light-sensitive emulsion having a spectral sensitivity peak in the wavelength region of at least 720 n.m. and a photographic composite comprising an infrared-sensitive silver halide photographic material enclosed in a packaging material in a deoxidized state. The desensitization upon storage of the infrared-sensitive silver halide photographic material is remarkably improved.

METHOD FOR STORING INFRARED-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL AND PHOTOGRAPHIC COMPOSITE COMPOSED OF INFRARED-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL AND PACKAGING MATERIAL THEREFOR

FIELD OF THE INVENTION

This invention relates to a method for storing an infrared-sensitive silver halide photographic material, and more particularly, to a storage method for preventing the change of photographic characteristics of a silver halide photographic material spectrally sensitized to an infrared wavelength region with the passage of time.

In particular, the invention relates to a storage method for maintaining the photographic characteristics of a silver halide color photographic material spectrally sensitized to an infrared wavelength region for laser scanning exposure with the passage of time.

Furthermore, the invention relates to a photographic composite composed of an infrared-sensitive silver halide photographic material and a packaging material therefor.

BACKGROUND OF THE INVENTION

Recently, for the storage and output of information, in particular, for the storage and output of information containing images, it has been common to store the processed information or display or output as a hard copy of the stored information after processing.

Conventional means for obtaining hard copies from soft information include methods using electric or magnetic signals, using light-insensitive recording materials such as an ink jet system, etc., and using light-sensitive recording materials such as silver halide photographic materials, electrophotographic materials, etc.

The last method is by recording using an optical system emitting light controlled with image information, and since the optical system has a high resolving power and can make not only a multi-value record but also a multi-gradient record, this method is useful for obtaining a high image quality. In particular, since in a silver halide photographic material, the image formation is performed chemically, the use of a silver halide photographic material gives a higher image quality and larger recorded amounts of information than when using an electrophotographic material.

On the other hand, since the image formation using a silver halide photographic material requires wet development processing, the system using the silver halide material is inferior to the system using an electrophotographic material in processing time, and hence the silver halide system has not been used much in fields not requiring a high image quality.

However, recently, a photographic image forming system using a silver halide color photographic material and a compact, simple and quick development system has been developed and photographic prints having a very high image quality have been obtained relatively easily and at a low cost. Thus, if images are obtained from soft information using this system, hard copies having a high image quality can be obtained easily and at a low cost.

For quickly and easily processing silver halide color photographic materials as described above, a specific system is required. Also, the silver halide color photographic material must have sufficient performance in the light-sensitive wavelength, optimum sensitivity, color separation, and further the stability of sensitivity, matching the optical system used.

Conventional color copying techniques include a copying system using an electrophotographic technique, a laser printer, and a combination of LED (light-emitting diode), heat development of silver halide, and a dye diffusion system.

Also, JP-A-61-137149 (the term "JP-A" as used herein means an unexamined published Japanese patent application") discloses a silver halide color photographic material having at least three silver halide emulsion layers each using an ordinary color coupler on a support, at least two emulsion layers having been spectrally sensitized for laser light of an infrared wavelength region.

JP-A-63-197947 discloses a full color recording material having at least three light-sensitive layers each containing a color coupler on a support, at least one layer having been spectrally sensitized to a longer wavelength region than about 670 n.m. in spectral sensitivity maximum wavelength so that the layer is sensitive to LED or a semiconductor laser, a color image being obtained by a scanning exposure and subsequent development. This patent application also discloses a particularly high sensitive and stable spectral sensitizing method and a method of using dyes.

Furthermore, JP-A-55-13505 discloses an image recording system for a color photographic material by controlling coloring of yellow, magenta, and cyan, respectively by three kinds of luminous fluxes each having a different wavelength, e.g., luminous fluxes of green, red, and infrared.

Also, in S.H. Baek, et al, Preliminary Reports , pages 245-247, 4th Non Impact Printing International Conference (SPSE) (April 20-25, 1988, New Orleans, La), there is described a continuous tone scanning type printer having a semiconductor laser output controlling mechanism.

A method using a silver halide color photographic material for obtaining hard copies from soft information can easily give stable copies having a high image quality as compared to light-insensitive recording methods and those using an electrophotographic material. Also, the use of a semiconductor laser for the scanning exposure is advantageous since the exposure apparatus is compact and inexpensive.

However, even at present, the wavelength of a semiconductor laser which can be used for the purpose can not be optionally selected. Recently a semiconductor laser having a wavelength of about 676 n.m. has been practically used, but many semiconductor lasers have been practically used in the infrared wavelength region.

In a color photographic system employing a subtractive color process as in the present invention, light-sensitive layers having spectral sensitivities to at least three different light-sensitive wavelength regions are required and hence one layer or two layers, or, as the case may be, three or more layers must have a spectral sensitivity in the infrared wavelength region.

Furthermore, in a semiconductor laser element in the visible region or the infrared region near a visible region, as the wavelength of the element is shorter, the output is weaker and the output itself is unstable.

Accordingly, among characteristics required for a silver halide photographic material used for such a semiconductor laser, it is very important that the photographic light-sensitive material have a high sensitivity; that stable performance is obtained even with deviations of the wavelength of the semiconductor laser, and that these features be attained in the infrared region.

Satisfying these requirements in the infrared wavelength region is difficulty, even when using silver iodobromide which is useful for obtaining a high sensitivity.

On the other hand, it is known that in order to quickly obtain a color image from the silver halide photographic material exposed by the above system, silver iodobromide is slow and silver chlorobromide is preferred. In particular, it is also known that a high silver chloride emulsion containing silver chloride in a high content is preferred.

However, it has been found that when using such a high silver chloride emulsion, it is more difficult to satisfy the above requirements in the infrared wavelength region. That is, it has been found that the silver chloride emulsion is very inconvenient for sensitization with an infrared spectral sensitizing dye. When using the silver chloride emulsion, it is difficult to obtain high sensitivity by efficiently spectrally sensitizing the emulsion as well, and the sensitivity obtained is greatly lowered when the photographic light-sensitive material containing the silver chloride emulsion is stored.

It is known that in general, when a silver halide photographic material containing silver halide emulsions sensitized using sensitizing dyes having insufficient adsorptive power to silver halide is stored, or a silver halide photographic material containing silver halide emulsions sensitized using sensitizing dyes having adequate adsorptive power to silver halide is stored under high-humidity conditions, the sensitizing dyes are desorbed and the spectral sensitivity is reduced with the passage of time.

On the other hand, desensitization on storing a silver halide photographic material containing silver halide emulsions sensitized using infrared spectral sensitizing dyes is different, since it is caused when the sensitivity of the silver halide emulsion itself having adsorbed thereto the infrared spectrally sensitizing dye is greatly reduced.

As a conventional method of preventing the change of photographic performance when a silver halide photographic material is stored, it is known to lower the temperature for storing the photographic material, that is, to store the photographic materials in a cold chamber or in a refrigerator. In particular, some commercial silver halide photographic materials having a spectral sensitivity in the infrared region are required to be stored under refrigerated storing conditions after purchase. However, practically, it is considerably difficult or impossible to provide such storage by the use.

JP-A-53-144727 (U.S. Patent 4,263,397) discloses a photographic product composed of a silver halide photographic material containing sensitizing dyes in a closed package with a packaging material having a low oxygen permeability under a low oxygen partial pressure, but it does not contain any practical description that such a system is effective for a sensitizing dye giving a spectrally sensitizing peak in the infrared region of a long wavelength as in this invention.

As the result of investigations on desensitization when storing a silver halide photographic material containing infrared spectrally sensitizing dyes for a long wavelength, the inventor has discovered that in the case of a silver halide photographic material using a spectrally sensitizing dye selected from a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, and a heptamethinerhodacyanine sensitizing dye, each having a spectral sensitizing peak in the wavelength region longer than 720 n.m., the desensitization upon the storage of the photographic material is severe.

Also, it has been discovered that when these long wavelength infrared spectrally sensitizing dyes are used for a high silver chloride emulsion containing at least 90 mol% silver chloride, desensitization at the storage becomes a more severe problem.

SUMMARY OF THE INVENTION

An object of this invention is, therefore, to provide a simple method for maintaining the sensitivity during storage of a silver halide photographic material containing high silver chloride emulsion(s) sensitized by using a long wavelength infrared spectrally sensitizing dye.

It has now been discovered that these and other objects of the present invention can be attained by a method for storing an infrared-sensitive silver halide photographic material, which comprises storing in a deoxidized state an infrared-sensitive silver halide photographic material comprising a support having thereon at least one silver halide light-sensitive emulsion layer spectrally sensitized with at least one sensitizing dye selected from a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, and a heptamethinerhodacyanine sensitizing dye, said light-sensitive emulsion having a spectral sensitivity peak in the wavelength region of at least 720 n.m.

The present invention also relates to a photographic composite i.e., a packaged photographic material comprising this infrared sensitive silver halide photographic material enclosed in a packaging material wherein the photograpic material is stored in a deoxidized state.

DETAILED DESCRIPTION OF THE INVENTION

The invention is now explained in greater detail.

The following are preferred embodiments of the present invention.

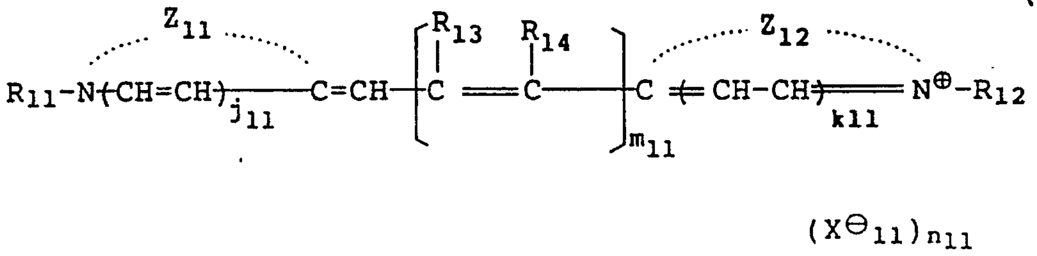
1. The method for storing an infrared-sensitive silver halide photographic material, wherein said silver halide light-sensitive emulsion layer comprises silver chlorobromide containing at least 90 mol% silver chloride.
2. The method for storing an infrared-sensitive silver halide photographic material, wherein the silver bromide in said silver chlorobromide is present as a local phase in the interior of the silver halide grains or at the surface of the silver halide grains.
3. The method for storing an infrared-sensitive silver halide photographic material, wherein said local phase has a silver bromide content of at least 15 mol%.
4. The method for storing an infrared-sensitive silver halide photographic material, wherein said silver chlorobromide grains have a surface phase containing 15 to 70 mol% silver bromide, said surface phase containing from 0.01 to 20 mol% of the total silver contained in said silver halide grains.
5. The method for storing an infrared-sensitive silver halide photographic material, wherein said silver chlorobromide grains have a surface phase containing 20 to 60 mol% silver bromide, said surface phase containing from 0.02 to 7 mol% of the total silver contained in said silver halide grains.
6. The method for storing an infrared-sensitive silver halide photographic material, wherein said silver halide emulsion is a monodisperse emulsion and the average grain size of the silver chlorobromide grains is from 0.1 μm to 1.5 μm.
7. The method for storing an infrared-sensitive silver halide photographic material, wherein said silver halide light-sensitive emulsion layer has a spectral sensitivity peak in the wavelength region of at least 735 n.m.
8. The method for storing an infrared-sensitive silver halide photographic material, wherein said silver halide light-sensitive emulsion layer has a spectral sensitivity peak in the wavelength region of at least

750 n.m.

9. The method for storing an infrared-sensitive silver halide photographic material, wherein said silver halide light-sensitive emulsion layer has a spectral sensitivity peak in the wavelength region of at least 770 n.m.

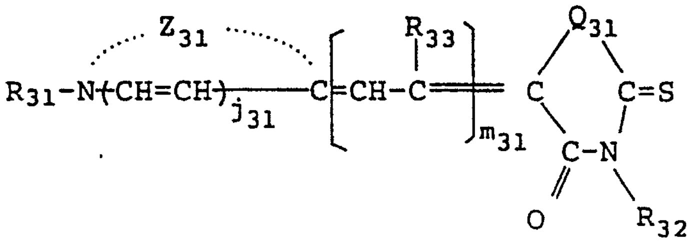
10. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said tricarbocyanine sensitizing dye is represented by formula (I):

(I)



wherein z_{11} and Z_{12} each represents an atomic group necessary for forming a heterocyclic nucleus; R_{11} and R_{12} each represents an alkyl group, an alkenyl group, an alkynyl group, or an aralkyl group; m_{11} is 3; R_{13} represents hydrogen; R_{14} represents hydrogen, a lower alkyl group or an aralkyl group or when R_{14} is hydrogen and m_{11} is 2 or 3, R_{13} combines with other R_{13} to form a hydrocarbon or a heterocyclic ring; j_{11} and k_{11} each is 0 or 1; X_{11} represents an acid anion; and n_{11} is 0 or 1.

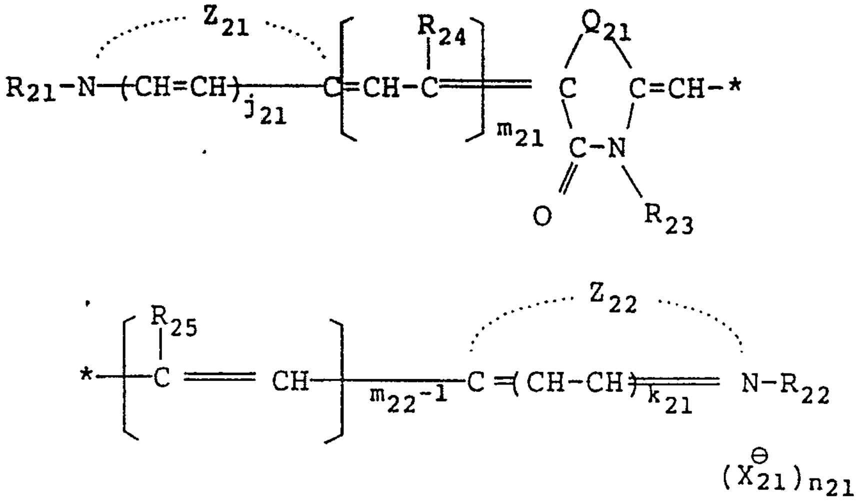
11. The method for storing an infrared-sensitive silver halide photographic material, wherein said hexamethinemerocyanine sensitizing dye is represented by formula (III):



(III)

wherein Z_{31} represents an atomic group necessary for forming a heterocyclic ring; Q_{31} represents sulfur, oxygen, selenium or N-R_{26}, wherein R_{26} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; R_{31} represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group; R_{32} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; m_{31} is 2 or 3; R_{33} represents hydrogen, a lower alkyl, or an aryl group or R_{33} combines with other R_{33} to form a hydrocarbon ring or a heterocyclic ring; and j_{31} is 0 or 1.

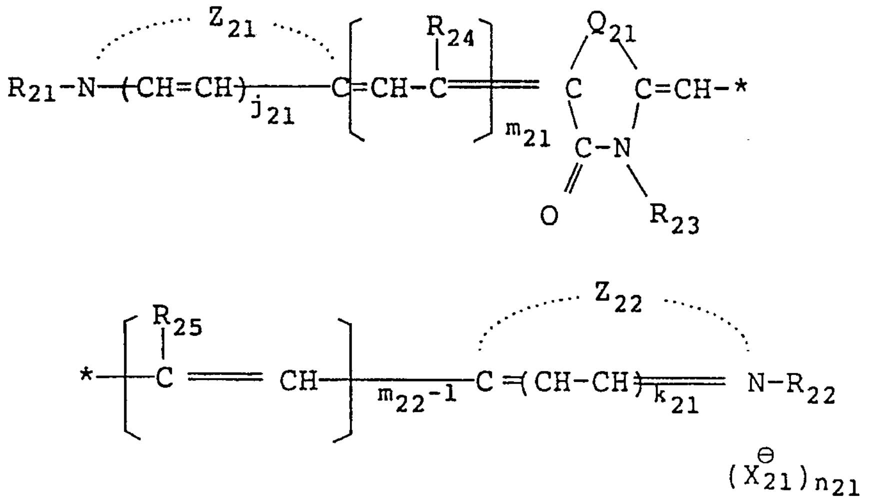
12. The method for storing an infrared-sensitive silver halide photographic material, wherein said pentamethinerhodacyanine sensitizing dye is represented by formula (II):



(II)

wherein Z_{21} and Z_{22} each represents an atomic group necessary for forming as heterocyclic nucleus; R_{21} and R_{22} each represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group; R_{23} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; m_{21} and m_{22} each represents 1, 2, or 3, provided that the sum of m_{21} and m_{22} is 3; R_{24} and R_{25} each represents hydrogen, a lower alkyl group, or an aryl group or when m_{21} is 2 or 3, R_{24} combines with other R_{13} or when m_{21} is 3, R_{25} combines with other R_{25}, to form a hydrocarbon ring or a heterocyclic ring; Q_{21} represents sulfur, oxygen, selenium or N-R_{26}, wherein R_{26} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; j_{21} and k_{21} each is 0 or 1; X_{21} represents an acid anion; and n_{21} is 0 or 1.

13. The method for storing an infrared-sensitive silver halide photographic material, wherein said heptamethinerhodacyanine sensitizing dye is represented by formula (II):



(II)

wherein z_{21} and Z_{22} each represents an atomic group necessary for forming as heterocyclic nucleus; R_{21} and R_{22} each represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group; R_{23} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; m_{21} and m_{22} each represents 1, 2, or 3, provided that the sum of m_{21} and m_{22} is 4; R_{24} and R_{25} each represents hydrogen, a lower alkyl group, or an aryl group or when m_{21} is 2 or 3, R_{24} combines with other R_{24} or when m_{21} is 3, R_{25} combines with other R_{25}, to form a hydrocarbon ring or a heterocyclic ring; Q_{21} represents sulfur, oxygen, selenium or N-R_{26}, wherein R_{26} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; j_{21} and k_{21} each is 0 or 1; X_{21} represents an acid anion; and n_{21} is 0 or 1.

14. The method for storing an infrared-sensitive silver halide photographic material, wherein said sensitizing dye is present in said silver halide emulsion in an amount from 5×10^{-7} mol to 5×10^{-3} mol per

mol of silver therein.

15. The method for storing an infrared-sensitive silver halide photographic material, wherein said infrared-sensitive silver halide photographic material is stored at an oxygen volume ratio of at most 2%.

16. The method for storing an infrared-sensitive silver halide photographic material, wherein said infrared-sensitive silver halide photographic material is stored at an oxygen volume ratio of at most 1%.

17. The method for storing an infrared-sensitive silver halide photographic material, wherein said infrared-sensitive silver halide photographic material is stored at an oxygen volume ratio of at most 0.5%.

18. The method for storing an infrared-sensitive silver halide photographic material, wherein said infrared-sensitive silver halide photographic material is stored in a nitrogen atmosphere.

19. The method for storing an infrared-sensitive silver halide material, wherein the silver halide photographic material has at least two silver haldie light-sensitive layers each having a spectral sensitivity peak in the wavelength region of not shorter than 720 n.m., and each silver halide light-sensitive emulsion layer contains one of a cyan coupler, a magenta coupler, and a yellow coupler.

20. The method for storing an infrared-sensitive silver halide photographic material, wherein the silver halide photographic material has at least three silver halide light-sensitive emulsion layers each containing a silver chlorobromide emulsion having a mean silver chloride content of at least 90 mol% or a silver chloride emulsion, each light-sensitive emulsion layer contains one of a cyan coupler, a magenta coupler, and a yellow coupler, respectively, and the three light-sensitive emulsion layers each has a different spectral sensitivity peak in the wavelength region of from 650 n.m. to 690 n.m., from 720 n.m. to 790 n.m., from 770 n.m. to 850 n.m., respectively.

The term "oxygen volume ratio" in this invention is as follows. That is, when the base content of oxygen atoms per unit volume of the atmosphere under 25°C and 1 atm. is defined as 21%, the content of oxygen atoms in the same unit volume under an optional temperature and pressure, i.e., the numerical value in direct proportional relation, is the oxygen volume ratio. The oxygen volume ratio is the product of the base oxygen ratio and the pressure, and the oxygen volume ratio is the content of oxygen per unit volume of certain gas for the atmosphere under normal conditions (25°C, 1 atm.).

For example, when an atmosphere containing 21% oxygen at 1 atm. is expanded at 0.5 atm., the oxygen volume ratio becomes 10.5%, and also when the atmosphere and nitrogen are mixed with other at 1:1 under 1 atm., the oxygen volume ratio is also 10.5%.

The control of the oxygen volume ratio can be attained by generally known various methods in this invention. Oxygen may be removed by physical or mechanical methods, or by a chemical method.

Specifically, the air may be mixed or replaced with other gas containing no oxygen, or vacuum degassing may be employed. After vacuum degassing, the remaining air may be replaced with a gas containing no oxygen. Also, oxygen in the air may be reacted with another compound or element. Also, oxygen may be removed using a gas separating membrane or an oxygen pump.

In this invention, the term "deoxidized state" means a state in which the content of oxygen is less than that of the atmosphere, or a state in which the oxygen volume ratio is low. In this invention, the oxygen volume ratio is preferably 2% or lower, and further is preferably as low as possible. The oxygen volume ratio is more preferably 1% or lower, and most preferably 0.5% or lower.

For storing the photographic light-sensitive material such that the oxygen volume ratio is as low as possible, the light-sensitive material can be stored or packed in an oxygen-free atmosphere, e.g., a nitrogen atmosphere, from production, or when the light-sensitive materials are stored in a closed vessel or closely packed in the air, the light-sensitive materials can be stored or packed with a deoxidizing agent such as an iron powder. This method is preferred to easily form a deoxidized state in a package form.

Such a deoxidized state may be maintained at any time after coating silver halide emulsions until the step of forming the product, or may be introduced to the when the product is packaged.

Furthermore, it is preferred that the deoxidized state is maintained after opening the package for using the light-sensitive materials.

As described above, the deoxidized state in this invention may be achieved in any step from the production of the light-sensitive materials to use thereof or throughout, whereby the charge of the performance or the light-sensitive materials can be prevented.

For keeping the deoxidized state for preventing the change of the photographic performance of the light-sensitive materials after opening the package a vacuum pump, an oxygen separating membrane, or a solid oxygen pump can be used. Such a device can be incorporated in the apparatus for exposing and processing the light-sensitive materials, or the device can be used individually.

In the case of using such an oxygen-removing device, it is useful to connect the device to an exposure apparatus, a holder or cartridge for the light-sensitive material, which is equipped with an exposure apparatus.

In the case of vacuum degassing using a vacuum pump, water contained in the light-sensitive material is also removed, which may retard the hardening reaction of gelatin, or cause the formation of fog, or curling of the light-sensitive material, but this technique is useful for stably storing the light-sensitive materials.

For attaining the object of this invention in the form of a photographic composite composed of a light-sensitive material and a packaging material therefor, a polymer or a metal foil substantially impermeable to oxygen is used as a packaging material, the light-sensitive material is closely packed by the packaging material, and before or after closely packaging, the deoxidized state is formed in the package.

The polymer which can be used for this purpose includes polyvinylidene chloride, polyethylene terephthalate, nylon, and polyvinyl alcohol, as a polymer having a low oxygen permeability. Also, even a polymer having a high oxygen permeability, such as polyethylene, or the material obtained by copolymerizing or blending polyethylene with polyvinyl alcohol, is preferably used. Furthermore, polyvinyl chloride, polyvinyl acetate, polypropylene can be used.

Also, as a metal foil, an aluminum foil or a lead foil can be used.

When a composite material formed by laminating the polymer film and the metal foil is used as the packaging material, very good results are obtained for the object of this invention.

Also, two or more packaging materials are preferably used as double or multiple package form.

For closely sealing the packaging material, a conventional method of heat-welding the polymer film may be used.

In this invention, at least one silver halide light-sensitive emulsion layer of a silver halide photographic material is spectrally sensitized by a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, or a heptamethinerhodacyanine sensitizing dye, each providing a spectral sensitivity peak in the wavelength region of at least 720 n.m., i.e. 720 n.m. or longer.

For the silver halide photographic material, these sensitizing dyes can be used with other sensitizing dyes such as ordinary cyanine dyes, merocyanine dyes, or complex cyanine dyes. Furthermore, complex cyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, or hemioxonol dyes can be also used in combination. Cyanine dyes include simple cyanine dyes, carbocyanine dyes, and dicarbocyanine dyes. Also, merocyanine dyes include zerimethinemerocyanine dyes, dimethinemerocyanine dyes, and tetramethinemerocyanine dyes.

When the silver halide photographic material is a color photographic material in this invention, at least one light-sensitive emulsion layer is spectrally sensitized by at least one sensitizing dye selected from a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, and a heptamethinerhodacyanine sensitizing dye each having a spectral sensitivity peak in the wavelength region of at least 720 n.m. and other light-sensitive emulsion layers may be layers having a spectral sensitivity peak shorter than 720 n.m.

That is, an ordinary color photographic light-sensitive material is composed of plural light-sensitive emulsion layers containing a cyan coupler, a magenta coupler, and a yellow coupler respectively and in this invention, at least one of the coloring coloring light-sensitive layers is required to be spectrally sensitized by a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, or a heptamethinerhodacyanine sensitizing dye each having a spectral sensitivity peak in the wavelength region of at least 720 n.m. It is preferable that two different coloring light-sensitive emulsion layers are each spectrally sensitized to have a spectral sensitivity peak in the wavelength region of at least 720 n.m.

In this invention, it is most preferred for three or more different coloring light-sensitive emulsion layers are all spectrally sensitized to have a spectral sensitivity peak in the region of at least 720 n.m.

In any case, at least one light-sensitive emulsion layer must be spectrally sensitized with a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, or a heptamethinerhodacyanine sensitizing dye giving spectral sensitivity peak in the region of at least 720 n.m.

When a silver halide photographic material has light-sensitive emulsion layer(s) having a spectral sensitivity peak in the region shorter than 720 n.m., it is, not necessary that all light-sensitive layers are spectrally sensitized to have a spectral sensitivity peak in the region of at least 720 n.m. That is, when a photographic light-sensitive material is exposed using a laser diode, the light-sensitive material can be exposed by light having a wavelength of shorter than 720 n.m., and also light having a wavelength of about 670 n.m.

Accordingly, in a color photographic light-sensitive material for laser diode exposure, each color light-sensitive emulsion layer may be selectively spectrally sensitized for matching with a laser diode emitting light having a wavelength in a different wavelength region of, for example, 650 n.m. to 690 n.m., 720 n.m. to

790 n.m., or 770 n.m. to 850 n.m. The term "selectively spectrally sensitized" as used herein means that when the light-sensitive material having the light-sensitive layer thus sensitized is exposed by the main wavelength of one laser diode, the sensitivity of the light-sensitive layer thus sensitized is sufficiently separated from that of other color light-sensitive layers to avoid mixing of colors is spectral sensitivity, which would cause an improper color reproduction.

The spectrally sensitizing dye which is preferably used in this invention, that is, the spectrally sensitizing dye which is used for visible sensitization to infrared sensitization, can be selected from the compounds represented by formulae (I), (II), and (III) shown below.

In the color photographic light-sensitive material in this invention, it is necessary that at least one light-sensitive emulsion layer is spectrally sensitized to have a spectral sensitivity peak in the wavelength region of at least 720 n.m. with at least one sensitizing dye selected from a tricarbocyanine sensitizing dye typified by a compound shown by following formula (I) wherein m_{11} is 3; a pentamethinerhodacyanine sensitizing dye or a heptamethinerhodacyanine sensitizing dye typified by a compound shown by following formula (II) wherein $m_{21} + m_{22}$ is 3 or 4, and a hexamethinemerocyanine sensitizing dye typified by a compound shown by following formula (III) wherein m_{31} is 3.

According to the general convention in the art, a sensitizing dye compound represented by formula (I) wherein m_{11} is 3 is called a tricarbocyanine sensitizing dye, and a sensitizing dye compound represented by formula (III) wherein m_{31} is 3 is called a hexamethinemerocyanine sensitizing dye, but it is not conventional that a sensitizing dye compound represented by formula (II) wherein $m_{21} + m_{22}$ is 3 is called a pentamethinerhodacyanine sensitizing dye and that a sensitizing dye typified by the compound shown by formula (II) wherein $m_{21} + m_{22}$ is 4 is called a heptamethinerhodacyanine sensitizing dye. In the invention, these definitions of the terms "pentamethinerhodacyanine dye" and "heptamethinerhodacyanine dye" in terms of formula (II) are employed for simplicity.

In this invention, the light-sensitive emulsion layer is spectrally sensitized by the specific sensitizing dye to give a spectral sensitivity peak in the wavelength region preferably of at least 735 n.m., more preferably of at least 750 n.m., and most preferably of at least 770 n.m.

In one preferred embodiment of this invention, two or more different color light-sensitive layers are spectrally sensitized to have a spectral sensitivity peak in the region of at least 720 n.m., each with a sensitizing dye selected from the compounds represented by formulae (I), (II), and (III) shown below.

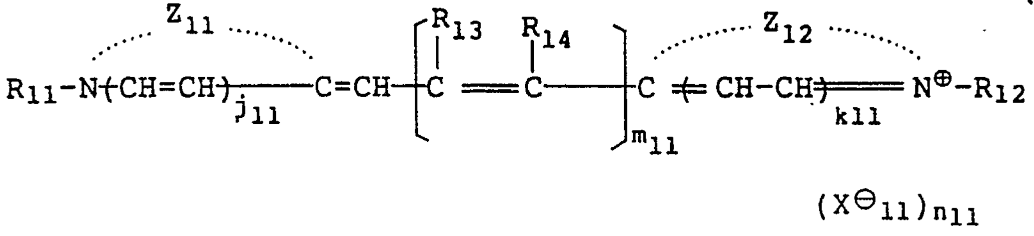
The compounds represented by formulae (I), (II), and (III) below include compounds which adsorb onto silver halide grains to spectrally sensitize the silver halide emulsion so that the emulsion has a spectral sensitivity peak in the region of at least 720 n.m. as described above but also include compounds capable of spectrally sensitizing such an emulsion to have a spectral sensitivity peak in the region shorter than 720 n.m.

Accordingly, if at least one light-sensitive emulsion layer is spectrally sensitized to have a spectral sensitivity peak in the wavelength region of at least 720 n.m. by the sensitizing dye, according to the invention, other light-sensitive emulsion layer(s) spectrally sensitized to have a spectral sensitivity peak in the region shorter than 720 n.m. may be spectrally sensitized by a compound included in the compounds represented by formulae (I), (II), and (III), or may be spectrally sensitized by other compounds not represented by these formulae.

The present invention relates to a method for retaining the storage performance of the silver halide photographic material after coating the silver halide emulsion(s) spectrally sensitized to have a spectral sensitivity peak in the region of at least 720 n.m. by the specific sensitizing dye according to the invention, and the spectrally sensitizing dyes for use in this invention are not to be construed as being limited to the compounds represented by formulae (I), (II), and (III).

The sensitising dyes represented by formulae (I), (II), and (III) are as follows:

(I)



$$R_{11}-N\!\left(CH=CH\right)_{j_{11}}\!-C=CH-\left[\overset{R_{13}}{\overset{|}{C}}=\overset{R_{14}}{\overset{|}{C}}\right]_{m_{11}}\!-C\!\left(=CH-CH\right)_{k_{11}}\!=N^{\oplus}-R_{12}\quad (Z_{11},\ Z_{12})\quad (X^{\ominus}_{11})_{n_{11}}$$

In the above formula, Z_{11} and Z_{12} each represents an atomic group necessary for forming a heterocyclic nucleus.

As the heterocyclic nucleus, a 5- or 6-membered heterocyclic nucleus containing nitrogen, sulfur, oxygen, selenium, or tellurium is preferred and the ring may be further combined with a condensed ring or may have a substituent.

Specific examples of the heterocyclic nucleus include a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a selenazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, an oxazole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, an imidazole nucleus, a benzimidazole nucleus, a naphthimidazole nucleus, a 4-quinoline nucleus, a pyrroline nucleus, a pyridine nucleus, a tetrazole nucleus, an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a tellurazole nucleus, a benzotellurazole nucleus and a naphthotellurazole nucleus.

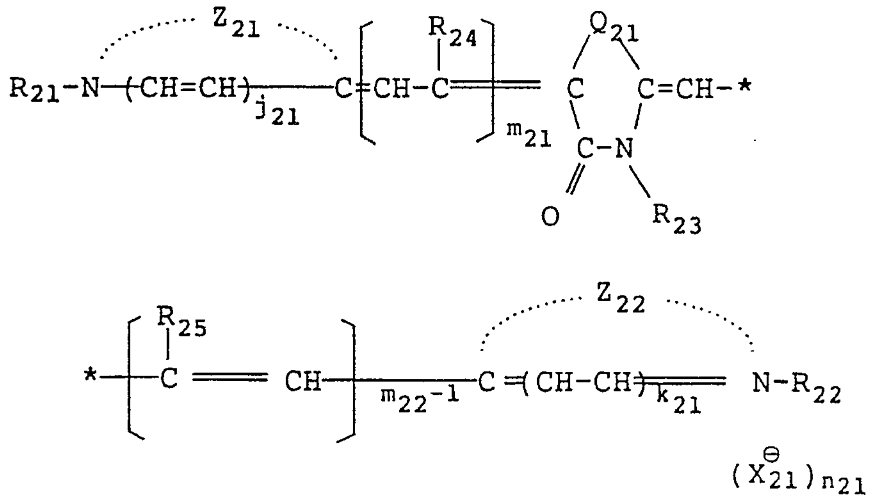
In formula (I), R_{11} and R_{12} each represents an alkyl group, an alkenyl group, an alkynyl group, or an aralkyl group. These groups and the groups described below may be substituted or unsubstituted. For example, the alkyl group include an unsubstituted alkyl group and a substituted alkyl group, and the alkyl group may be a straight chain, branched, or cyclic alkyl group. The carbon atom number of the alkyl group is preferably from 1 to 8.

Specific examples of the substituent of the substituted alkyl group include a halogen atom (e.g., chlorine, bromine, and fluorine), a cyano group, an alkoxy group, a substituted or unsubstituted amino group, a carboxylic acid group, a sulfonic acid group, and a hydroxy group, and alkyl group may have one or plural substituents.

Specific examples of the alkenyl group include a vinylmethyl group.

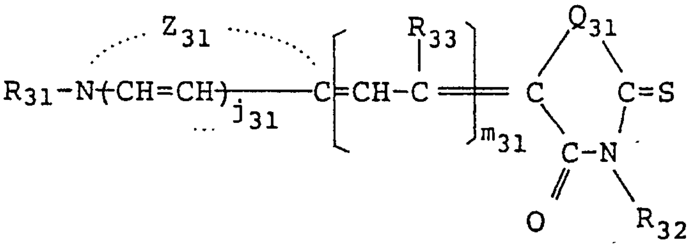
Specific examples of the aralkyl group include benzyl and phenetyl.

In formula (I), m_{11} represents 1, 2, or 3; R_{13} represents hydrogen; R_{14} represents hydrogen, a lower alkyl group, or an aralkyl group, and further R_{14} may combine with R_{12} to form a 5- or 6-membered ring. Also, when R_{14} represents hydrogen and m_{11} is 2 or 3, R_{13} may combine with other R_{13} to form a hydrocarbon ring or a heterocyclic ring such as, preferably, a 5- or 6-membered ring; j_{11} and k_{11} each represents 0 or 1; X_{11} represents an acid anion; and n_{11} represents 0 or 1.



(II)

In the above formula, Z_{21} and Z_{22} have the same meaning as Z_{11} and Z_{12} in formula (I); R_{21} and R_{22} have the same meaning as R_{11} and R_{12} in formula (I); R_{23} represents an alkyl group, an alkenyl group, an alkynyl group, or an aryl group (e.g., a substituted or unsubstituted phenyl group); m_{21} and m_{22} each represents 1, 2, or 3; R_{24} and R_{25} each represents hydrogen, a lower alkyl group, or an aryl group, and m_{21} is 2 or 3, R_{24} may combine with other R_{24} or m_{21} is 3, said R_{25} may combine with other R_{25} to form a hydrocarbon ring or a heterocyclic ring such as, preferably, a 5- or 6=membered ring; Q_{21} represents sulfur, oxygen, selenium, or N-R_{26} (wherein R_{26} has the same meaning as R_{23} above); and j_{21}, k_{21}, X_{21}, and n_{21} are same as j_{11}, k_{11}, X_{11}, and n_{11} in formula (I), respectively.



(III)

In the above formula, Z_{31} represents an atomic group necessary for forming a heterocyclic ring. Specific examples of the heterocyclic ring include those described above for to Z_{11} and Z_{12} in formula (I), and in addition, nuclei of thiazolidine, thiazoline, benzothiazoline, naphthothiazoline, selenazolidine, selenazoline, benzoselenazoline, naphthoselenazoline, benzoxazoline, naphthoxazoline, dihydropyridine, dihydroquinoline, benzimidazoline, and naphthimidazoline.

In formula (III), Q_{31} has the same meaning as Q_{21} in formula (II); R_{31} has the same meaning as R_{11} or R_{12} in formula (I); and R_{32} has the same meaning as R_{23} in formula (II); m_{31} represents 2 or 3; R_{33} has the same meaning as R_{24} in formula (II) and R_{33} may combine with other R_{33} to form a hydrocarbon ring or a heterocyclic ring; and j_{31} has the same meaning as j_{11} in formula (I).

In this invention, the sensitizing dye represented by formula(I) wherein Z_{11} and/or Z_{12} comprises a naphthothiazole nucleus, a naphthoselenazole nucleus, a naphthoxazole nucleus, a naphthimidazole nucleus, or a 4-quinoline nucleus is preferred. Sensitizing dyes represented by formula (II) wherein Z_{21} and/or Z_{22} in formula (II) is selected from the same nuclei, and those represented by formula (III) wherein Z_{31} is selected from the same nuclei, are also preferred. Also, sensitizing dyes wherein the methine chain forms a hydrocarbon ring or a heterocyclic ring are preferred.

Since infrared sensitization uses the sensitization by the M band of a sensitizing dye, the spectral sensitivity distribution is generally broader than the sensitization by the J band. Thus, it is preferred to correct the spectral sensitivity distribution by forming a colored layer containing a dye on a colloid layer closer to the exposed side than a definite light-sensitive layer. The colored layer is effective for inhibiting color mixing by a filter effect.

As a red-sensitive or infrared-sensitive sensitizing dye, a compound having a reduction potential of -1,00 (VvsSCE) or lower is preferred. The sensitizing dye having this characteristic is useful for increasing the sensitivity, in particular, for stabilizing the sensitivity and latent images.

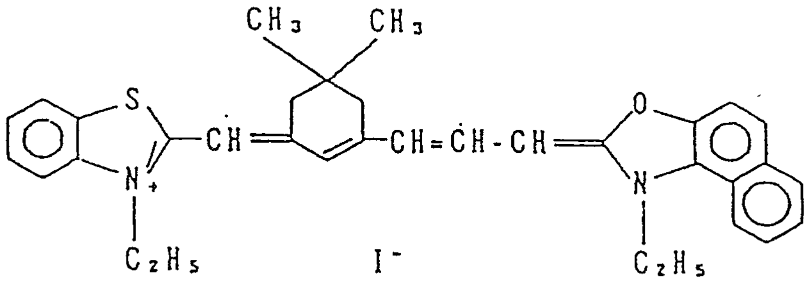
The reduction potential can be measured by phase discrimination type second harmonics AC polarography. As the working electrode, a dropping mercury electrode is used, as a reference electrode, a saturated calomel electrode is used, and as a counter electrode, platinum is used.

Also, the measurement of the reduction potential by phase discrimination type second harmonic AC voltametry using platinum as the working electrode is described in Journal of Imaging Science , Vol. 30, 27-35 (1986).

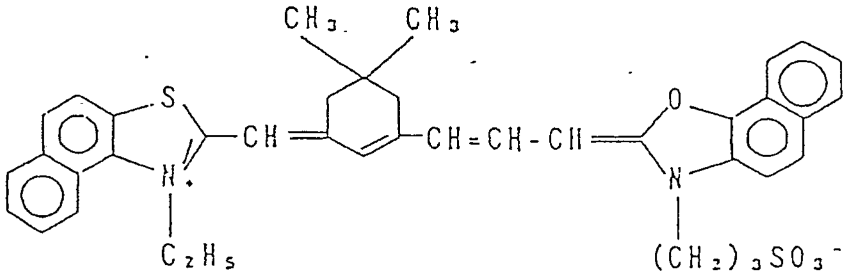
Furthermore, the combination of a compound selected from compounds represented by formulae (IV), (V), (VI) and (VII) described in JP-A-2-157749 and a compound selected from the formaldehyde condensation products of the compounds represented by formulae (VIII-a), (VIII-b) and (VIII-c) described in JP-A-2-157749 is preferably used together with the sensitizing dye according to the present invention.

Specific examples of the sensitizing dyes represented by formulae (I), (II), and (III) are as follows, but the present invention is not to be construed as being limited thereto.

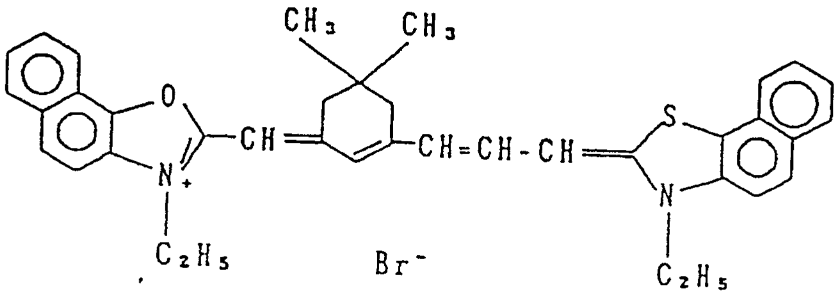
(V-1)


CH₃
CH₃
S
CH
CH=CH-CH
O
N+
N
C₂H₅
I⁻
C₂H₅

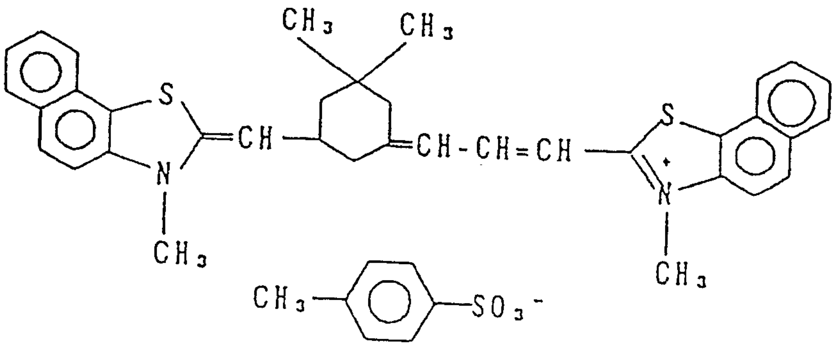
(V-2)


CH₃
CH₃
S
CH
CH=CH-CH
O
N+
N
C₂H₅
(CH₂)₃SO₃⁻

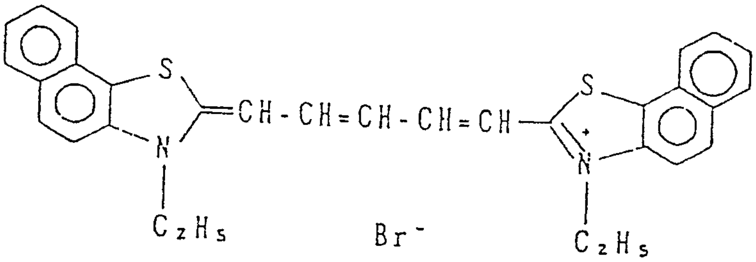
(V - 3)


CH3
CH3
O
CH
CH=CH-CH
S
N+
N
C2H5
Br-
C2H5

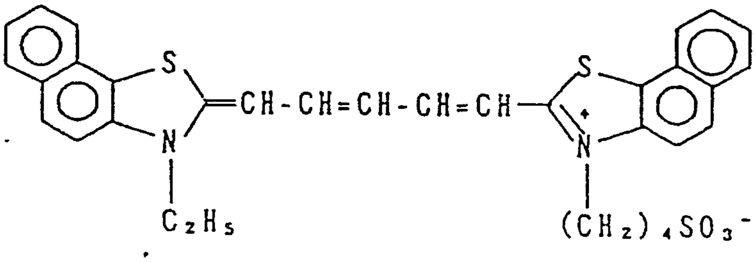
(V - 4)


CH3
CH3
S
CH
CH-CH=CH
S
N
+
N
CH3
CH3
CH3
SO3-

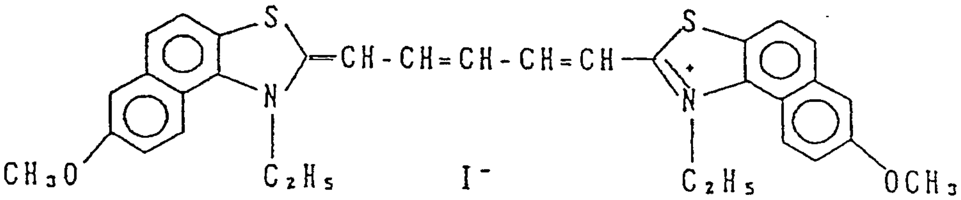
(V - 5)


S
CH-CH=CH-CH=CH
S
N
+
N
C2H5
Br-
C2H5

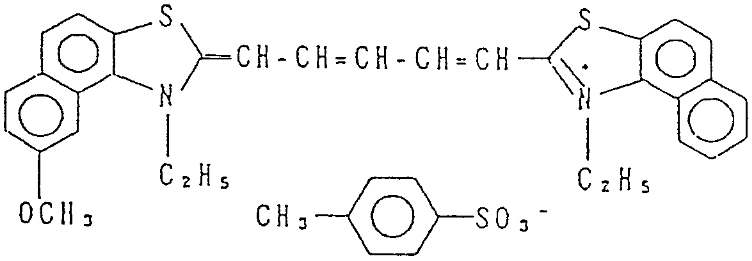
(V − 6)


S
CH-CH=CH-CH=CH
N
C₂H₅
S
N
(CH₂)₄SO₃⁻

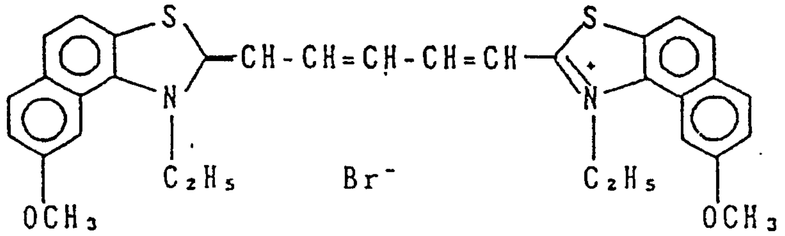
(V − 7)


S
CH-CH=CH-CH=CH
N
CH₃O
C₂H₅
I⁻
S
N
C₂H₅
OCH₃

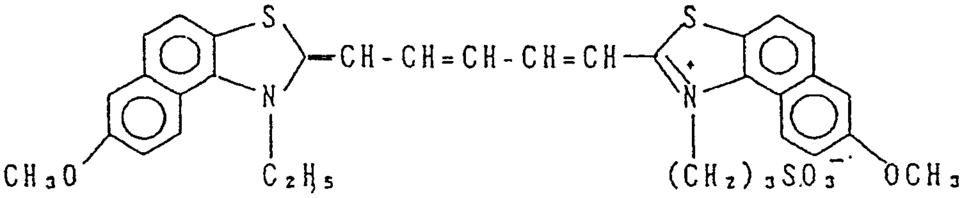
(V − 8)


S
CH-CH=CH-CH=CH
N
C₂H₅
OCH₃
CH₃
SO₃⁻
S
N
C₂H₅

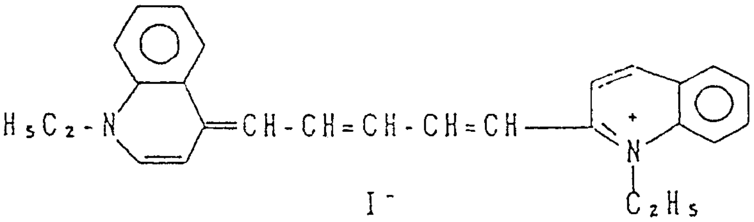
(V－9)


S
CH-CH=CH-CH=CH
N
C₂H₅
Br⁻
S
N
C₂H₅
OCH₃
OCH₃

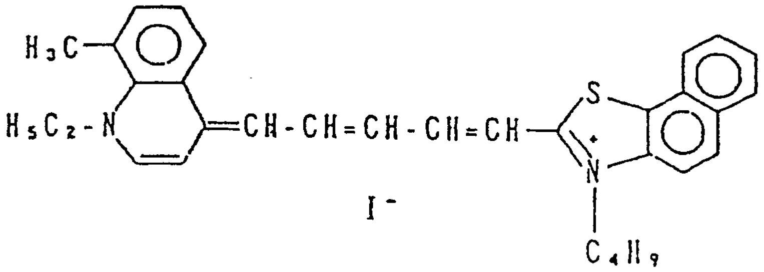
(V－10)


S
CH-CH=CH-CH=CH
N
C₂H₅
CH₃O
S
N
(CH₂)₃SO₃⁻
OCH₃

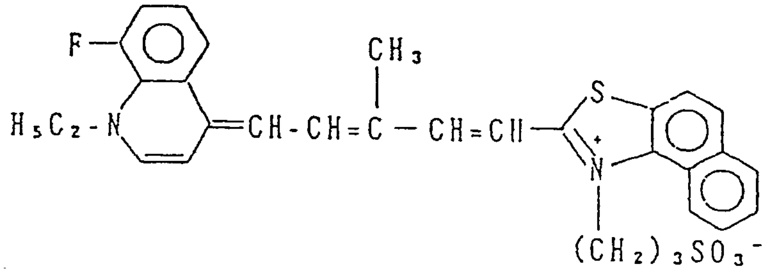
(V－11)


H₅C₂-N
=CH-CH=CH-CH=CH
N
C₂H₅
I⁻

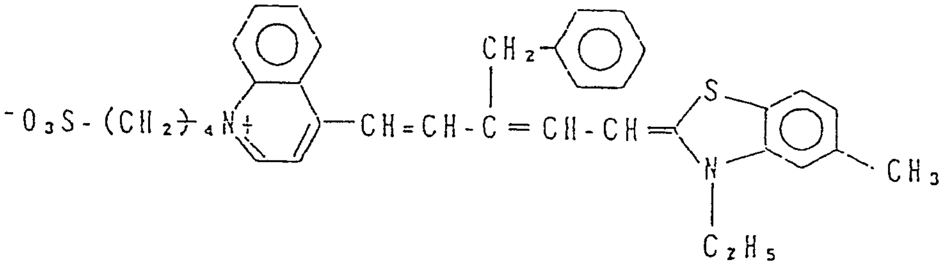
(V－12)


H₃C
H₅C₂-N
=CH-CH=CH-CH=CH
S
N
+
C₄H₉
I⁻

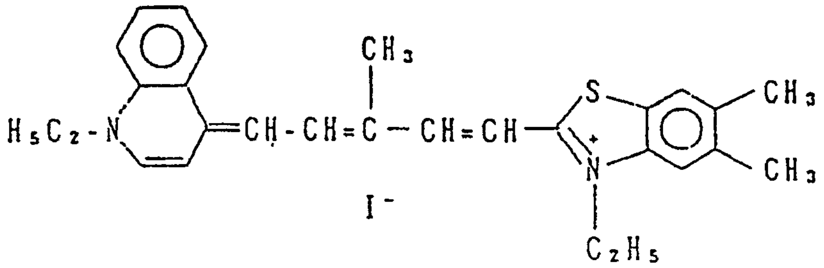
(V－13)


F
H₅C₂-N
=CH-CH=C－CH=CH
CH₃
S
N
+
(CH₂)₃SO₃⁻

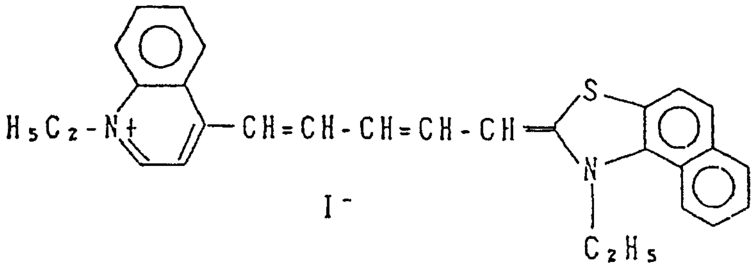
(V－14)


⁻O₃S-(CH₂)₄N+
CH=CH-C=CH-CH=
CH₂
S
N
C₂H₅
CH₃

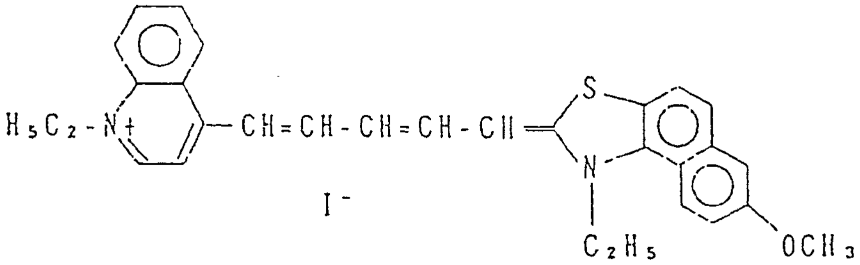
(V－15)


H₅C₂-N
=CH-CH=C－CH=CH－
CH₃
S
N
+
CH₃
CH₃
I⁻
C₂H₅

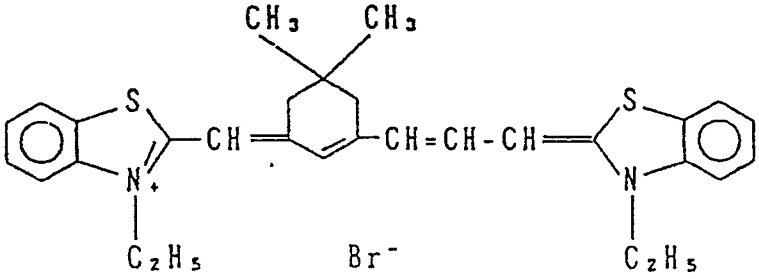
(V－16)


H₅C₂-N+
－CH=CH-CH=CH-CH=
S
N
I⁻
C₂H₅

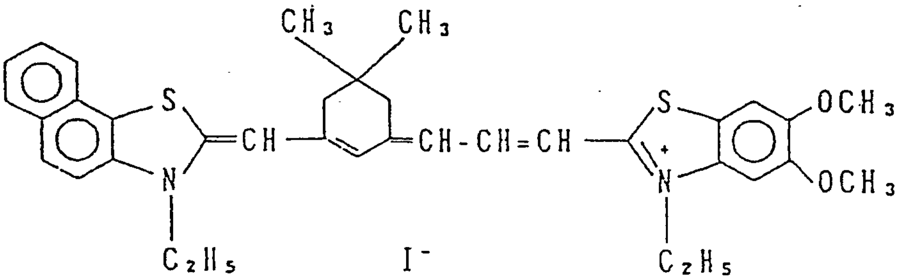
(V－17)


H₅C₂-N+
－CH=CH-CH=CH-CH=
S
N
I⁻
C₂H₅
OCH₃

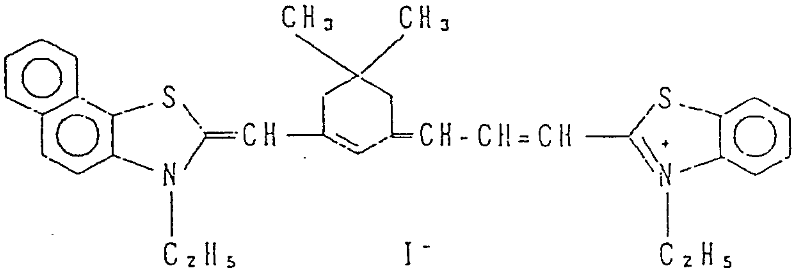
(V－18)


CH3
CH3
S
CH
CH=CH-CH
S
N+
N
C2H5
Br-
C2H5

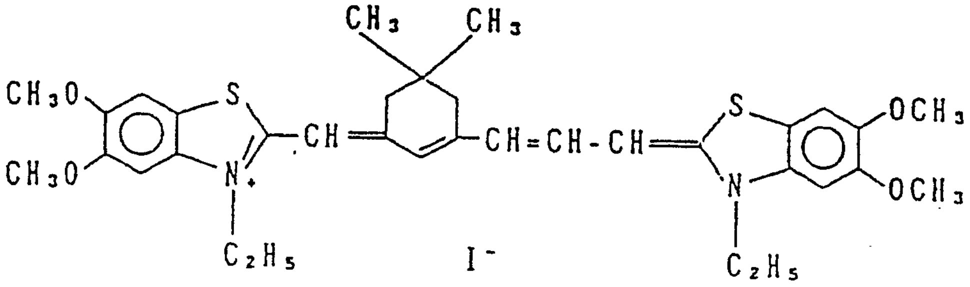
(V－19)


CH3
CH3
S
CH
CH-CH=CH
S
OCH3
N
N+
OCH3
C2H5
I-
C2H5

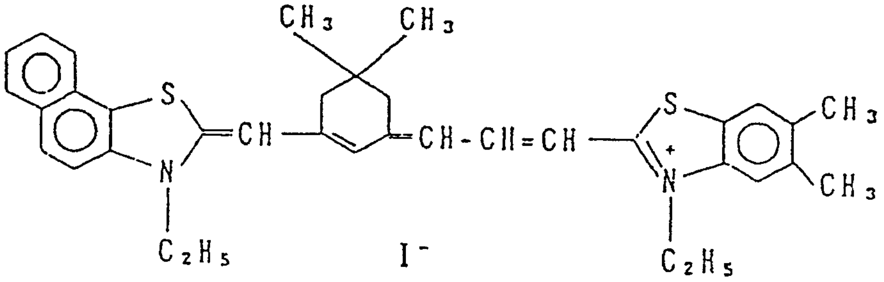
(V－20)


CH3
CH3
S
CH
CH-CH=CH
S
N
N+
C2H5
I-
C2H5

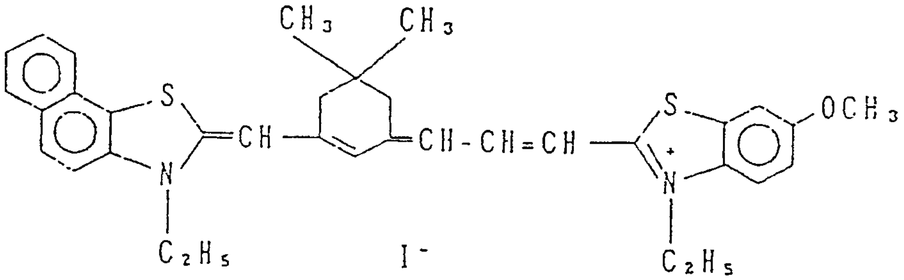
(V－21)


CH₃
CH₃
CH₃O
CH₃O
S
N+
CH
C₂H₅
I⁻
CH=CH-CH
S
N
OCH₃
OCH₃
C₂H₅

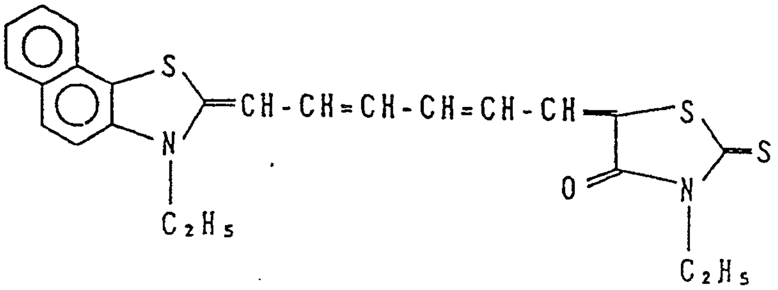
(V－22)


CH₃
CH₃
S
N
CH
C₂H₅
I⁻
CH-CH=CH
S
N+
CH₃
CH₃
C₂H₅

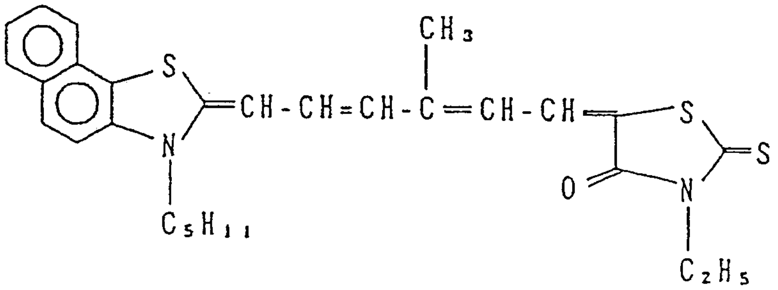
(V－23)


CH₃
CH₃
S
N
CH
C₂H₅
I⁻
CH-CH=CH
S
N+
OCH₃
C₂H₅

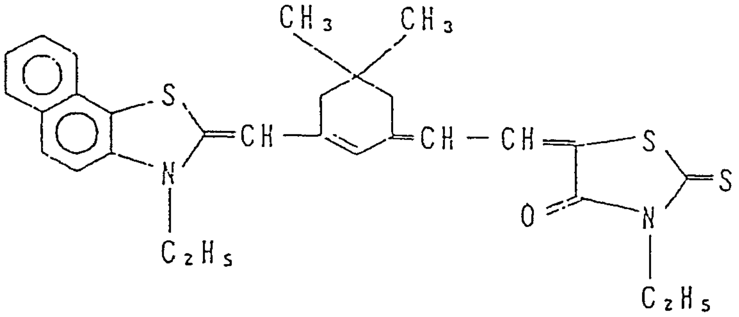
(V-24)


S
CH-CH=CH-CH=CH-CH
S
S
N
O
N
C₂H₅
C₂H₅

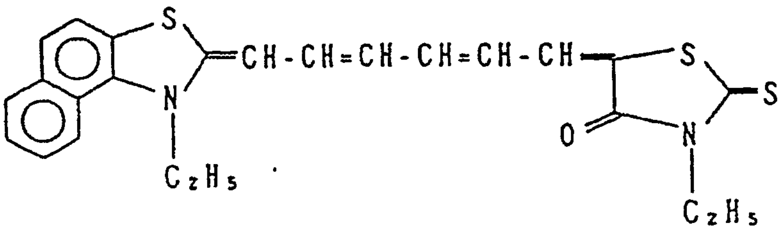
(V-25)


CH₃
S
CH-CH=CH-C=CH-CH
S
S
N
O
N
C₅H₁₁
C₂H₅

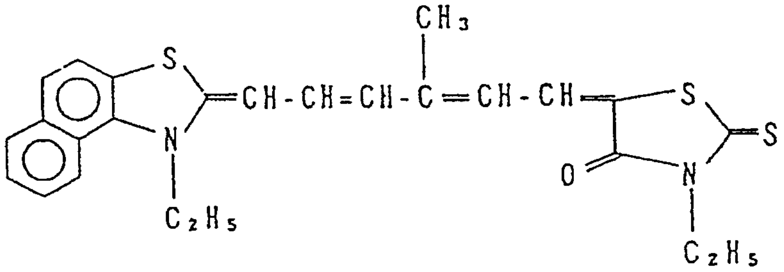
(V-26)


CH₃
CH₃
S
CH
CH - CH
S
S
N
O
N
C₂H₅
C₂H₅

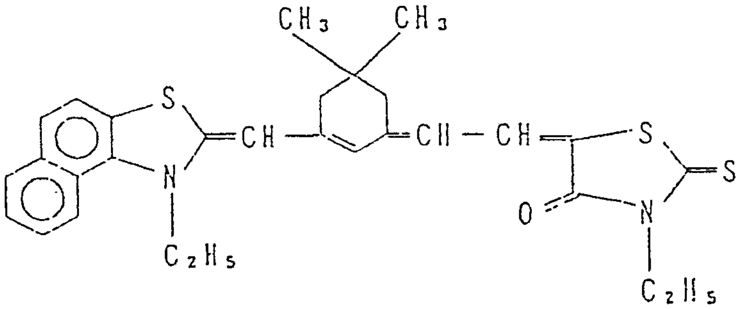
(V－27)


S
CH-CH=CH-CH=CH-CH
S
S
N
O
N
C₂H₅
C₂H₅

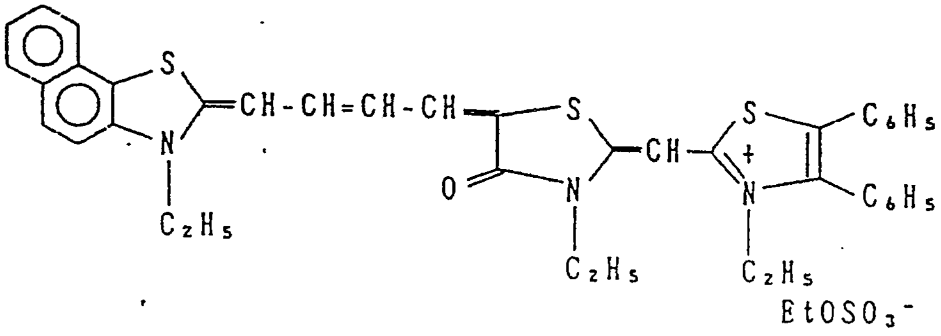
(V－28)


CH₃
S
CH-CH=CH-C=CH-CH
S
S
N
O
N
C₂H₅
C₂H₅

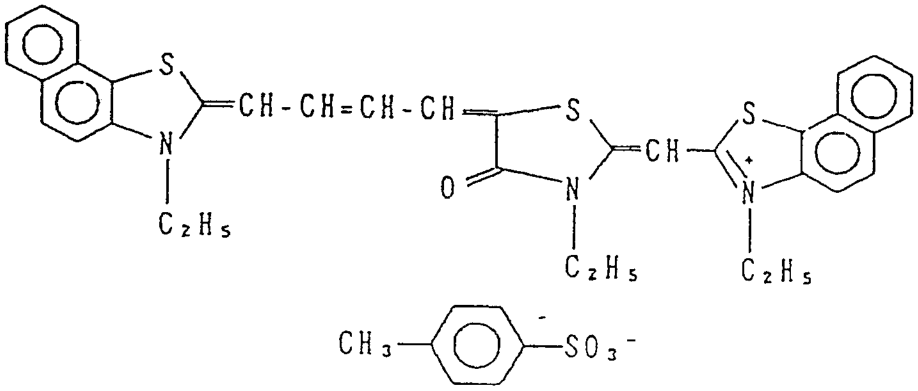
(V－29)


CH₃
CH₃
S
CH
CH－CH
S
S
N
O
N
C₂H₅
C₂H₅

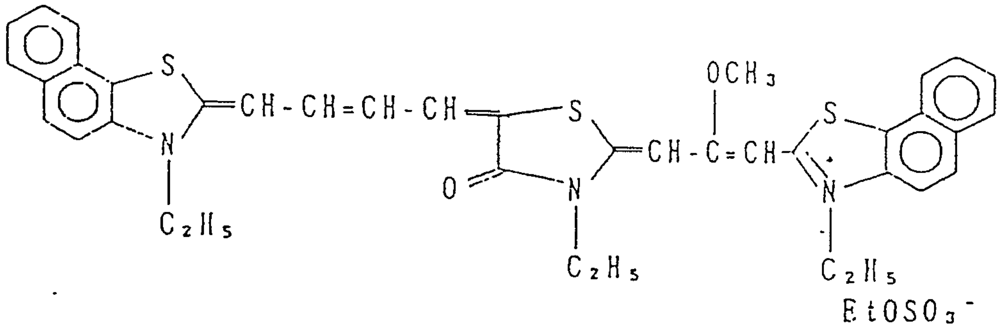
(V－30)



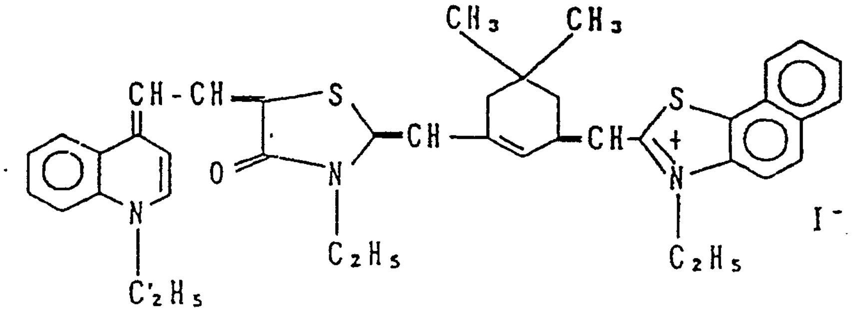
(V－31)



(V－32)

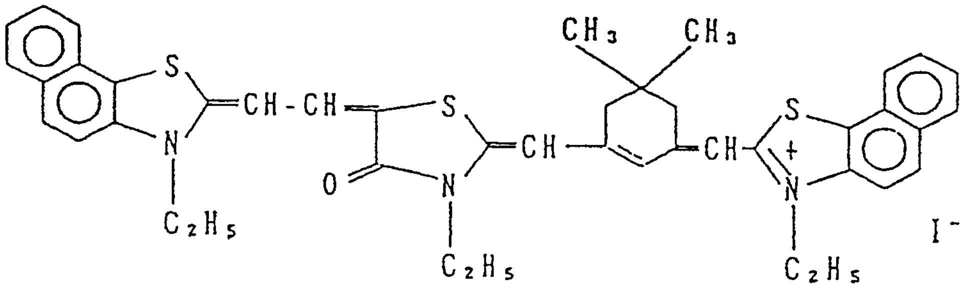


(V－33)



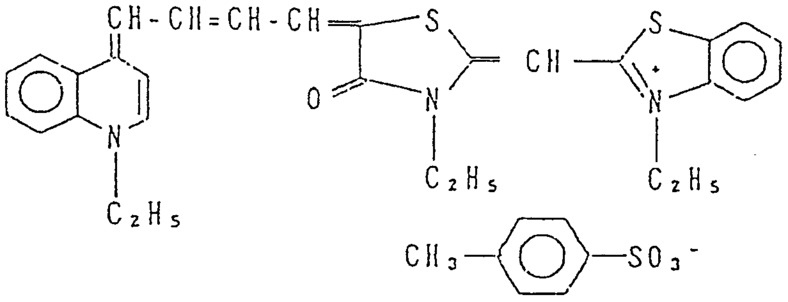
CH₃
CH₃
CH-CH
S
CH
CH
S
+
O
N
N
N
I⁻
C₂H₅
C₂H₅
C₂H₅

(V－34)



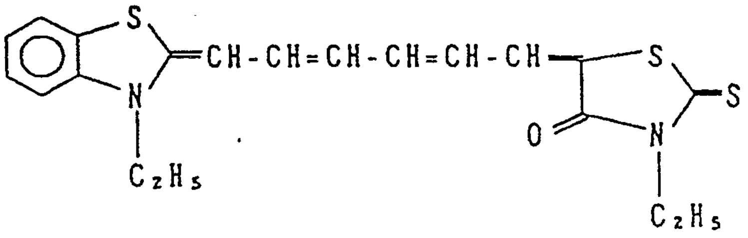
CH₃
CH₃
S
=CH-CH
S
=CH
CH
S
+
N
O
N
N
I⁻
C₂H₅
C₂H₅
C₂H₅

(V－35)

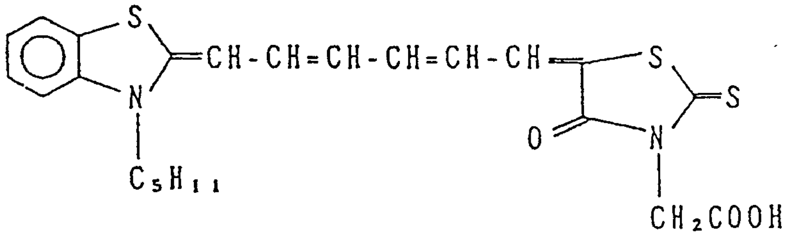


CH-CH=CH-CH
S
CH
S
+
O
N
N
N
C₂H₅
C₂H₅
C₂H₅
CH₃
SO₃⁻

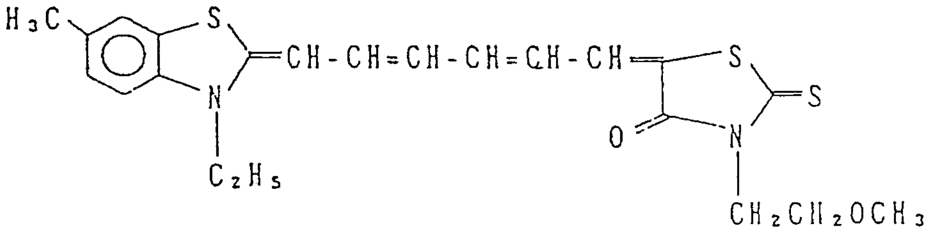
(V－36)



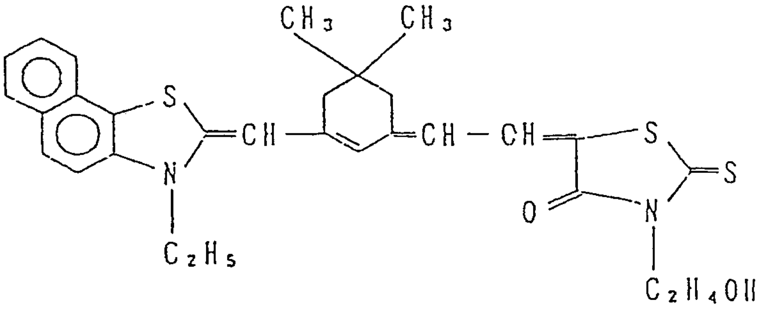
(V－37)



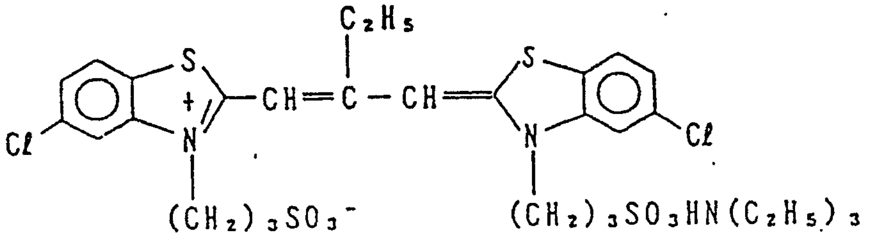
(V－38)



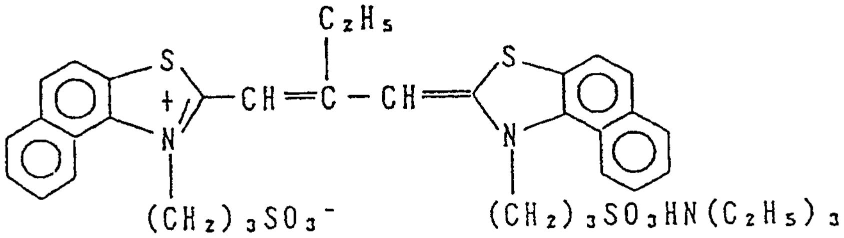
(V－39)



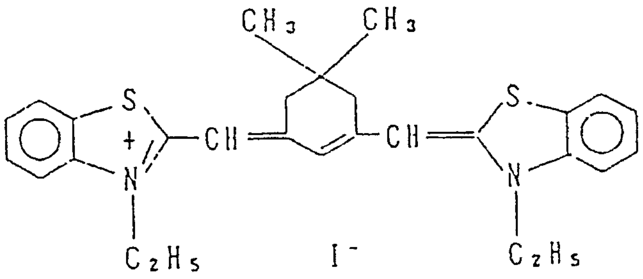
(V-40)



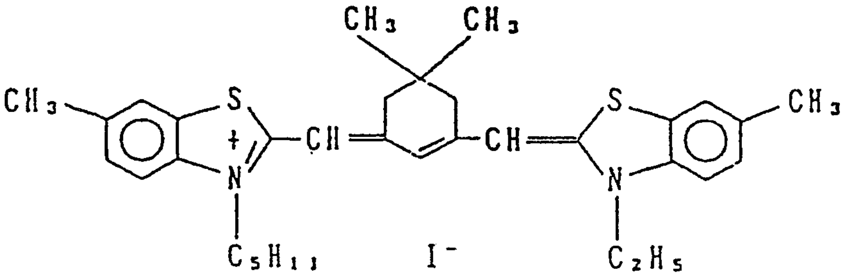
(V-41)



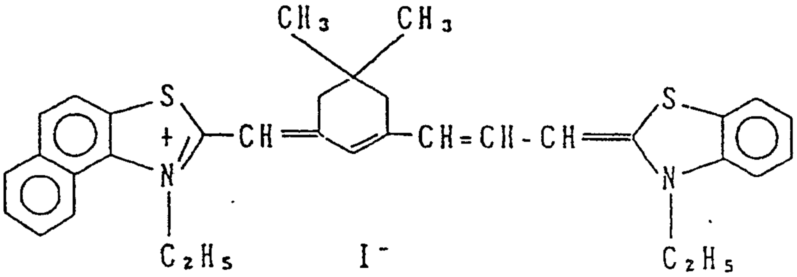
(V-42)



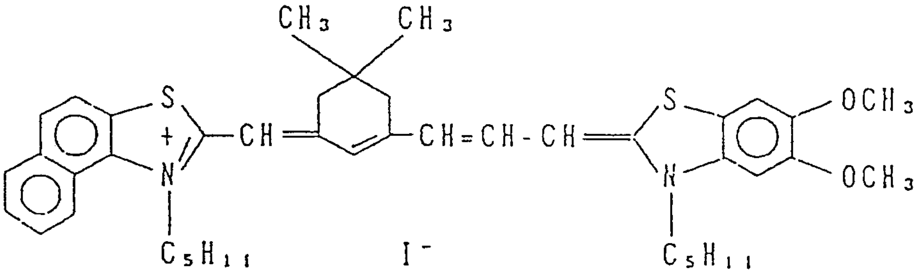
(V－43)


CH3
CH3
CH3
S
+
N
CH
CH
S
N
CH3
C5H11
I⁻
C2H5

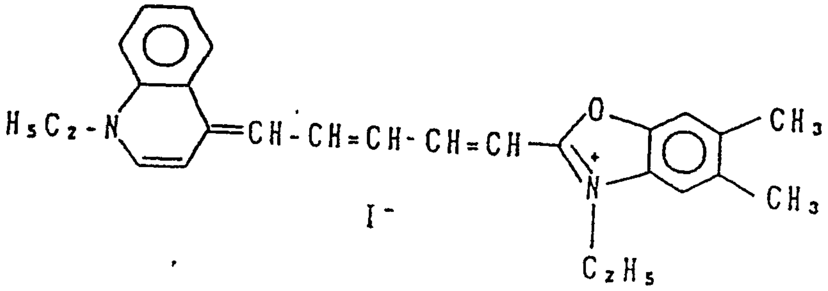
(V－44)


CH3
CH3
S
+
N
CH
CH=CH-CH
S
N
C2H5
I⁻
C2H5

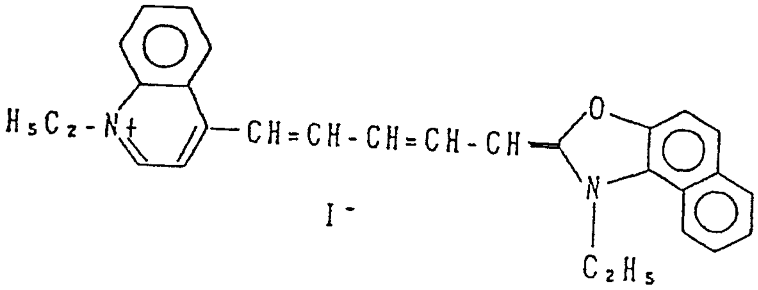
(V－45)


CH3
CH3
S
+
N
CH
CH=CH-CH
S
N
OCH3
OCH3
C5H11
I⁻
C5H11

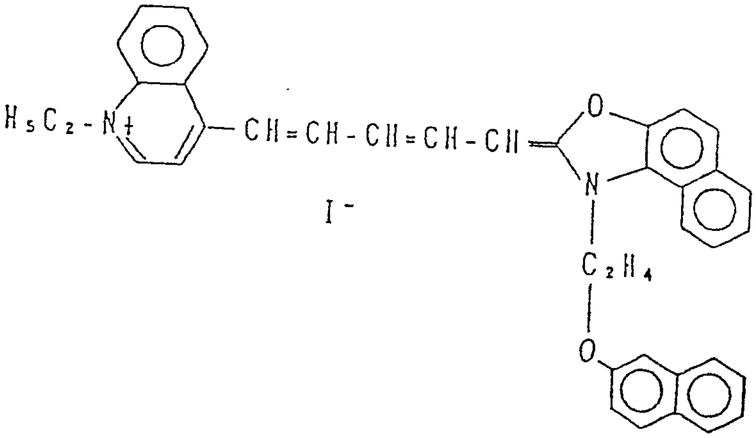
(V－46)


H5C2-N
=CH-CH=CH-CH=CH—
O
N+
CH3
CH3
I-
C2H5

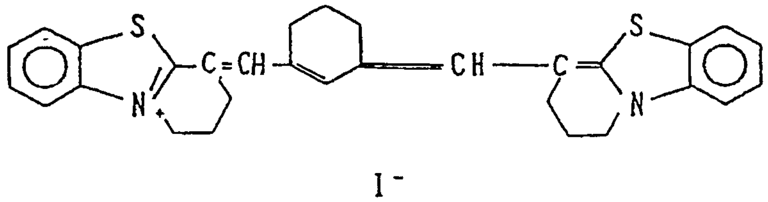
(V－47)


H5C2-N+
—CH=CH-CH=CH-CH=
O
N
I-
C2H5

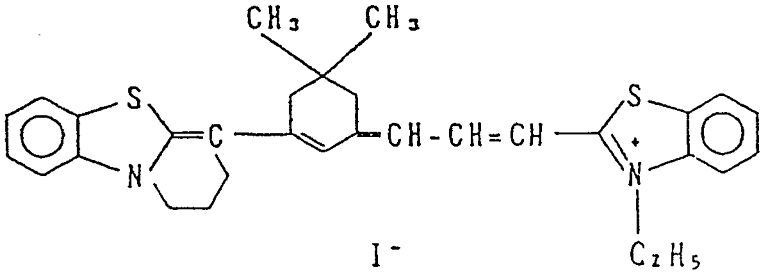
(V－48)


H5C2-N+
—CH=CH-CH=CH-CH=
O
N
I-
C2H4
O

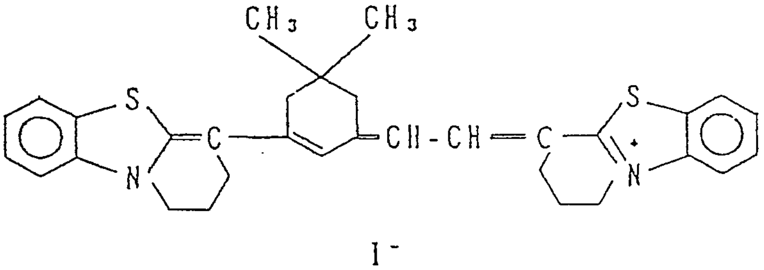
(V-49)



(V-50)



(V-51)



The sensitizing dye for use in this invention is contained in a silver halide emulsion in an amount, per mol of silver halide, of from $5x10^{-7}$ mol to $5x10^{-3}$ mol, preferably from $1x10^{-6}$ mol to $1x10^{-3}$ mol, and particularly preferably from $2x10^{-6}$ mol to $5x10^{-4}$ mol

The sensitizing dye for use in this invention can be directly dispersed in a silver halide emulsion. Also, the sensitizing dye can be added to an emulsion as a solution thereof in a proper solvent such as methanol, ethanol, methylcellosolve, acetone, water, pyridine or a mixture thereof. Also, in the case of dissolving the sensitizing dye, ultrasound can be used.

Furthermore, methods of adding the infrared sensitizing dye, include a method of dissolving the dye in a volatile organic solvent, dispersing the solution in an aqueous solution of a hydrophilic colloid, and adding the dispersion to a silver halide emulsion as described in U.S. Patent 3,469,987; a method of dispersing the water-insoluble dye in a water-soluble solvent without dissolving the dye and adding the dispersion to an emulsion as described in JP-B-46-24185 (the term "JP-B" as used herein means an "examined published Japanese patent application"), a method of dissolving the dye in a surface active agent and adding the solution to an emulsion as described in U.S. Patent 3,822,135; a method of dissolving the dye in a solvent using a compound capable of red-shifting the dye and adding the solution to an emulsion as described in JP-A-51-74624; and a method of dissolving the dye in an acid containing substantially no water and adding the solution to an emulsion as described in JP-A-50-80826.

Other methods described in U.S. Patents 2,912,343, 3,342,605, 2,996,287, and 3,429,835 can be also used for adding the dye to an emulsion.

Also, the infrared sensitizing dye may be uniformly dispersed in a silver halide emulsion before the emulsion is coated on a proper support. Furthermore, the dye may be added to a silver halide emulsion before the chemical sensitization or during the latter half of the formation of silver halide grains.

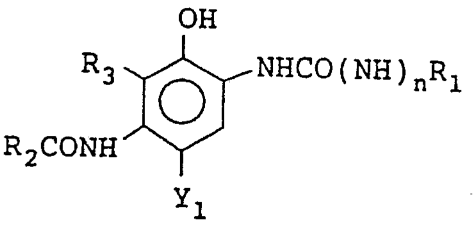
It is preferable to use a coupler having a high mol ratio of the colored coupler to developed silver halide for a silver halide color photographic material in this invention for quick color photographic processing, whereby the amount of a light-sensitive silver halide can be reduced. In particular, two equivalent couplers are preferably used. Furthermore, a one-equivalent coupler, wherein a one-electron oxidation coloring step subsequent to the coupling reaction of the quinonediimine compound of the aromatic amine of a color developing agent and a color coupler is performed with an other oxidizing agent than silver halide may be used in combination.

Usually, for a color photographic material, a color coupler is used such that the maximum coloring color density is at least 3 as a transmission density and at least 2 as a reflection density. In the image-forming process using the exposure portion unit in this invention, color gradation conversion processing is conducted with color correction processing by an image processing apparatus, and hence an excellent color image can be obtained at the maximum coloring reflection density of about 1.2, and preferably from about 1.6 to 2.0. Accordingly, the amounts of color couplers and light-sensitive silver halide can be decreased.

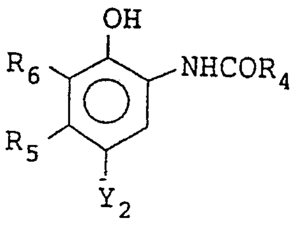
The amounts of yellow coupler, magenta coupler, and cyan coupler for the color photographic light-sensitive material, in particular, a reflection color photographic light-sensitive material in this invention are from 2.5×10^{-4} to 10×10^{-4}; from 1.5×10^{-4} to 8×10^{-4}; and from 1.5×10^{-4} to 7×10^{-4} mol/m^2, respectively.

Color couplers suitable for the color photographic light-sensitive material in this invention are now described in greater detail.

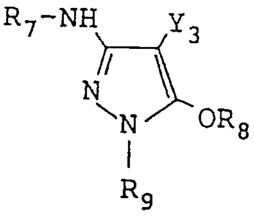
The cyan couplers, magenta couplers, and yellow couplers which are preferably used in this invention are represented by formulae (C - I), (C - II); (M - I), (M -II); and (Y), respectively.



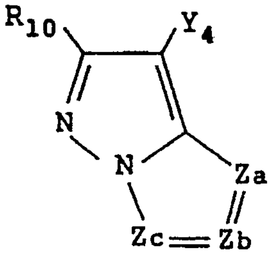
(C-I)



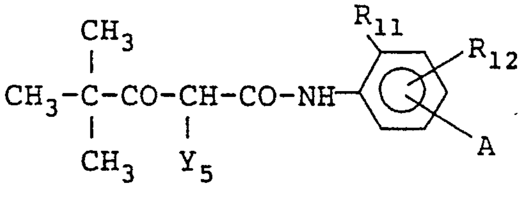
(C-II)



(M-I)



(M-II)



(Y)

In formulae (C - I) and(C - II), R_1, R_2, and R_4 each represents a substituted or unsubstituted aliphatic group, a substituted or unsubstituted aromatic group, or a substituted or unsubstituted heterocyclic group,

R_3, R_5, and R_6 each represents hydrogen, a halogen atom, an aliphatic group, an aromatic group, or an acylamino group, R_3 and R_2 together may form a non-metallic atomic group forming a nitrogen-containing 5- or 6-membered ring; Y_1 and Y_2 each represents hydrogen or a coupling-off group capable of being cleaved upon the coupling reaction with the oxidation product of a color developing agent; and n represents 0 or 1.

In formula (C - II), R_5 is preferably an aliphatic group such as, for example, methyl, ethyl, propyl, butyl, pentadecyl, tert-butyl, cyclohexyl, cyclohexylmethyl, phenylthiomethyl, dodecyloxyphenylthiomethyl, butaneamidomethyl, and methoxymethyl.

Preferred examples of the cyan couplers represented by formulae (C - I) and (C - II) are as follows.

In formula (C - I), R_1 is preferably an aryl group or a heterocyclic group, and is more preferably an aryl group substituted by a halogen atom, an alkyl group, an alkoxy group, an aryloxy group, an acylamino group, an acyl group, a carbamoyl group, a sulfonamido group, a sulfamoyl group, a sulfonyl group, a sulfamido group, an oxycarbamoyl group, or a cyano group.

When a ring is not formed by R_3 and R_2 in formula (C - I), R_2 is preferably a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group and particularly preferably an alkyl group substituted by a substituted aryloxy group and R_3 is preferably hydrogen.

In formula (C - II), R_4 is preferably a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, and particularly preferably an alkyl group substituted by a substituted aryloxy group.

In formula (C - II), R_5 is preferably an alkyl group having from 2 to 15 carbon atoms or a methyl group having a substituent of one or more carbon atoms. Preferred examples of the substituent are an arylthio group, an alkylthio group, an acylamino group, an aryloxy group, and an alkyloxy group.

In formula (C - II), R_5 is more preferably an alkyl group having from 2 to 15 carbon atoms, and particularly preferably an alkyl group having from 2 to 4 carbon atoms.

In formula (C - II), R_6 is preferably hydrogen or a halogen atom, and particularly preferably chlorine or fluorine.

In formulae (C - I) and (C - II), Y_1 and Y_2 each is preferably hydrogen, a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, or a sulfonamido group.

In formula (M - I), R_7 and R_9 each represents an aryl group; R_8 represents hydrogen, an aliphatic acyl group, an aromatic acyl group, an aliphatic sulfonyl group, or an aromatic sulfonyl group; Y_3 represents hydrogen or a coupling-off group.

The substituent for the aryl group (preferably a phenyl group) shown by R_7 and R_9 is same as the above substituent for R_1 and when two or more substituents exist, they may be the same or different.

In formula (M - I), R_8 is preferably hydrogen, an aliphatic acyl group or an aliphatic sulfonyl group, and particularly preferably hydrogen.

Y_3 is preferably a coupling-off group of a type released by sulfur, oxygen, or nitrogen and the sulfur atom-releasing type magenta couplers described in U.S. Patent 4,351,897 and PCT WO088/04795 are particularly preferred.

In formula (M - II), R_{10} represents hydrogen or a substituent; Y_4 represents hydrogen or a releasable group, and is particularly preferably a halogen atom or an arylthio group; Za, Zb, and Zc each represents methine, substituted methine, =N-, or -NH-, and one of the Za-Zb bond and the Zb-Zc bond is a double bond and the other is a single bond.

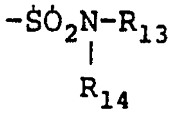
When the Zb-Zc bond is a carbon-carbon double bond, the double bond can be part of an aromatic ring. Also, the coupler includes a dimer or higher polymer formed at R_{10} or Y_4 and when Za, Zb, and Zc is a substituted methine, the coupler includes a dimer or higher polymer formed at the substituted methine.

In the pyrazoloazole series magenta couplers represented by formula (M - II), imidazo[1,2-b]pyrazoles described in U.S. Patent 4,500,630 are preferred for reduced yellow side absorption and light fastness of colored dyes formed and also pyrazolo[1,5-b][1,2,4]triazoles described in U.S. patent 4,540,654 are particularly preferred.

R_{10} and the substituents to the pyrazoloazoles are described in detail in U.S. Patent 4,540,654, column, 2 line 41 to column 8, line 27.

Moreover, pyrazolotriazole couplers having a branched alkyl group directly bonded to the 2-, 3-, or 6-position of the pyrazolotriazole ring as described in JP-A-61-65245, pyrazoloazole couplers containing a sulfonamido group in the molecule as described in JP-A-61-65246, pyrazoloazole couplers having an alkoxyphenylsulfonamido ballast group as described in JP-A-61-147254, and pyrazolotriazole couplers having an alkoxy group or an aryloxy group at the 6-position as described in European Patent Applications (unexamined published) 226,849 and 294,785 can be preferably used in this invention.

In formula (Y), R_{11} represents a halogen atom, an alkoxy group, a trifluoromethyl group, or an aryl group; R_{12} represents hydrogen, a halogen atom, or an alkoxy group; A represents $-NHCOR_{13}$, $-NHSO_2-R_{13}$, $-SO_2NHR_{13}$, $-COOR_{13}$, or



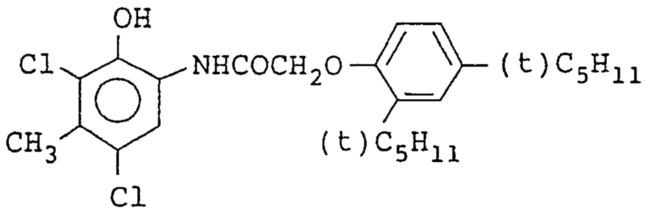
$$-SO_2\underset{\substack{|\\R_{14}}}{N}-R_{13}$$

(wherein R_{13} and R_{14} each represents an alkyl group, an aryl group, or an acyl group); and Y_5 represents a coupling-off group.

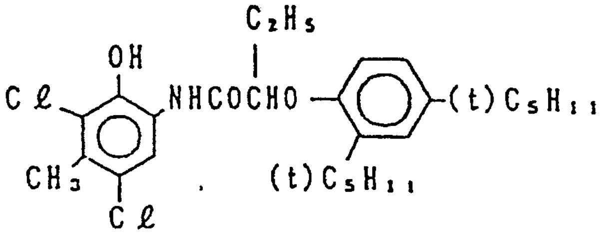
The substituents for R_{12}, R_{13}, and R_{14} are same as the substituents for R_1 and Y_5 is preferably a coupling-off group of the type of being released by oxygen or nitrogen, and is particularly preferably of a nitrogen atom-releasing type.

Specific examples of the couplers represented by formulae (C - I), (C - II), (M - I), (M - II) and (Y) are illustrated below, but the present invention is not to be construed as being limited thereto.

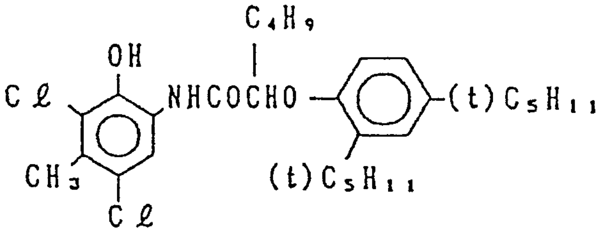
(C-I)



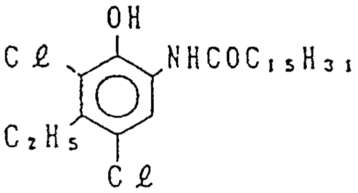
(C－2)



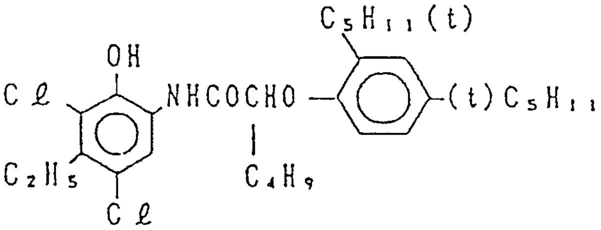
(C－3)



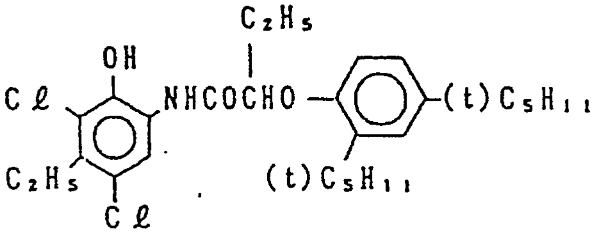
(C－4)



(C－5)

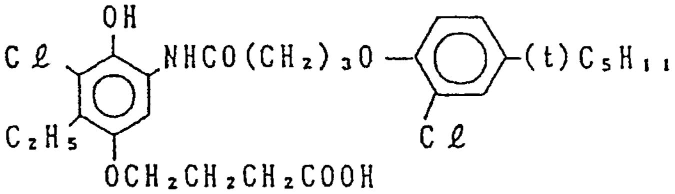


(C－6)



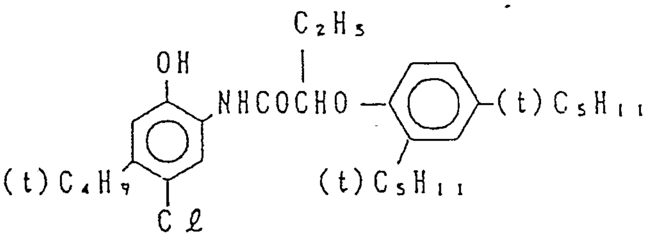
OH
C$_2$H$_5$
Cℓ
NHCOCHO
(t)C$_5$H$_{11}$
C$_2$H$_5$
(t)C$_5$H$_{11}$
Cℓ

(C－7)



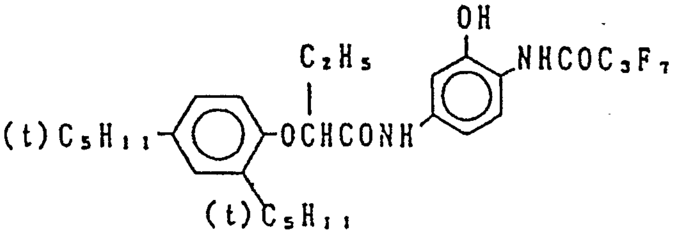
OH
Cℓ
NHCO(CH$_2$)$_3$O
(t)C$_5$H$_{11}$
C$_2$H$_5$
Cℓ
OCH$_2$CH$_2$CH$_2$COOH

(C－8)

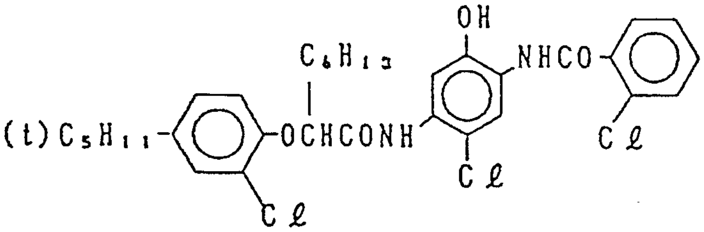


C$_2$H$_5$
OH
NHCOCHO
(t)C$_5$H$_{11}$
(t)C$_4$H$_9$
(t)C$_5$H$_{11}$
Cℓ

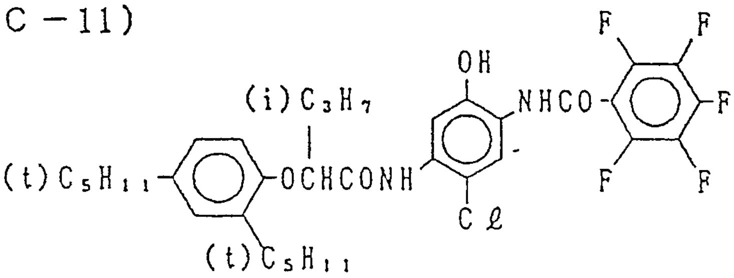
(C－9)



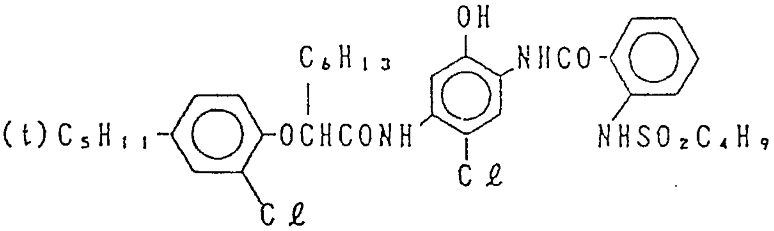
(C－10)



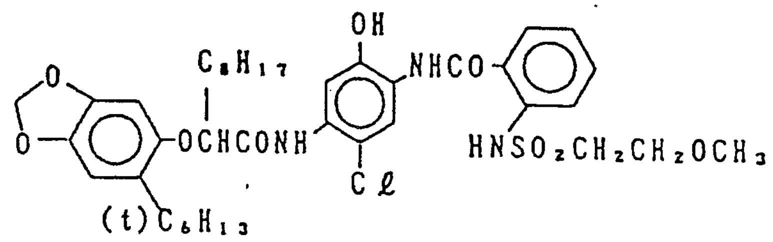
(C－11)



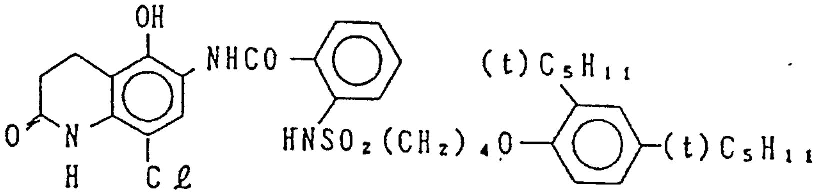
(C－12)



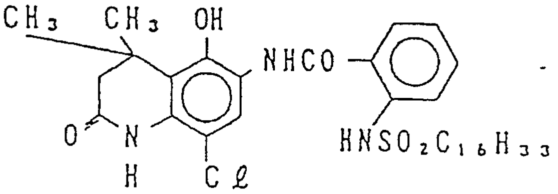
(C-13)



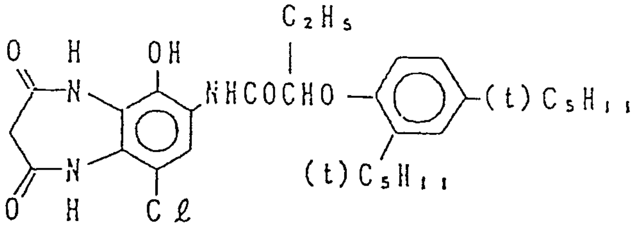
(C-14)



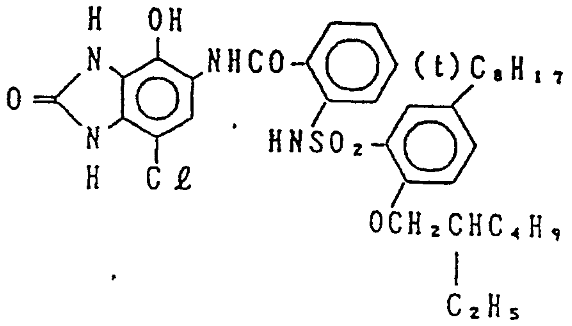
(C-15)



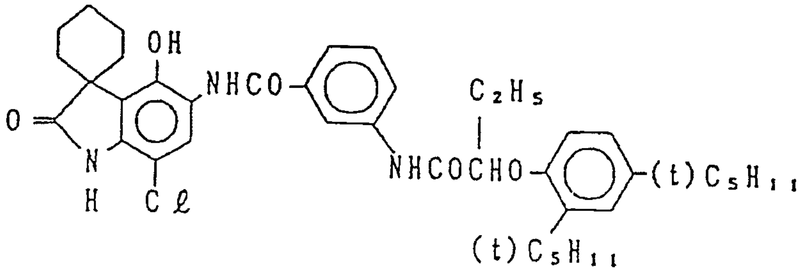
(C-16)



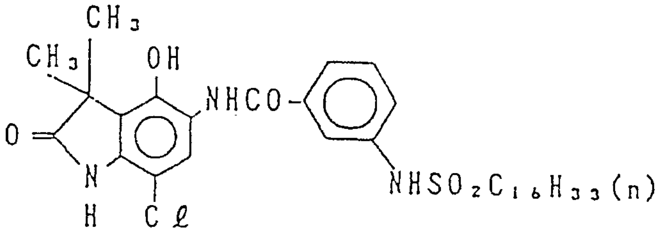
(C－17)


H
OH
N
NHCO
(t)C8H17
O
N
HNSO2
H
Cℓ
OCH2CHC4H9
C2H5

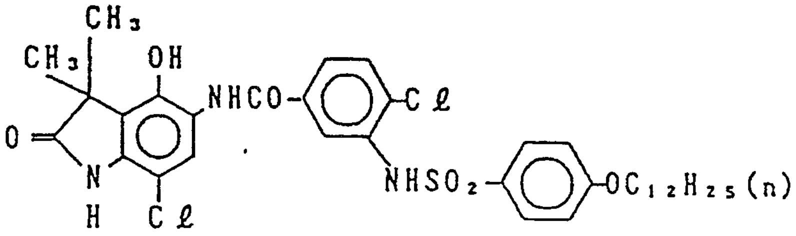
(C－18)


OH
NHCO
C2H5
O
N
NHCOCHO
(t)C5H11
H
Cℓ
(t)C5H11

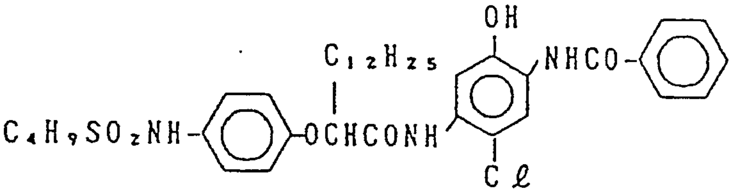
(C－19)


CH3
CH3
OH
NHCO
O
N
NHSO2C16H33(n)
H
Cℓ

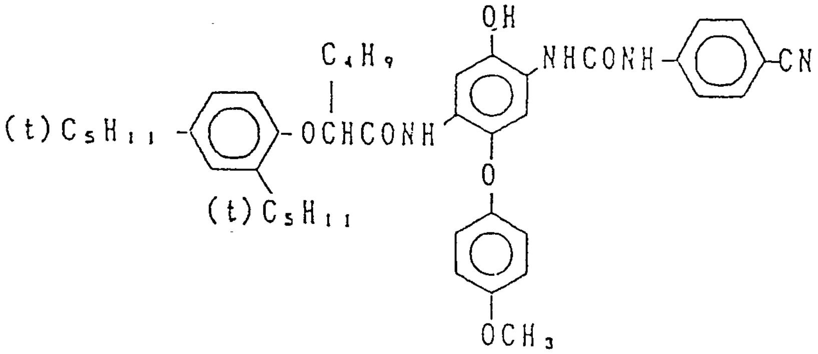
(C−20)



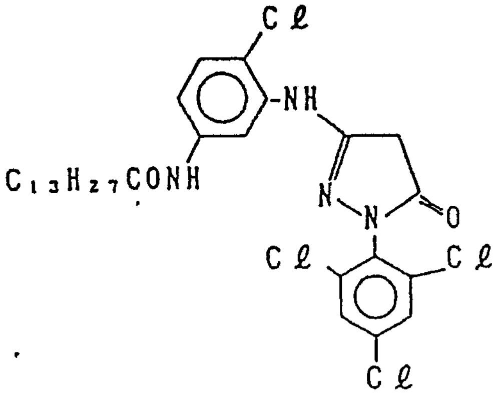
(C−21)



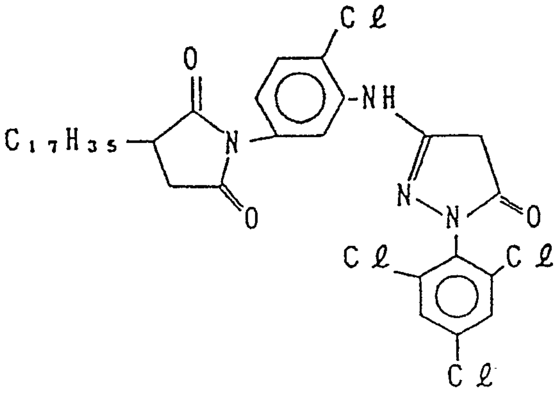
(C−22)



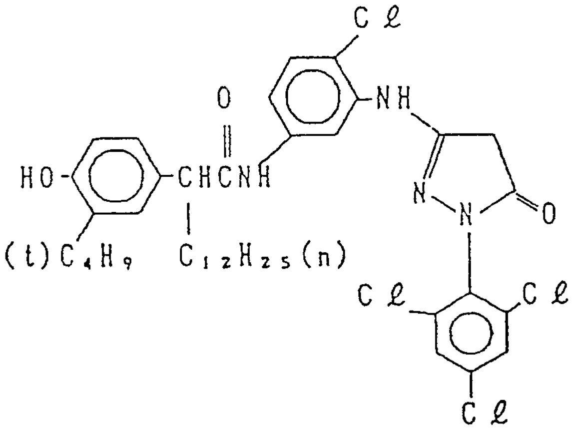
(M－1)


Cℓ
-NH
C13H27CONH
N
N
O
Cℓ
Cℓ
Cℓ

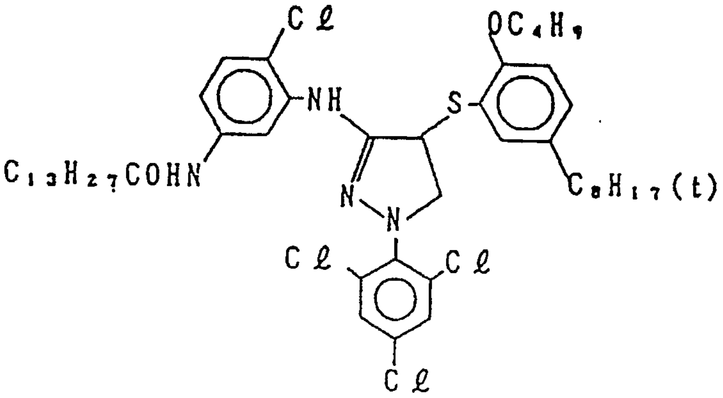
(M－2)


Cℓ
O
-NH
C17H35
N
O
N
N
O
Cℓ
Cℓ
Cℓ

(M－3)

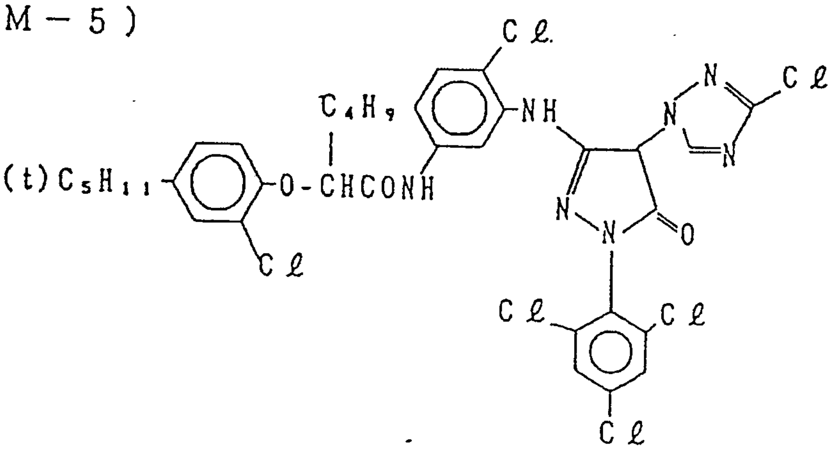

Cℓ
O
NH
HO
CHCNH
(t)C4H9
C12H25(n)
N
N
O
Cℓ
Cℓ
Cℓ

(M－4)



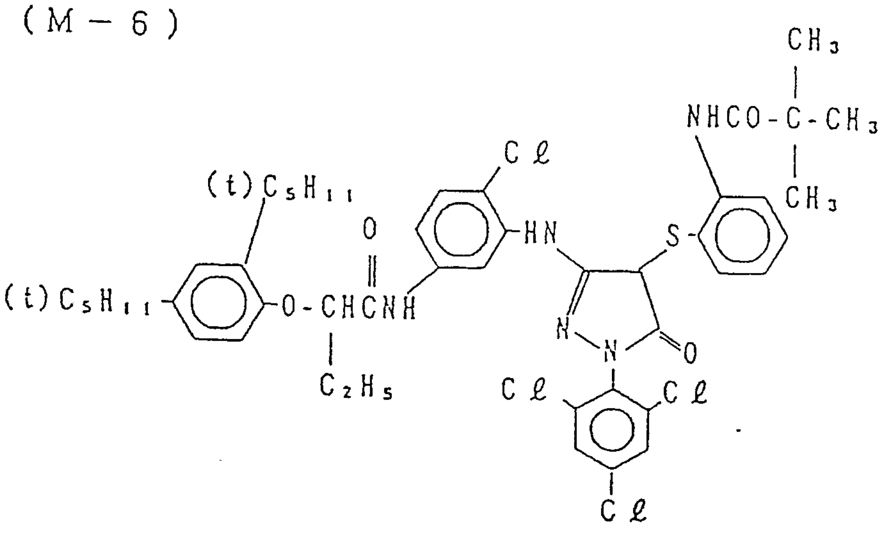
Cℓ
OC4H9
NH
S
C13H27COHN
C8H17(t)
N
N
Cℓ
Cℓ
Cℓ

(M－5)



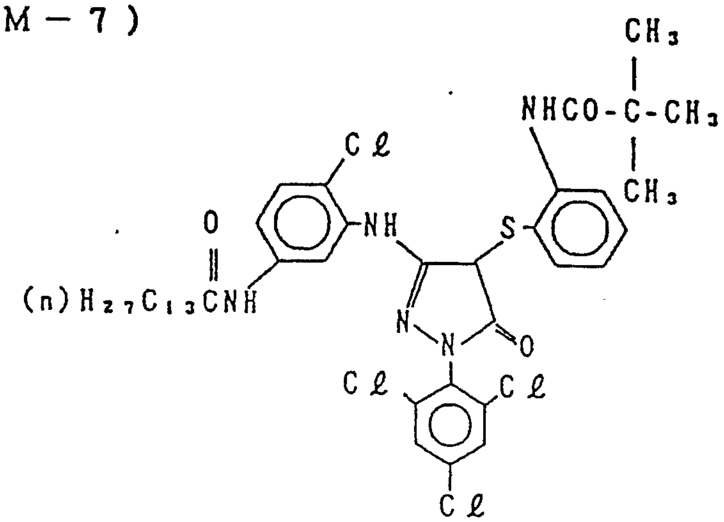
Cℓ
N
Cℓ
C4H9
NH
N
N
(t)C5H11
O-CHCONH
N
N
O
Cℓ
Cℓ
Cℓ
Cℓ

(M－6)

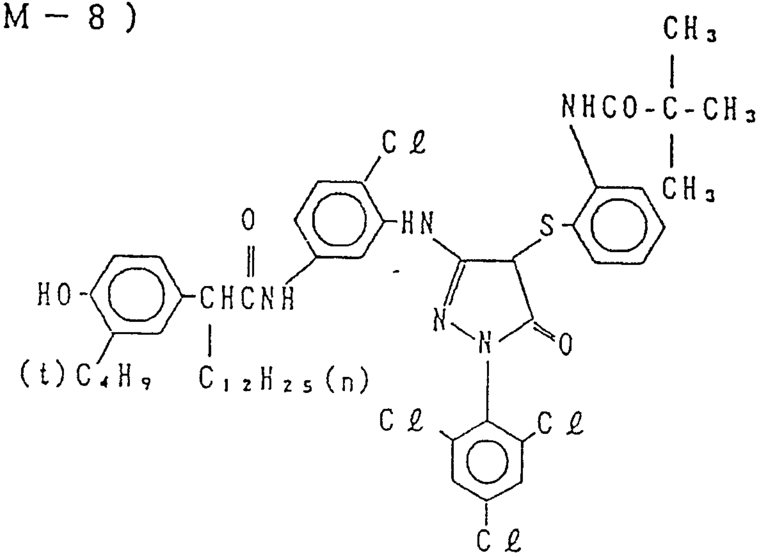


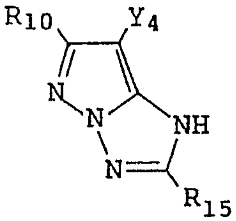
CH3
NHCO-C-CH3
Cℓ
CH3
(t)C5H11
O
HN
S
(t)C5H11
O-CHCNH
N
N
O
C2H5
Cℓ
Cℓ
Cℓ

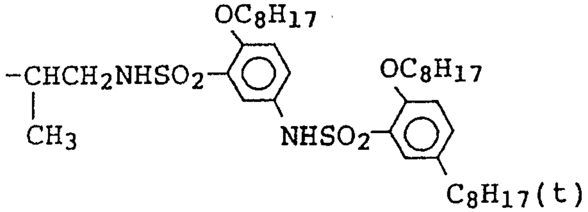
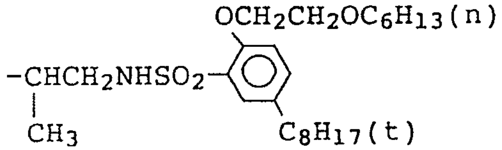
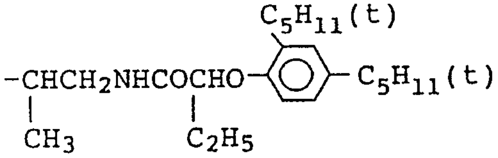
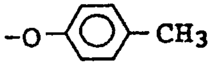
(M − 7)

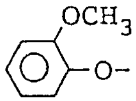
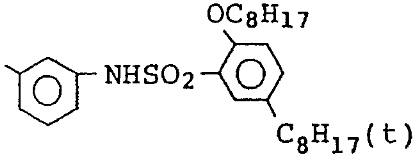
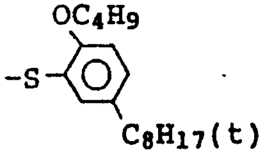
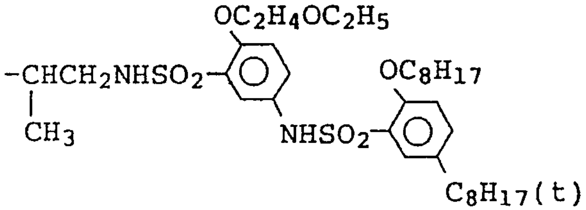
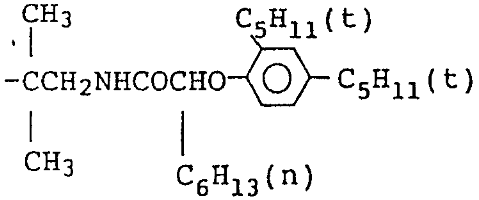
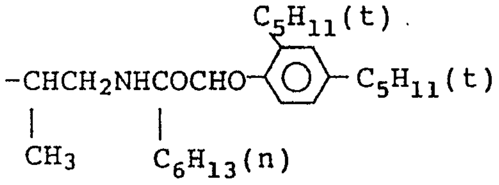

CH₃
NHCO-C-CH₃
CH₃
Cℓ
S
O
NH
(n)H₂₇C₁₃CNH
N
N
O
Cℓ
Cℓ
Cℓ

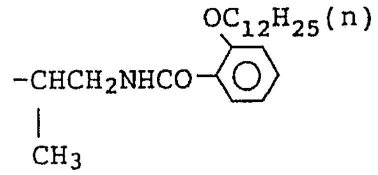
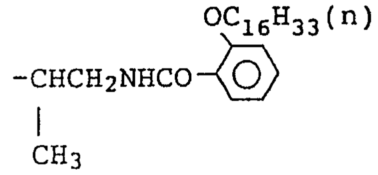
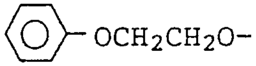
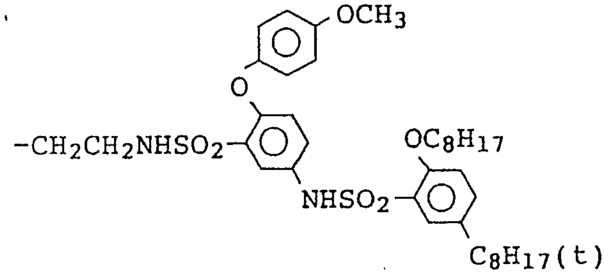
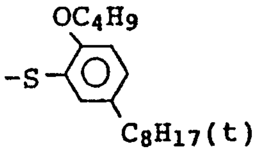
(M − 8)

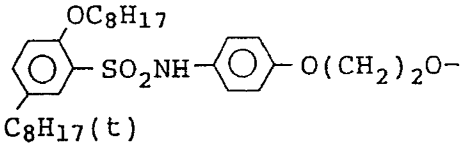
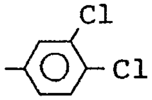
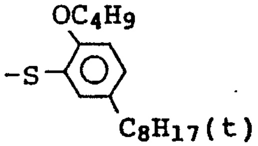
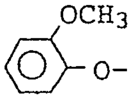
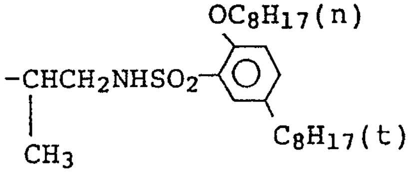

CH₃
NHCO-C-CH₃
CH₃
Cℓ
S
O
HN
HO
CHCNH
(t)C₄H₉
C₁₂H₂₅(n)
N
N
O
Cℓ
Cℓ
Cℓ

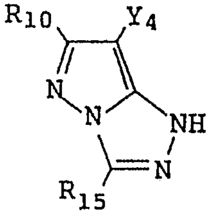


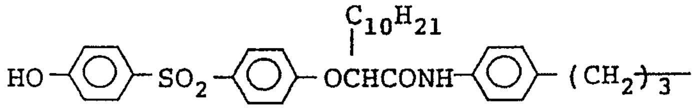
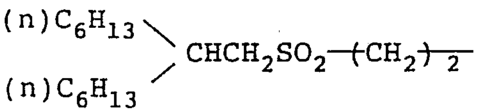
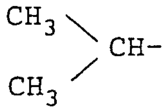
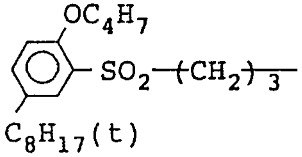
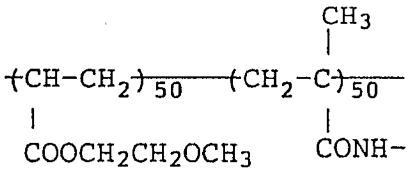
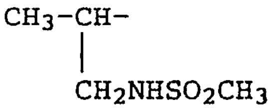
Compound	R_{10}	R_{15}	Y_4
M-9	CH_3-		Cℓ
M-10	"		"
M-11	$(CH_3)_3C$-		

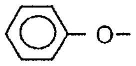
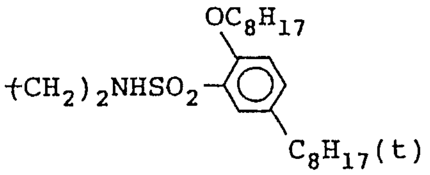
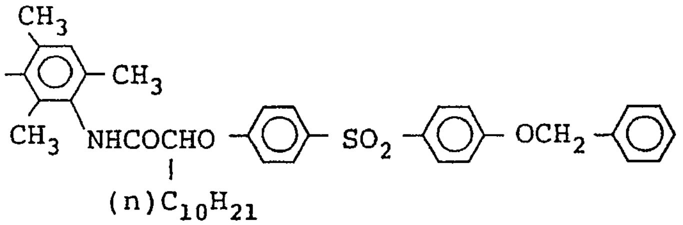
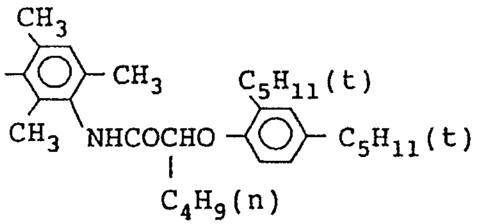
Compound	R_{10}	R_{15}	Y_4
M-12			
M-13	CH_3-		Cl
M-14	"		"
M-15	"		"

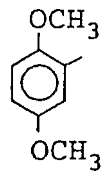
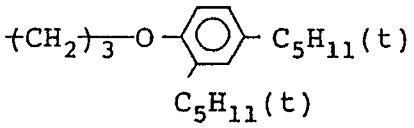
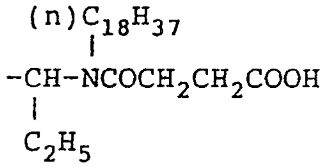
Compound	R_{10}	R_{15}	Y_4
M-16	CH_3-		Cl
M-17	"		"
M-18			
M-19	CH_3CH_2O-	"	"

Compound	R_{10}	R_{15}	Y_1
M-20			
M-21			Cℓ

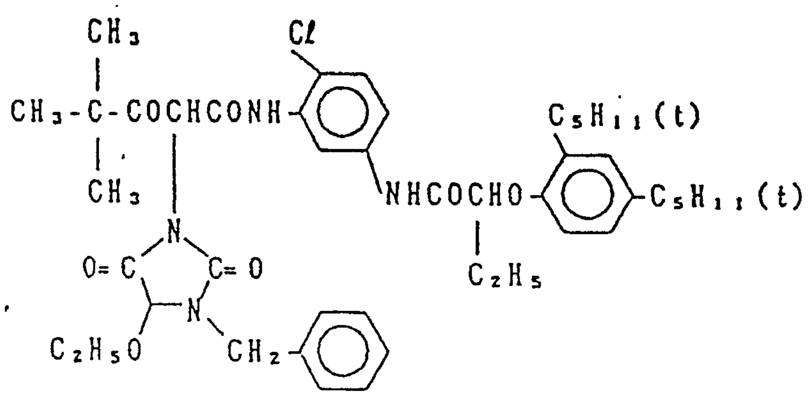


Compound	R_{10}	R_{15}	Y_4
M-22	CH_3		Cl
M-23	"		"
M-24			"
M-25	 $\underset{COOCH_2CH_2OCH_3}{(CH-CH_2)_{50}}\underset{CONH-}{(CH_2-\overset{CH_3}{C})_{50}}$	 $\underset{CH_2NHSO_2CH_3}{CH_3-CH-}$	"

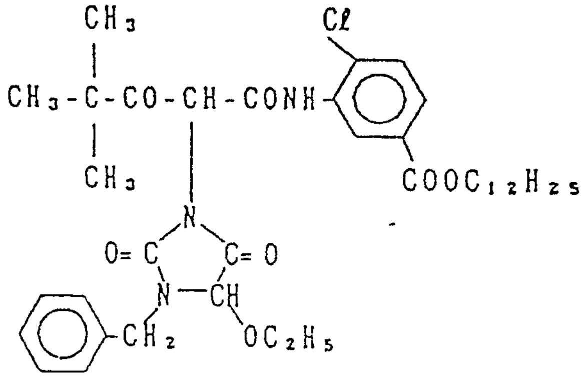
Compound	R_{10}	R_{15}	Y_4
M-26			Cℓ
M-27	CH_3-		"
M-28	$(CH_3)_3C$-		"

Compound	R_{10}	R_{15}	Y_4
M-29			Cℓ
M-30	CH_3-	 $-\underset{C_2H_5}{CH}-\overset{(n)C_{18}H_{37}}{N}COCH_2CH_2COOH$	"

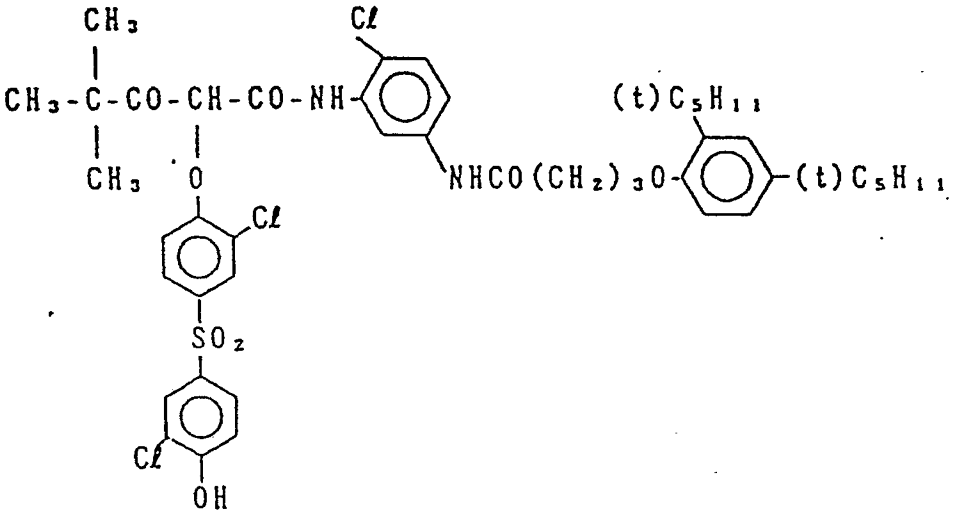
(Y-1)



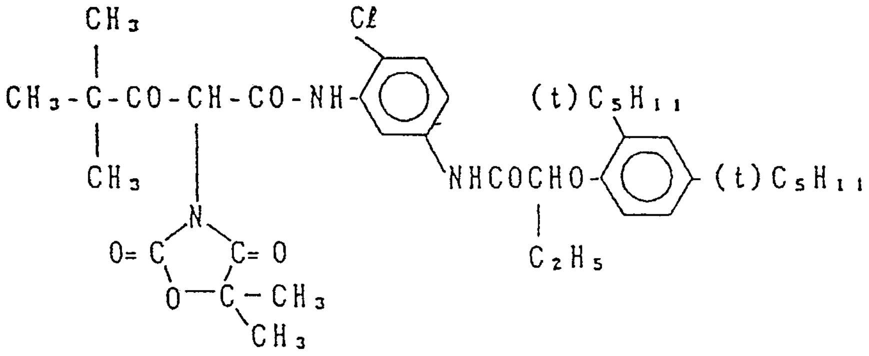
(Y-2)



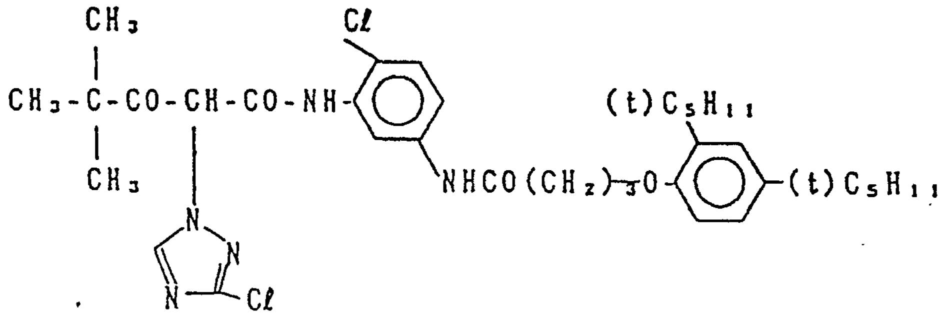
(Y－3)



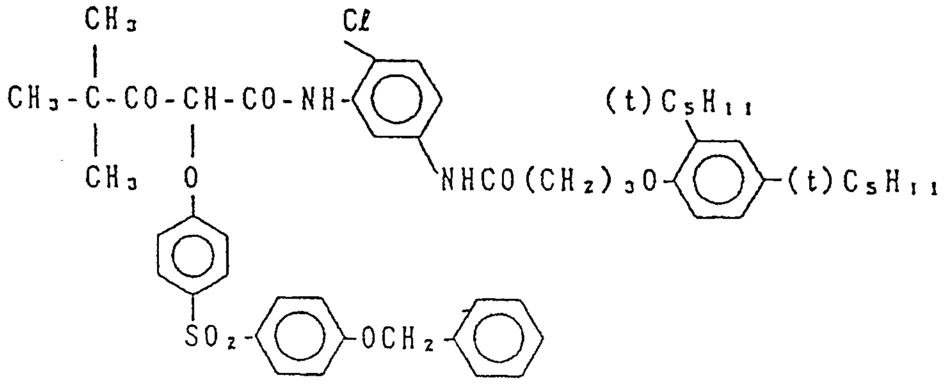
(Y－4)



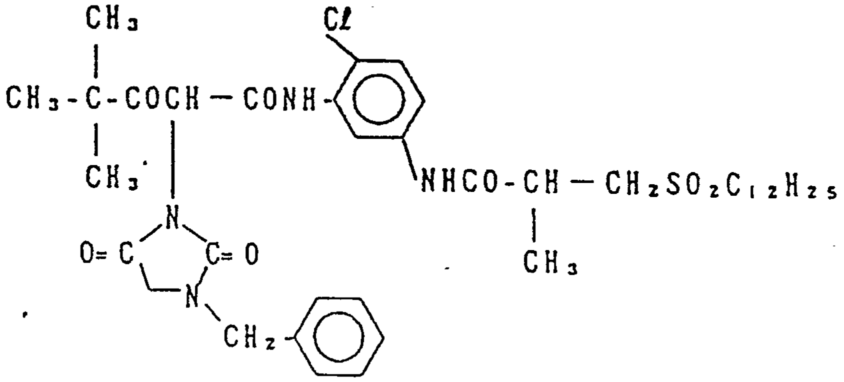
(Y－5)



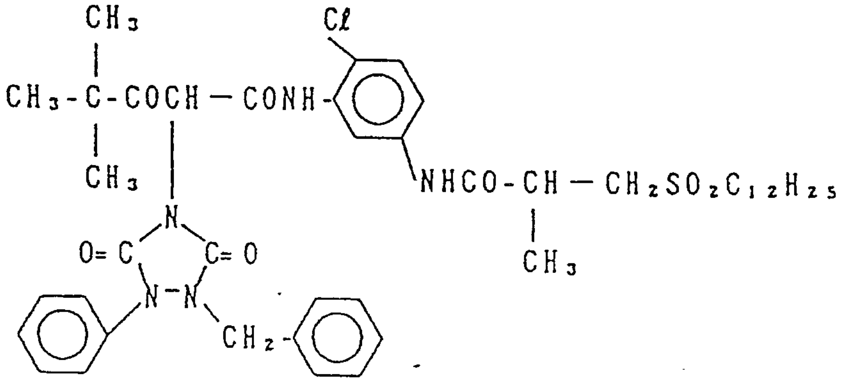
(Y－6)



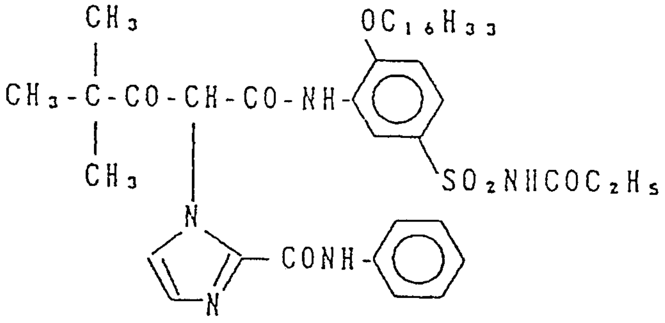
(Y－7)



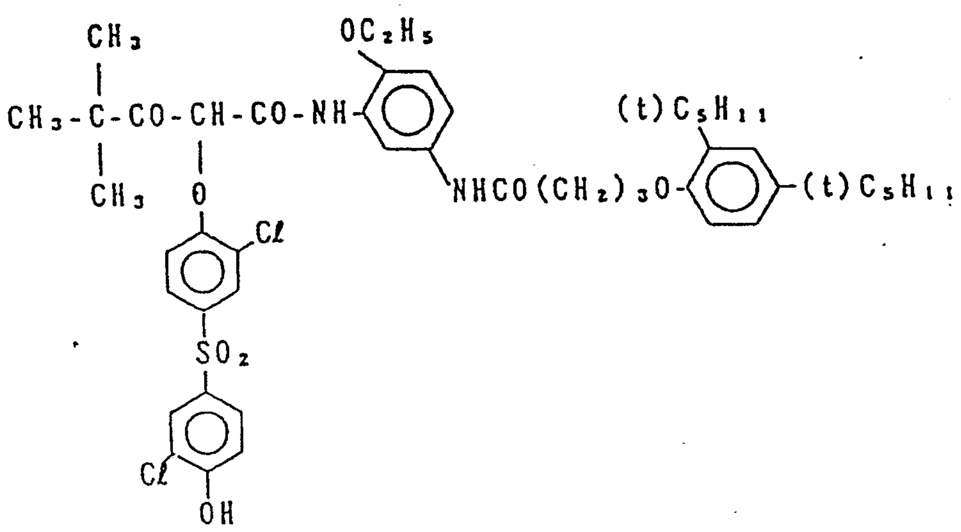
(Y－8)



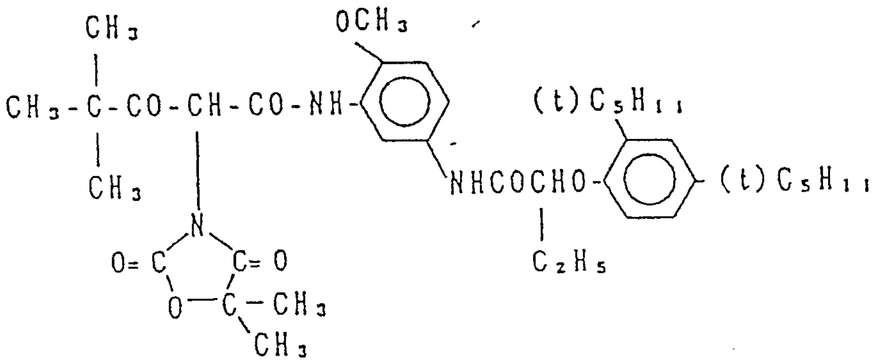
(Y－9)



(Y－10)



(Y－11)



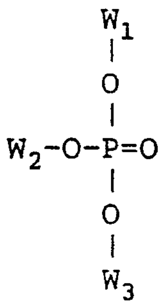
Each of the couplers shown by the aforesaid formulae (C-I), (C-II), (M-I), (M-II), and (Y) is contained in a silver halide emulsion constituting the light-sensitive emulsion layer in an amount of from 0.1 to 1.0 mol, and preferably from 0.1 to 0.5 mol per mol of silver halide.

In this invention, for adding these couplers to light-sensitive emulsion layers, various techniques can be applied. Usually, the coupler can be added by an oil drop-in-water dispersion method known as an "oil product" method. That is, after dissolving a coupler in an organic solvent, the solution is dispersed by emulsification in an aqueous gelatin solution containing a surface active agent. Or water or an aqueous gelatin solution is added to a coupler solution containing a surface active agent and an oil drop-in-water dispersion may be formed from the mixture with phase inversion.

Also, when a coupler is alkali soluble, the coupler can be dispersed by a Fischer's dispersion method. After removing a low-boiling organic solvent from a coupler dispersion by distillation, a noodle washing method, or ultrafiltration, the dispersion may be added to a silver halide emulsion.

As the dispersion medium for such a coupler, a high-boiling organic solvent and/or a water-insoluble polymer. each having a dielectric constant of from 2 to 20 (25° C), and a refractive index of from 1.5 to 1.7 (25° C) is preferably used.

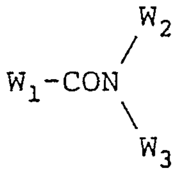
As the high-boiling organic solvent, the high-boiling organic solvent represented by formulae (A) to (E) is preferably used.



$$\begin{array}{c} W_1 \\ | \\ O \\ | \\ W_2\text{-}O\text{-}P{=}O \\ | \\ O \\ | \\ W_3 \end{array}$$

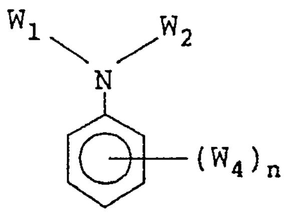
(A)

$W_1\text{-}COO\text{-}W_2$ (B)



$$W_1\text{-}CON\begin{array}{l} \diagup W_2 \\ \diagdown W_3 \end{array}$$

(C)



(D)

$W_1\text{-}O\text{-}W_2$ (E)

In the above formulae, W_1, W_2, and W_3 each represents an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, or a heterocyclic group, and each may be substituted; W_4 represents W_1, OW_1, or $S\text{-}W_1$; and n represents an integer of from 1 to 5. When n is 2 or more, W_4s may be the same or different. In formula (E), W_1 and W_2 may form a condensed ring.

Other high-boiling organic solvents than those represented by formulae (A) to (E) can be also used in this invention, if they are compounds immiscible with water having a melting point of up to 100° C and a boiling point of at least 140° C, and are a good solvent for the coupler. The melting point of the high-boiling organic solvent is preferably up to 80° C and the boiling point of the high boiling organic solvent is preferably at least 160° C, and more preferably at least 170° C.

Details of these high-boiling organic solvents are described in JP-A-62-215272, page 137, right column to page 144, right column.

Also, the coupler can be dispersed by emulsification in an aqueous gelatin solution by impregnating a loadable latex polymer (described, e.g., in U.S. Patent 4,203,716) with the coupler in the presence or absence of the high-boiling organic solvent or by dissolving in a polymer which is insoluble in water and soluble in an organic solvent.

The homopolymer or copolymer described in PCT WO 088/00723, pages 12-30 is preferably used and the use of the acrylamide series polymer is particularly preferred for color image stabilization.

The silver halide photographic material in this invention may contain a hydroquinone derivative, an aminophenol derivative, a gallic acid derivative, or an ascorbic acid derivative as a color fogging inhibitor.

Also, for the photographic light-sensitive materials in this invention, various fading inhibitors can be used. Organic fading inhibitors for cyan, magenta, and/or yellow images include hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols, hindered phenols (such as bisphenols), gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines, and the ether or ester derivatives thereof formed by silylating or alkylating the phenolic hydroxy groups of these compounds. Also, metal complexes such as (bis-salicylaldoximate)nickel complex and (bis-N,N-dialkyldithiocarbamate)nickel complex can be used.

Practical examples of the organic inhibitor are described in the following patent specifications.

Hydroquinones are described in U.S. Patents 2,360,290, 2,418,613, 2,700,453, 2,701,197, 2,728,659, 2,732,300, 2,735,765, 3,982,944, and 4,430,425, British Patent 1,363,921, U.S. Patents 2,710,801, and 2,816,028; 6-hydroxychromans, 5-hydroxycoumarans, and spirochromans are described in U.S. Patents 3,432,300, 3,573,050, 3,574,627, 3,698,909, and 3,764,337, and JP-A-52-152225; spiroindanes are described in U.S. Patent 4,360,589; p-alkoxyphenols are described in U.S. Patent 2,735,765, British Patent 2,066,975, JP-A-59-10539, and JP-B-57-19765; hindered phenols are U.S. Patent 3,700,455, JP-A-52-72224, U.S. Patent 4,228,235, and JP-B-52-6623; gallic acid derivatives, methylenedioxybenzenes, and aminophenols are described in U.S. Patents 3,457,079 and 4,332,886, and JP-B-56-21144; hindered amines are described in U.S. Patents 3,336,135 and 4,268,593, British patents 1,326,889, 1,354,313, and 1,410,846, JP-B-51-1420, JP-A-58-114036, JP-A-59-53846, and JP-A-59-78344; and metal complexes are described in U.S. Patents 4,050,938 and 4,241,155, and British Patent 2,027,731(A).

The aforesaid compound is coemulsified with each corresponding color coupler in an amount of from 5 to 100% by weight to the coupler and added to a silver halide emulsion.

For preventing the deterioration of cyan dye images by heat and, in particular,light, it is more effective to introduce an ultraviolet absorbent into the cyan coloring layer or layers adjacent to both sides thereof.

Examples of the ultraviolet absorbent which can be used in this invention are benzotriazole compounds substituted by an aryl group described, e.g., in U.S. Patent 3,533,794, 4-thiazolidone compounds described, e.g., in U.S. Patents 3,314,794 and 3,352,681, benzophenone compounds described, e.g., in JP-A-46-2784, cinnamic acid ester compounds described, e.g., in U.S. Patents 3,705,805 and 3,707,395, butadiene compounds described, e.g., in U.S. Patent 4,045,229, and benzoxazole compounds described, e.g., in U.S. Patents 3,406,070, 3,677,762, and 4,271,307.

Ultraviolet absorptive couplers (e.g., α-naphtholic cyan dye-forming couplers) or ultraviolet absorptive polymers may be used.

These ultraviolet absorbents may be mordanted in a specific layer.

Of these compounds, the benzotriazole compounds substituted by an aryl group are preferred.

Also, it is preferred to use the following compounds together with the couplers. In particular, the use of the following compounds with pyrazoloazole couplers is preferred.

The use of a compound (F) which causes chemical bonding with an aromatic amine color developing agent remaining after color development processing to form a chemically inactive and substantially colorless compound and/or a compound (G) which causes chemical bonding with the oxidized aromatic amino color developing agent remaining after color development processing is preferred for preventing the occurrence of stains by the formation of colored dyes by the reaction of the color developing agent or the oxidation product thereof remaining in the emulsion layers with couplers, or the occurrence of other side reaction during the storage of the photographic materials after processing.

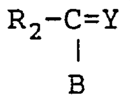
As the compound (F), a compound which reacts with p-anisidine at a secondary reaction rate constant k_z (in trioctyl phosphate at 80°C) in the range of from 1.0 liter/mol•sec. to 1×10^{-5} liter/mol•sec. is preferably used.

The secondary reaction rate constant can be measured by the method described in JP-A-63-158545.

If the value of k_z is larger than this range, the compound itself becomes unstable and may decomposed by causing a reaction with gelatin or water. On the other hand, if the value of k_z is less than this range, the reaction with the remaining aromatic amine developing agent is delayed, which reduces the prevention of the side reaction of the remaining aromatic amine developing agent.

More preferred compounds among such compounds (F) are represented by formulae (FI) or (FII);

$$R_1-(A)_n-X \qquad (FI)$$



$$R_2-\underset{\displaystyle B}{\underset{|}{C}}=Y \qquad (FII)$$

wherein R_1 and R_2 each represents an aliphatic group, an aromatic group, or a heterocyclic group; n represents 0 or 1; A represents a group forming a chemical bond by reacting with an aromatic amino developing agent; X represents a group capable of being cleaved by reacting with an aromatic amino developing agent; B represents hydrogen, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, or a sulfonyl group; and Y represents a group capable of accelerating the addition of an aromatic amino developing agent to the compound of formula (FII). In this case, R_1 and X or Y and R_2 or B may be linked with each other to form a cyclic structure.

The typical system of chemically bonding with a remaining aromatic amino developing agent is a substitution reaction and an addition reaction.

Specific examples of preferred compounds represented by formula (FI) and (FII) are described in JP-A-63-158545 and JP-A-62-283338, and European Patent Applications (unexamined published) 298,321 and 277,589.

Preferred compounds among the compounds (G) which cause chemical bonding with the oxidation product of an aromatic amino developing agent remaining after color development processing are represented by formula (GI):

R-Z (GI)

wherein R represents an aliphatic group, an aromatic group, or a heterocyclic group and Z represents a nucleophilic group or a group which is decomposed in a photographic light-sensitive material to release a nucleophilic group.

In the compound represented by formula (GI), Z is preferably a group having a Pearson's nuoleophilic $^{n}CH_3I$ value (R.G. Pearson, et al, Journal of Americal Chemical Society , 90 , 319 (1968)) of at least S or a group derived from this group.

Specific examples of the preferred compounds shown by formula (GI) are described in European Patent Applications (unexamined published) 255,722, 298,321, and 277,589, JP-A-62-143048, JP-A-62-229145, JP-A-1-57259 and Japanese Patent Application No. 63-136724.

Also, details of the combination of compound (G) and compound (F) are described in European Patent Application (unexamined published) 277,589.

The photographic light-sensitive material in this invention may contain ultraviolet absorbent(s) in the hydrophilic colloid layer(s). Examples of the ultraviolet absorbent are benzotriazole compounds substituted by an aryl group described, e.g., in U.S. Patent 3,533,794, 4-thiazolidone compounds described, e.g., in U.S. Patents 3,314,794 and 3,352,681, benzophenone compounds described, e.g., in JP-A-46-2784, cinnamic acid ester compounds described, e.g., in U.S. Patents 3,705,805 and 3,707,375, butadiene compounds described, e.g., in U.S. Patent 4,045,229, and benzooxidol compounds described, e.g., in U.S. Patent 3,700,455. An ultraviolet absorptive coupler (e.g., α-naphtholic cyan dye-forming couplers) or an ultraviolet absorptive polymer may be used. The ultraviolet absorbent may be mordanted in a specific hydrophilic colloid layer.

For the photographic light-sensitive materials in this invention, colloidal silver or dyes are used for anti-irradiation, anti-halation, and in particular, the separation of the spectral sensitivity distribution of each light-sensitive emulsion layer and ensuring safety to a safelight of a visible wavelength region.

Examples of dyes which are used for this purpose are oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Of these dyes, oxonol dyes, hemioxonol dyes, and merocyanine dyes are useful. Also, indolenine dyes are particularly useful.

As a longest wavelength red or infrared dye, decolorable dyes described in JP-A-62-3250, JP-A-62-181381, JP-A-62-123454, and JP-A-63-197947 and dyes for backing layers are described in JP-A-62-39682, JP-A-62-123192, JP-A-62-158779, and JP-A-62-174741, or dyes introduced with a water-soluble group which can flow out during processing can be used. The infrared dye for use in this invention may be a colorless dye having substantially no light absorption in a visible wavelength region.

When the infrared dye for use in this invention is mixed with a silver halide emulsion spectrally sensitized to the longest wavelength side of red region or infrared wavelength region, occasionally the emulsion is desensitized, fog is formed, or in some cases, the dye itself adsorbs to silver halide grains to cause a weak and broad spectral sensitization. It is preferred that the infrared dye is incorporated in other colloid layer(s) only than light-sensitive emulsion layers. For this purpose, it is preferable that the dye is incorporated in a specific colored layer in a nondiffusible state. Thus, first, the dye is rendered nondiffusible by introducing a ballast group into the dye. However, in this case, residual color or processing stain is liable to form.

Second, the anionic dye for use in this invention is mordanted using a polymer or a polymer latex providing a cation site. Third, a dye which is insoluble in water having pH of 7 or lower and decolored and dissolved off during processing is used as a dispersion of fine particles thereof. For the purpose, the dye is dissolved in a low-boiling organic solvent or solubilized in a surface active agent and dispersed in an aqueous solution of a hydrophilic protective colloid such as gelatin. It is preferred that the solid dye is kneaded with an aqueous solution of a surface active agent, the mixture is mechanically ground by a mill to fine particles and the fine particles are dispersed in an aqueous solution of a hydrophilic colloid such as gelatin.

As a binder or a protective colloid which can be used for the photographic layers of the photographic light-sensitive material in this invention, gelatin is advantageously used but other hydrophilic colloids can be used singly or together with gelatin.

Gelatin for use in this invention may be lime-processed gelatin or acid-processed gelatin. Details of the production process of gelatin are described in Arther Weiss, The Macromolecular Chemistry of Gelatin (published by Academic Press, 1964).

For the color photographic light-sensitive materials in this invention, known photographic additives, in particular, materials which are used in commercially available color photographic papers using high silver chloride emulsions (grain mean silver chloride content of at least 96 mol%) can be used. They are described in Research Disclosures (RD) as shown below.

Additive	RD 17643	RD 18716
1. Chemical Sensitizers	Page 23	Page 648, right column
2. Sensitivity Increasing Agent	Page 23	Page 648, right column
3. Spectral Sensitizer	Pages 23 to 24	Page 648, right column to page 649, right column
4. Super Color Sensitizer	Pages 23 to 24	Page 648, right column to page 649, right column
5. Whitening Agent	Page 24	Page 648, right column to page 649, right column
6. Antifoggant and Stabilizer	Pages 24 to 25	Page 649, right column
7. Coupler	Page 25	Page 649, right column
8. Organic Solvent	Page 25	Page 649, right column
9. Light Absorbent and Filter Dye	Pages 25 to 26	Page 649, right column to page 650, left column
10. Ultraviolet Absorbent	Pages 25 to 26	Page 649, right column to page 650, left column
11. Stain Inhibitor	Page 25, right column	Page 650, left column to right column
12. Dye Image Stabilizer	Page 25	Page 650, left column to right column
13. Hardening Agent	Page 26	Page 651, left column
14. Binder	Page 26	Page 651, left column
15. Plasticizer and Lubricant	Page 27	Page 650, right column
16. Coating Aid and Surface Active Agent	Pages 26 to 27	Page 650, right column
17. Antistatic Agent	Page 27	Page 650, right column

The halogen composition for a silver halide emulsion which is used for the silver halide light-sensitive emulsion layers of the silver halide photographic material in this invention may be silver chloride, silver bromide, silver chlorobromide, silver chloroiodo-bromide, or silver iodochloride, but a high silver chloride content such as that of a silver chlorobromide emulsion containing at least 90 mol% silver chloride is preferred for rapid development processing and increasing the storage stability of this invention. A silver chlorobromide emulsion containing at least 96 mol% silver chloride or a silver chloride emulsion is more preferably used. When silver bromide is contained in the emulsion, it is preferred that silver bromide exist in the interior of silver halide grain or at the surface of the grain as a local phase. In this invention, when silver halide grains have a local partial structure having a different silver bromide content at least in the inside of the grain or localized in the surface thereof, the silver halide grain has a "local phase". Also, in pure silver chloride, if the silver halide grains have a local partial structure having a different content of a metal ion other than a silver ion, such as iridium, rhodium, or iron, the silver chloride grains are said to have a "local phase" in this invention. JP-A-1-183647 discloses that high silver chloride grains having a silver bromide local phase were doped with iron ions.

In this invention, when silver halide grains are composed of silver chlorobromide, silver chlorobromide having a mean silver chloride content of at least 96 mol% and having local phases having a silver bromide content of over 15 mol% is preferred.

Such a local phase having a high content of silver bromide may be optionally disposed as required, i.e., may be in the inside of the silver halide grains, at the surface of the grain, near the surface of the grain, or may simultaneously exist at two or more positions. Also, the local phase may have a layer structure surrounding the grain, a discontinuous isolated structure, a network structure, or a composite structure thereof.

In a preferred example of the disposition of the local phase, silver chlorobromide having a silver bromide content of at least 15 mol% is present locally at the surface of silver chlorobromide grains. It is preferred that the silver bromide content of the local phase is over 15 mol% but less than 70 mol%. If the silver bromide content of the local phase is too high, pressure desensitization occurs when exposing the light- sensitive material using the silver halide emulsion after applying a mechanical pressure, or the photographic properties of the photographic light-sensitive material are varied with changes in the composition of a processing solution.

Accordingly, the silver bromide content in the local phase is preferably in the range of from 15 to 70 mol%, more preferably from 20 to 60 mol%, and particularly preferably from 30 to 50 mol%.

The local phases are preferably composed of silver in an amount from 0.01 to 20 mol% of the total silver constituting the silver halide grains for use in this invention, and are more preferably composed of silver of from 0.02 to 7 mol% of total silver.

The interface between the local phase having a high silver bromide content and other phase may have a distinct boundary or may have a boundary wherein the halogen composition is gradually and continuously changed.

The silver bromide content in such a local phase can be analyzed using an X-ray diffraction method (described, e.g., in Shin Jikken Kagaku Koza (New Experimental Chemical Course) 6 Kozokaiseki (Structure Analysis) , edited by Chemical Society of Japan, published by Maruzen) or an XPS method (described, e.g., in Hyomen Bunseki (Surface Analysis)-IMA , Application of Auger Electron. Photoelectric Spectrum-, published by Kodansha). The existence of the local phase can be seen by an electromicroscope.

In this invention, for forming the silver bromide local phase or a metal salt local phase, various methods can be used.

For example, the local phase can be formed by reacting a soluble silver salt and a soluble bromide or metal salt by a single jet method or a double jet method. The local phase can be also formed using a halogen conversion method including a step of converting a silver halide already formed into a silver halide having a lower solubility product. Furthermore, the local phase can be also formed by mixing silver halides each having a different halogen composition followed by ripening to cause recrystallization. When the silver chlorobromide local phase is formed at the surface of silver chloride grains, it is preferred to form the local phase by adding fine silver bromide grains having relatively small grain sizes to silver chloride grains already formed followed by ripening to cause recrystallization.

By changing the period of adding a halide solution for forming a local phase, adding a sparingly soluble halide, adding a silver salt solution, adding a halide solution, and/or adding fine grain silver halide, or changing the ripening time and temperature, and the silver ion concentration at the addition and ripening thereof, the extent of the halogen conversion or the recrystallization is changed, thereby the silver halide emulsion formed can be controlled to have a desired performance.

The silver halide emulsion having the aforesaid local phases may contain silver iodide. In this case, it is preferred that silver iodide is present locally. In this case, the content of silver iodide is preferably from 0 to 3 mol%, more preferably from 0 to 1 mol%, and most preferably from 0 to 0.6 mol%.

The silver halide emulsion for use in this invention may further contain an inorganic silver salt other than silver halide as described above, such as silver rhodanate or silver phosphate.

The form of the crystal grains of the silver halide for use in this invention may be a regular grain form such as cubic, octahedral, tetradecahedral, or rhombic dodecahedral, or may be an irregular grain for such as sphere or tabular. Also, the grain form may be a complicated form having a combination of these crystal planes or may be grains having higher crystal planes. Furthermore, a mixture of these silver halide grains may be used.

Also, when the silver halide emulsion for use in this invention contains tabular grains having a mean aspect ratio (the ratio of the circle equivalent diameter of the main plane of the grain to the thickness of the grain) of at least 5, and particularly preferably at least 8 account for at least 50% of the total projected area of the grains, the emulsion is useful for quick processing.

The grain size distribution of the silver halide grains may be broad or narrow but a monodisperse silver halide emulsion is preferable for sensitivity stability. The value S/d obtained by dividing the standard deviation S of the distribution of the circle equivalent diameters from the projected areas of the silver halide grains by the mean diameter d is preferably 20% or less, and more preferably 15% of less.

A monodisperse silver halide emulsion containing silver halide grains having a regular crystal form in a grain number or weight of at least 50%, preferably at least 70%, and more preferably at least 90% is preferably used in this invention, and a silver halide emulsion containing silver halide grains of cubic or tetrahedral form having a (100) crystal plane and having the aforesaid local phase at the corner portions or edge portions if particularly preferred in this invention. The local phase of a metal salt may preferably exist at another portion than the edge and the corner, such as, at the (100) plane in this invention.

Such discontinuous isolated local phases existing at the surfaces of silver halide grains can be formed by supplying a bromide ion or a metal ion to a silver halide emulsion containing the silver halide grains as the case material while controlling the silver ion concentration, hydrogen ion concentration, temperature or time, to cause halogen conversion. In this case, however, if it is necessary to uniformly supply the ion to each silver halide grain in the system, it is preferred to supply the ion while stirring the system. It is also preferred to simultaneously supply the ions at a low concentration or gradually supply the ions. For gradually supplying the ion, an organic halogen compound such as bromosuccinimide or bromopropionic acid or a halogen compound covered by a semipermeable capsule can be used.

Also, the local phases can be formed by supplying a silver ion and a halogen ion to a silver halide emulsion containing silver halide grains as a base material while controlling the silver ion concentration, to grow silver halide at limited sites of the grains, or by mixing silver halide grains as the base material with fine grain silver halide crystals having a finer grain size than the base material to grow silver halide at limited sites of the silver halide grains as the base material, such as the edges or corners thereof. In this case, if necessary, a silver halide solvent can be used together.

Also, controlling compounds for halogen conversion or recrystallization described in JP-A-1-105940, JP-A-1-26840, and JP-A-1-183647 can be used. The silver halide grains having such local phases can be also prepared using fine crystals of silver iodobromide, silver chlorobromide, as in the case of using fine silver bromide crystals.

The grain sizes of the silver halide grains contained in the silver halide emulsion for use in this invention are preferably from 0.05 µm to 2 µm, and more preferably from 0.1 µm to 1.5 µm as the mean value of the diameters of spheres corresponding to the volumes thereof.

The silver halide emulsions for use in this invention can be prepared by utilizing the methods described in P. Glafkides, Chemie et Phisique Photographique , (Paul Montel Co., 1967); G.F. Duffin, Photographic Emulsion Chemistry , (Focal Press Co., 1966); and V.L. Zelikman et al, Making and Coating of Photographic Emulsion , (Focal Press Co., 1964).

That is, an acid method, a neutralization method, or an ammonia method, can be used for the preparation of the emulsion but an acid method and a neutralization method are preferred in this invention for reducing the formation of fog. For obtaining a silver halide emulsion of a high sensitivity, it is preferred to prepare the emulsion at a hydrogen ion concentration lower than neutral. Also, for obtaining a silver halide emulsion by reacting a soluble silver salt and a soluble halide, a single jet method, a double jet method or a combination thereof may be used. A reverse mixing method of forming silver halide grains in an excess of silver ion can be also used. For obtaining a monodisperse silver halide emulsion which is preferably used in this invention, a double jet method is preferably used. As one system of the double jet method, a double jet method keeping a constant silver ion concentration in a liquid phase while forming silver halide grains is more preferably used. When this method is used, a preferred silver halide emulsion containing silver halide grains having a regular crystal form and a narrow grain size distribution can be obtained.

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

At or after the grain formation, a silver halide solvent (e.g., ammonia, thiocyanates, or the ethers and the thione compounds described in U.S. Patent 3,271,157, JP-A-51-12360, JP-A-53-82408, JP-A-53-144319, JP-A-54-100717, and JP-A-54-155828) may be used, and when the silver halide solvent is used a preferred silver halide emulsion containing silver halide grains having a regular silver halide crystal form and a narrow grain size distribution is obtained.

For removing soluble salts from the silver halide emulsion after physical ripening, a noodle washing method, a flocculation method, or an ultra-filtration method can be utilized.

The silver halide emulsion for use in this invention can be chemically sensitized by sulfur sensitization, selenium sensitization, reduction sensitization, or noble metal sensitization, alone or as a combination thereof. A sulfur sensitization method using active gelatin or a compound containing a sulfur compound capable of reacting with a silver ion (e.g., a thiosulfate, a thiourea compound, a mercapto compound, a rhodanine compound), a reduction sensitization method using a reducing material (e.g., stannous salts, amines, hydrazine derivatives, formamidinesulfinic acid, silane compounds, ascorbic acid), and a noble metal sensitization method using a noble metal compound (e.g., a gold complex salt, a salt of a metal belonging to group VIII of the periodic table, such as platinum, iridium, palladium, rhodium, iron) or a complex salt thereof can be used solely or as a combination of them.

For the silver halide emulsion for use in this invention, sulfur sensitization or a selenium sensitization is preferably used and it is also preferred to use gold sensitization together with this sensitization. Also, it is preferred for controlling the sensitivity and gradation to perform the chemical sensitization in the presence of a hydroxyazaindene compound or nucleic acid.

It is preferred for obtaining the high sensitivity stabilizing effect of this invention under various conditions that the silver halide grains for use in this invention contain a metal ion other than a silver ion (e.g., a metal ion belonging to group VIII of the periodic table, a transition metal ion of group II, a lead ion of group IV, or a gold ion or a copper ion of group I) or a complex ion thereof. The metal ion or the complex ion thereof may be incorporated uniformly in the silver halide grains, the local phases or other phases.

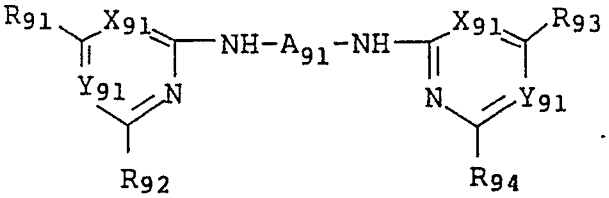
Of the metal ions and the complex ions, an iridium ion, a zinc ion, an iron ion, a palladium ion, a rhodium ion, a platinum ion, a gold ion, and a copper ion are preferred.

When these metal ions or complex ions are used as a combination thereof, desired photographic properties are frequently obtained, and also it is preferred to change the kind and the amount of the addition ion between the local phases and other portions of the grains. It is particularly preferred that an iridium ion or a rhodium ion be present in the local phases.

For incorporating the metal ion or the complex ion in the local phases of silver halide grains or other portions of the grains, the metal ion or the complex ion may be directly added to a reaction vessel before or during the formation of the silver halide grains or at physical ripening after formation of the grains, or may be previously added to a solution of a water-soluble halide or a water-soluble silver salt. In the case of forming the local phases with fine grain silver bromide, the metal ion or complex ion is incorporated in the fine grains of silver bromide or silver iodide and they may be added to a silver chloride emulsion or a high-silver chloride emulsion. Also, by adding a relatively sparingly soluble bromide of the aforesaid metal ion other than silver salt as a solid or a powder, the metal ion may be incorporated while forming the local phases.

In the silver halide emulsion prepared as described above, high sensitivity, the stability of sensitivity, and the stability of latent images, which are problems of a high-silver chloride emulsion sensitized from a red-sensitive region to an infrared sensitive region, are improved overall and the high-silver chloride emulsion is suitable for rapid processing.

For the M band sensitization in the red to infrared sensitizations in this invention, super color sensitization by a compound represented by formula (IX) is preferred:



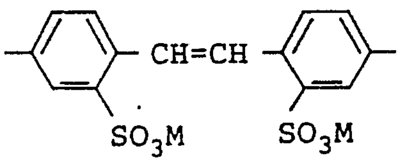
(IX)

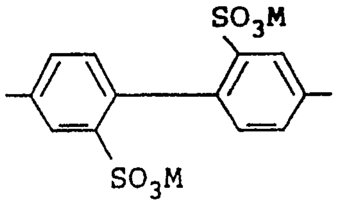
wherein, A_{91} represents a divalent aromatic residue; R_{91}, R_{92}, R_{93}, and R_{94} each represents hydrogen atom, a hydroxy group, an alkyl group, an alkoxy group, an aryloxy group, a halogen atom, a heterocyclic nucleus, a heterocyclylthio group, an arylthio group, an amino group, an alkylamino group, an arylamino group, an aralkylamino group, or a mercapto group, and each group may be substituted; at least one of A_{91}, R_{91}, R_{92}, R_{93}, and R_{94} contains a sulfo group; and X_{91} and Y_{91} each represents -CH= or -N=, provided that at least one of X_{91} and Y_{91} represents -N=.

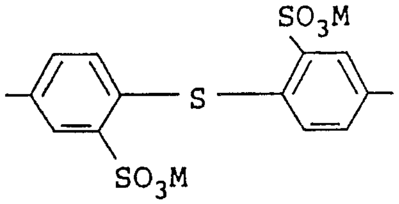
In more detail, in formula (IX), $-A_{91}-$represents a divalent aromatic group which may be substituted with $-SO_3M$ (wherein M represents hydrogen or a cation providing water solubility (e.g., sodium and potassium)).

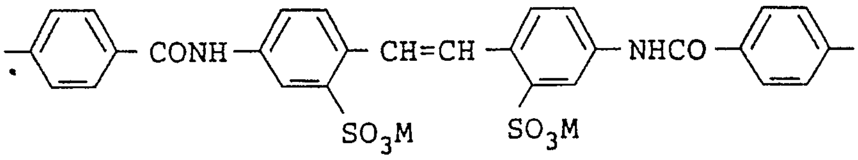
Useful examples of $-A_{91}-$ are those selected from $-A_{92}-$ or $-A_{93}-$ shown below. However, when R_{91}, R_{92}, R_{93}, or R_{94} does not contain $-SO_3M$, $-A_{91}-$ is represented by $-A_{92}-$.

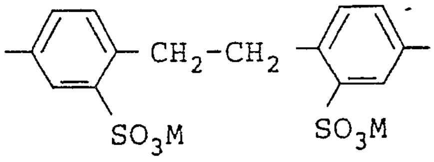
A_{92} represents the following groups:

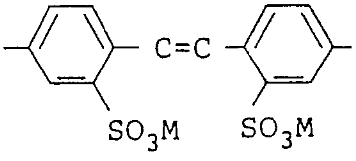
 :

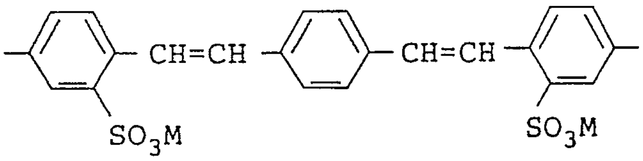
 :

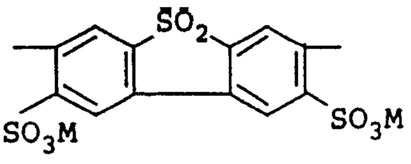
 :

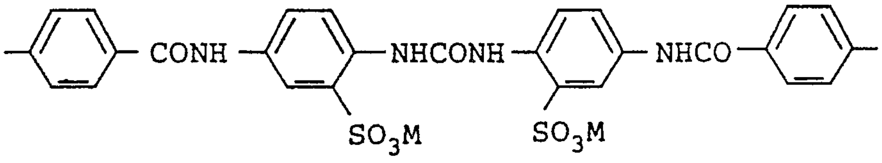


 :

 :

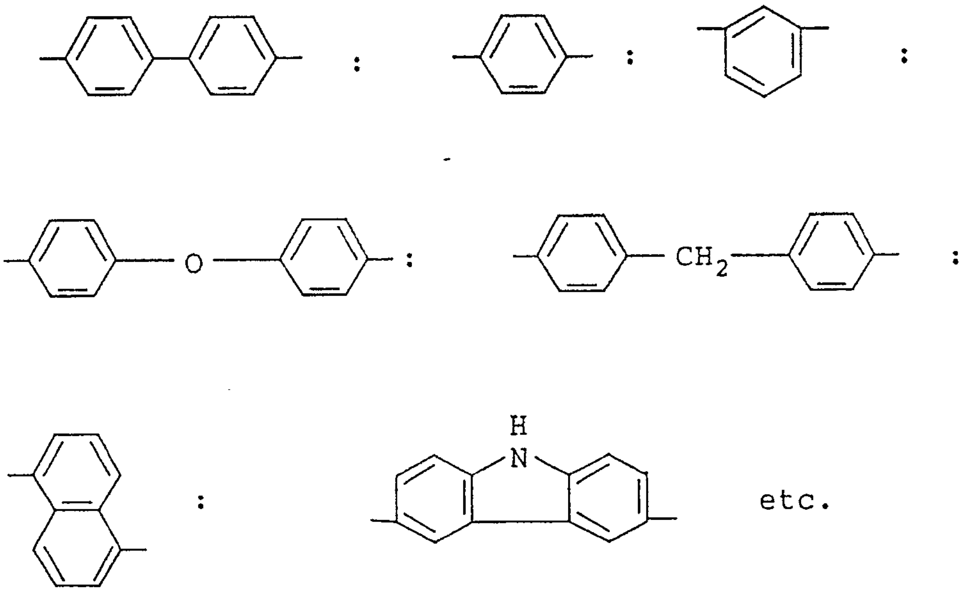
 :

 :

 :

(wherein M represents a hydrogen atom or a cation giving water solubility).

A_{93} represents the following groups:


etc.

In formula (IX), R_{91}, R_{92}, R_{93}, and R_{94} each represents hydrogen, a hydroxy group, an alkyl group (having preferably from 1 to 8 carbon atoms, e.g., methyl, ethyl, n-propyl, and n-butyl), an alkoxy group (having preferably from 1 to 8 carbon atoms, e.g., methoxy, ethoxy, propoxy, and butoxy), an aryloxy group (e.g., phenoxy, naphthoxy, o-tolyloxy, and p-sulfophenoxy), a halogen atom (e.g., chlorine and bromine), a heterocyclic nucleus (e.g., morpholinyl and piperidyl), an alkylthio group (e.g., methylthio and ethylthio), a heterocyclicthio group (e.g., benzothiazolylthio, benzimidazolylthio, and phenyltetrazolylthio), an arylthio group (e.g., phenylthio and tolylthio), an amino group, an alkylamino group or a substituted alkylamino group [e.g., methylamino, ethylamino, propylamino, dimethylamino, diethylamino, dodecylamino, cyclohexylamino, β-hydroxyethylamino, di-(β-hydroxyethyl)amino, and β-sulfoethylamino], an arylamino group or substituted arylamino group (e.g., anilino, o-sulfoanilino, m-sulfoanilino, p-sulfoanilino, o-toluidino, m-toluidino, p-toluidino, o-carboxyanilino, m-carboxyanilino, p-carboxyanilino, o-chloroanilino, m-chloroanilino, p-chloroanilino, p-aminoanilino, o-anisidino, m-anisidino, p-anisidino, o-acetaminoanilino, hydroxyanilino, disulfophenylamino, naphthylamino, and sulfonaphthylamino), a heterocyclicamino group (e.g., 2-benzothiazolylamino, and 2-pyrizylamino), a substituted or unsubstituted aralkylamino group (e.g., benzylamino, o-anisylamino, m-anisylamino, and p-anisylamino), an aryl group (e.g., phenyl), or a mercapto group.

R_{91}, R_{92}, R_{93}, and R_{94} may be the same or different.

When $-A_{91}-$ is selected from the group represented by $-A_{93}-$, at least one of R_{91}, R_{92}, R_{93}, and R_{94} must have at least one sulfo group (which may be a free acid group or form a salt). X_{91} and Y_{91} each represents -CH= or -N= and it is preferred that X_{91} represents -CH= and Y_{91} represents -N=.

Specific examples of the compound represented by formula (IX), which can be used in this invention, are illustrated below, but the invention is not to be construed as being limited thereto:

(A-1) 4,4'-Bis[2,6-di(2-naphthoxy)pyrimidin-4-ylamino] stilbene-2,2'-disulfonic acid di-sodium salt

(A-2) 4,4'-Bis[2,6-di(2-naphthothylamino)pyrimidin-4-ylamino]stilbene-2,2'-disulfonic acid di-sodium salt

(A-3): 4,4'-Bis(2,6-dianilinopyrimidin-4-ylamino)stilbene-2,2'-disulfonic acid di-sodium salt

(A-4): 4,4'-Bis[2-(2-naphthylamino)-6-anilinopyrimidin-4-ylamino]stilbene-2,2'-disulfonic acid disodium salt

(A-5) 4,4'-Bis(2,6-diphenoxypyrimidin-4-ylamino]stilbene-2,2'-disulfonic acid triethylammonium salt

(A-6): 4,4'-Bis[2,6-di(benzimidazolyl-2-thio)pyrimidin-4-ylamino]stilbene-2,2'-disulfonic acid di-sodium salt

(A-7): 4,4'-Bis[4,6-di(benzothiazolyl-2-thio)pyrimidin-2-ylamino]stilbene-2,2'-disulfonic acid di-sodium salt

(A-8): 4,4'-Bis[4,6-di(benzothiazolyl-2-amino)pyrimidin-2-ylamino]stilbene-2,2'-disulfonic acid di-sodium salt

(A-9): 4,4'-Bis(4,6-di(naphthyl-2-oxy)pyrimidin-2-ylamino]stilbene-2,2'-disulfonic acid di-sodium salt

(A-10): 4,4'-Bis(4,6-diphenoxypyrimidin-2-ylamino)stilbene-2,2'-disulfonic acid di-sodium salt

(A-11): 4,4'-Bis(4,6-di-phenylthiopyrimidin-2-ylamino)stilbene-2,2'-disulfonic acid di-sodium salt

(A-12): 4,4'-Bis(4,6-dimercaptopyrimidin-2-ylamino)biphenyl-2,2'-disulfonic acid di-sodium salt

(A-13): 4,4'-Bis(4,6-dianilinotriazin-2-ylamino)stilbene-2,2'-disulfonic acid di-sodium salt

(A-14): 4,4'-Bis(4-anilino-6-hydroxy-triazin-2-ylamino)stilbene-2,2'-disulfonio acid di-sodium salt

(A-15): 4,4′-Bis[4,6-di(naphthyl-2-oxy)pyrimidin-2-ylamino]bibenzyl-2,2′-disulfonic acid di-sodium salt

(A-16): 4,4′-Bis(4,6-dianilinopyrimidin-2-ylamino)stilbene-2,2′-disulfonic acid di-sodium salt

(A-17): 4,4′-Bis[4-chloro-6-(2-naphthyloxy)pyrimidin-2-ylamino)biphenyl-2,2′-disulfonic acid di-sodium salt

(A-18) 4,4′-Bis[4,6-di(1-phenyltetrazolyl-5-thio)pyrimidin-2-ylamino]stilbene-2,2′-disulfonic acid di-sodium salt

(A-19): 4,4′-Bis(4,6-di(benzimidazolyl-2-thio)pyrimidin-2-ylamino)stilbene-2,2′-disulfonic acid di-sodium salt

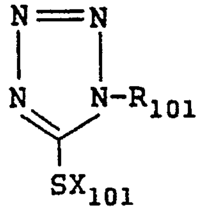
(A-20): 4,4′-Bis(4-naphthylamino-6-anilino-triazin-2-ylamino)stilbene-2,2′-disulfonic acid di-sodium salt.

Of these compounds, (A-1) to (A-6) are preferred and also, (A-1), (A-2), (A-4), (A-5), (A-9), (A-15), and (A-20) are particularly preferred.

The compound represented by formula (IX) is used in an amount of from 0.01 to 5 g per mol of silver halide and also, advantageously used in an amount of from about 5 times to 2,000 times, and preferably from 20 times to 1,500 times by weight the amount of a sensitizing dye.

Then, compounds which are preferably used with this supersensitizing compound are explained.

It is preferred to add a mercaptoazole represented by following formula (X), (XI), or (XII) to the coating compositions for an interlayer and a silver halide emulsion layer. The addition amount thereof is preferably from $1x10^{-5}$ to $5x10^{-2}$ mol, and more preferably from $1x10^{-4}$ to $1x10^{-2}$ mol per mol of silver halide.



(X)

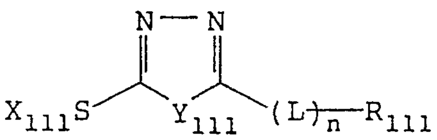
wherein R_{101} represents an alkyl group, an alkenyl group, or an aryl group and X_{101} represents hydrogen, an alkali metal atom, an ammonium group, or a precursor thereof.

Examples of the alkali metal atom ate sodium and potassium and examples of the ammonium group are tetramethylammonium and trimethylbenzylammonium. A "precursor" is a group of becoming $X_{104} = H$ or an alkali metal under alkaline conditions, and examples thereof ate acetyl, cyanoethyl, and methanesulfonylethyl groups.

In the groups represented by R_{101} described above, the alkyl group and the alkenyl group include unsubstituted groups and substituted groups, and further include alicyclic groups.

The substituent of the substituted alkyl group include a halogen atom, a nitro group, a cyano group, a hydroxy group, an alkoxy group, an aryl group, an acylamino group, an alkoxycarbonylamino group, a ureido group, an amido group, a heterocyclic group, an acyl group, a sulfamoyl group, a sulfonamido group, a thioureido group, a carbamoyl group, an alkylthio group, an arylthio group, a heterocyclic thio group, a carboxylic acid group, a sulfonic acid group, and the salt thereof.

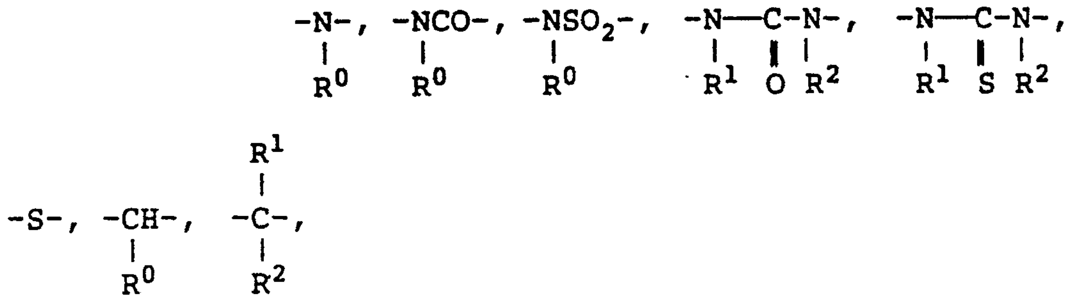
The ureido group, thioureido group, sulfamoyl group, carbamoyl group, and amino group each includes an unsubstituted group, an N-alkyl-substituted group, and an N-aryl-substituted group. Examples of the aryl group are a phenyl group and a substituted phenyl group, and examples of the substituent of the substituted phenyl group are an alkyl group and the substituents illustrated above for the substituted alkyl group.



(XI)

wherein Y_{111} represents oxygen or sulfur; L represents a divalent linkage group; and R_{111} represents hydrogen, an alkyl group, an alkenyl group, or an aryl group. X_{111} has the same meaning as X_{101} in formula (X), and the alkyl group and alkenyl group represented by R_{111} are the same as those in formula (X).

Specific examples of the divalent linkage group shown by L are

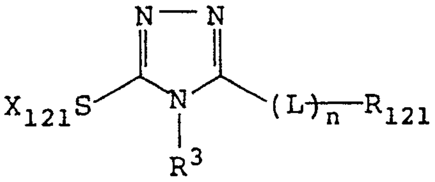


$$-\underset{R^0}{\underset{|}{N}}-,\ -\underset{R^0}{\underset{|}{N}}CO-,\ -\underset{R^0}{\underset{|}{N}}SO_2-,\ -\underset{R^1}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-\underset{R^2}{\underset{|}{N}}-,\ -\underset{R^1}{\underset{|}{N}}-\underset{S}{\underset{\|}{C}}-\underset{R^2}{\underset{|}{N}}-,$$

$$-S-,\ -\underset{R^0}{\underset{|}{C}}H-,\ -\overset{R^1}{\overset{|}{\underset{R^2}{\underset{|}{C}}}}-,$$

and a combination thereof (wherein R^0, R^1, and R^2 each represents hydrogen, an alkyl group, or an aralkyl group).

In formula (XI), n represents 0 or 1.

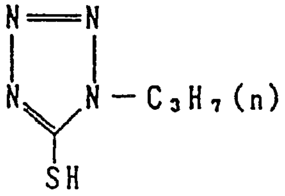


(XII)

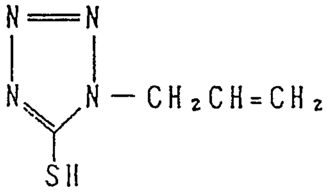
wherein R_{121} and X_{121} have the same meaning as R_{101} and X_{101} in formula (X); L and n have the same meaning as L and n in formula (XI); R^3 has the same meaning as R_{121}, and they may be the same or different.

Specific examples of the compounds represented by formulae (X), (XI), and (XII) are shown below but the invention is not to be construed as being limited to them.

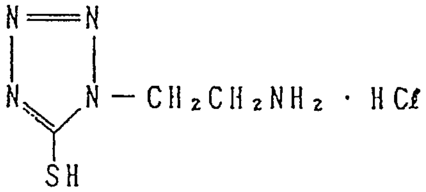
(X－1)



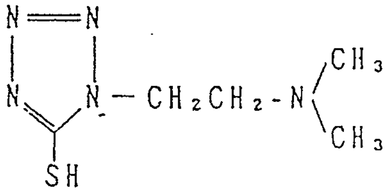
(X－2)



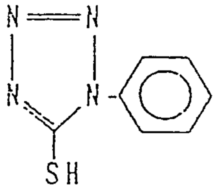
(X－3)



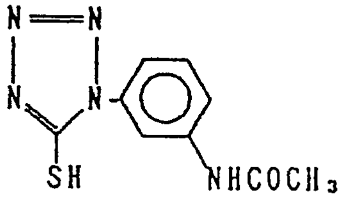
(X－4)



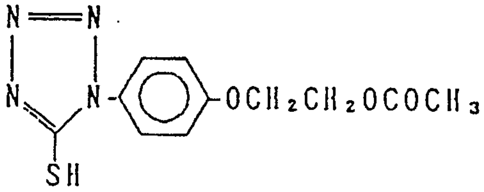
(X－5)



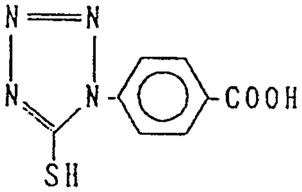
(X－6)



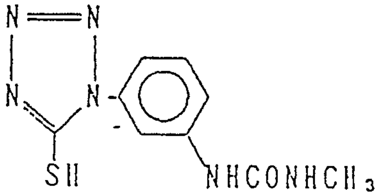
(X－7)



(X－8)

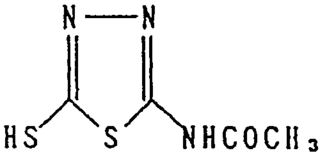


(X－9)

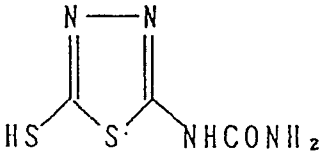


(X－10)

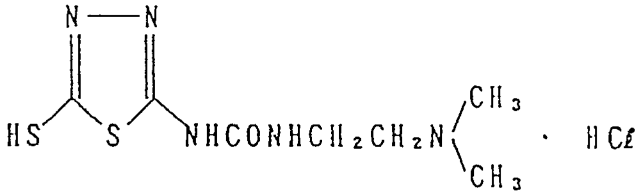
(XI－11)



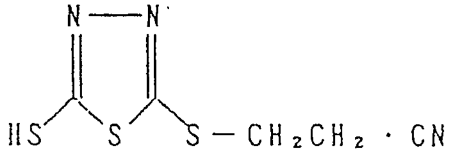
(XI－12)



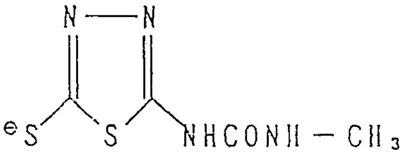
(XI－13)



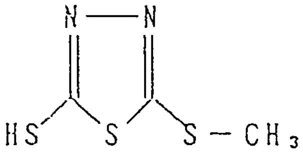
(XI－14)



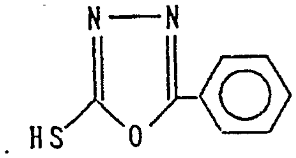
(XI－15)



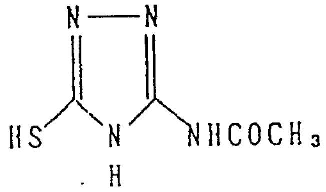
(XI－16)



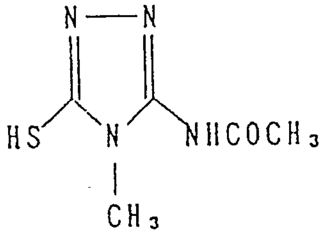
(XII-17)



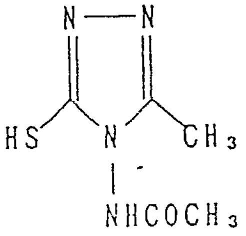
(XII-18)



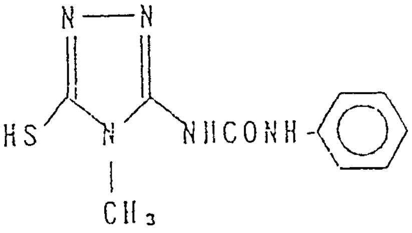
(XII-19)



(XII-20)



(XII-21)



The invention is now described in greater detail with reference to the following examples but the present invention is not to be construed as being limited thereto. Unless otherwise indicated, all part percents and ratios are by weight.

EXAMPLE 1

A silver halide color photographic material having the layer structure shown below was prepared as Sample A.

The silver halide emulsion use for each emulsion layer was prepared as follows.

Emulsion for Cyan Coupler-Containing Layer:

In 1000 ml of distilled water was dissolved 30 g of lime-processed gelatin at 40° C and then the pH of the solution was adjusted to 3.8 with sulfuric acid. Then, after adding thereto 5.5 g of sodium chloride and 0.02 g of N,N′-dimethylimidazolidine-2-thione, the temperature of the mixture was raised to 52/5° C. Then, a solution of 62.5 g of silver nitrate dissolved in 750 ml of distilled water and a solution of 21.5 g of sodium chloride dissolved in 500 ml of distilled water were added to the aforesaid solution while keeping the temperature at 52.5° C over a period of 40 minutes. Furthermore, a solution of 62.5 g of silver nitrate dissolved in 300 ml of distilled water and a solution of 21.5 g of sodium chloride dissolved in 300 ml of distilled water were added thereto at 52.5° C over a period of 20 minutes.

Then, di-potassium iridium hexachloride and hexacyano iron(II) potassium were added in amounts of 1x10^{-8} mol/mol-Ag and 1.5x10^{-5} mol/mol-Ag, respectively, based on the total silver halide amount.

When the emulsion obtained was observed by an electromicroscope, the emulsion contained silver halide grains having a mean side length of about 0.46 μm and a variation coefficient of the grain size distribution of 0.09.

After desalting and washing the emulsion, 0.2 g of nucleic acid and a monodisperse silver bromide emulsion (containing 1.2x10^{-4} mol/mol-Ag of di-potassium iridium hexachloride) having a mean grain size of 0.05 μm in an amount of 1.0 mol% as silver halide were added to the above emulsion, the emulsion was chemically sensitized with about 2x10^{-6} mol/mol-Ag of tri-ethylthiourea, and then 5x10^{-6} mol/mol-Ag of compound (V-23), 1.1x10^{-3} mol/mol-Ag of compound (I-1), and 1.8x10^{-3} mol/mol-Ag of compound (F-1) were added thereto to provide the desired emulsion.

Emulsion for Magenta Coupler-Containing Layer:

After dissolving 30 g of lime-processed gelatin in 1000 ml of distilled water at 40° C, 5.5 g of sodium chloride and 0.02 g of N,N′-dimethylimidazolidine-2-thione were added to the solution and the temperature thereof was raised to 50° C. Then, a solution of 62.5 g of silver nitrate dissolved in 750 ml of distilled water and a solution of 21.5 g of sodium chloride dissolved in 500 ml of distilled water were added to the solution at 50° C over a period of 40 minutes. Furthermore, a solution of 62.5 g of silver nitrate dissolved in 500 ml of distilled water and a solution of 21.5 g of sodium chloride dissolved in 300 ml of distilled water were also added thereto at 50° C over a period of 20 minutes.

Then, di-potassium iridium hexachloride and hexacyano iron(II) potassium were added thereto in amounts of 1.2x10^{-8} mol/mol-Ag and 1.8x10^{-5} mol/mol-Ag, respectively, based on the total silver halide amount.

When the emulsion obtained was observed by means of an electromicroscope, the emulsion contained silver halide grains having a mean side length of about 0.44 pm and a variation coefficient of grain size distribution of 0.08.

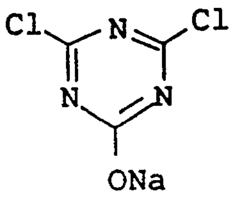
After desalting and washing the emulsion, 0.2 g of nucleic acid and a monodisperse silver bromide emulsion (containing 1.5x10^{-4} mol/mol-Ag) having a mean grain size of 0.05 μm of 0.5 mol% as silver halide were added to the emulsion, the emulsion was chemically sensitized with about 2.4x10^{-6} mol/mol-Ag of triethylurea, and further, 1.1x10^{-5} mol/mol-Ag of compound (V-46), 0.6x10^{-3} mol/mol-Ag of compound (I-1), and 0.9x10^{-3} mol/mol-Ag of compound (F-1) were added thereto to provide the desired emulsion.

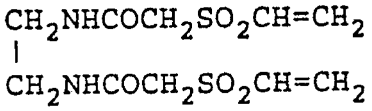
Emulsion for Yellow Coupler-Containing Layer:

By following the same procedure for producing the emulsion for the magenta coupler-containing layer, except that 0.6x10^{-4} mol/mol-Ag of compound (V-40) and the same amount of compound (V-41) were added in place of compound (V-4), and compound (F-1) was omitted, the desired emulsion was prepared.

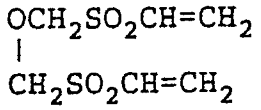
To these samples were added compounds (D-1), (D-2), (D-3), (D-4), (D-5), and (D-6) in amounts of 0.016 g/m^2, 0.006 g/m^2, 0.008 g/m^2, 0.013 g/m^2, 0.018 g/m^2, and 0.022 g/m^2, respectively, for improving the safety to safelight and further improving image sharpness.

Also, as hardening agents for gelatin, the following 3 compounds were used in a 3:2:1 by mol ratio.





$$\begin{array}{l} CH_2NHCOCH_2SO_2CH=CH_2 \\ | \\ CH_2NHCOCH_2SO_2CH=CH_2 \end{array}$$

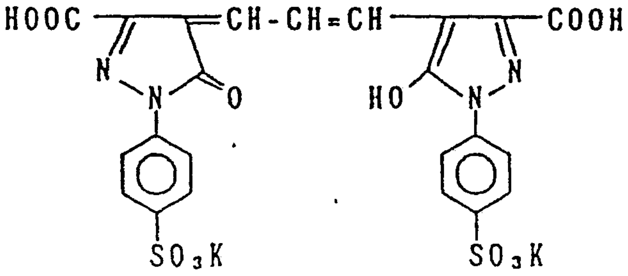


$$\begin{array}{l} OCH_2SO_2CH=CH_2 \\ | \\ CH_2SO_2CH=CH_2 \end{array}$$

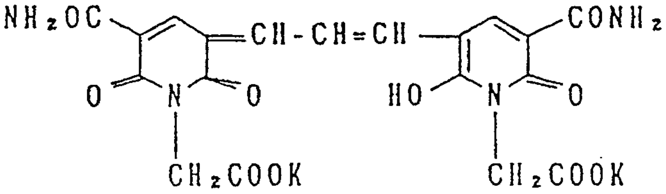
Sample A was kept for 3 days under conditions of 25 °C and 60% RH, then stored for 4 weeks at 25 °C under the storage conditions shown in Table 1, and the photographic properties were compared.

The compounds used were as follows.

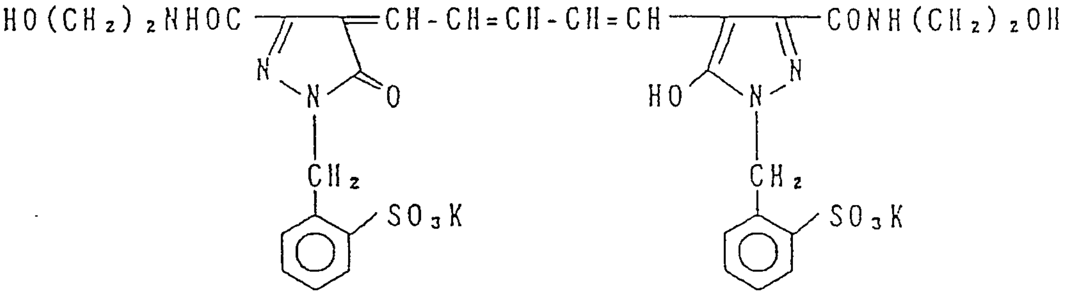
(D－1)


HOOC
CH-CH=CH
COOH
N
N
O
HO
N
N
SO3K
SO3K

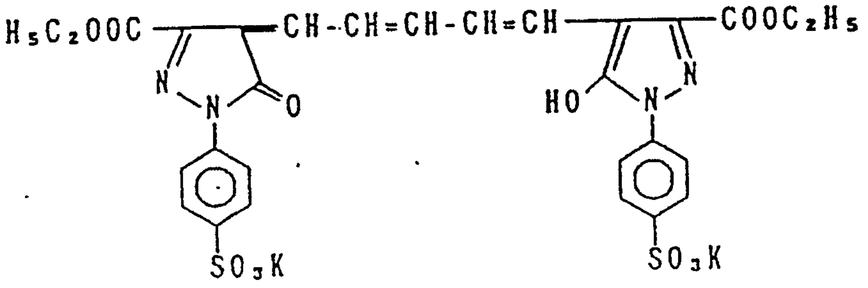
(D－2)


NH2OC
CH-CH=CH
CONH2
O
N
O
HO
N
O
CH2COOK
CH2COOK

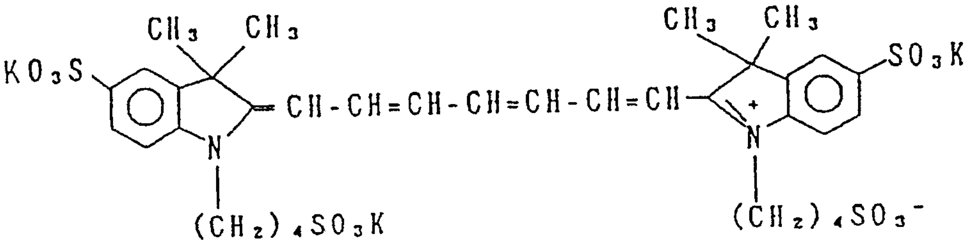
(D－3)


HO(CH2)2NHOC
CH-CH=CH-CH=CH
CONH(CH2)2OH
N
N
O
HO
N
N
CH2
SO3K
CH2
SO3K

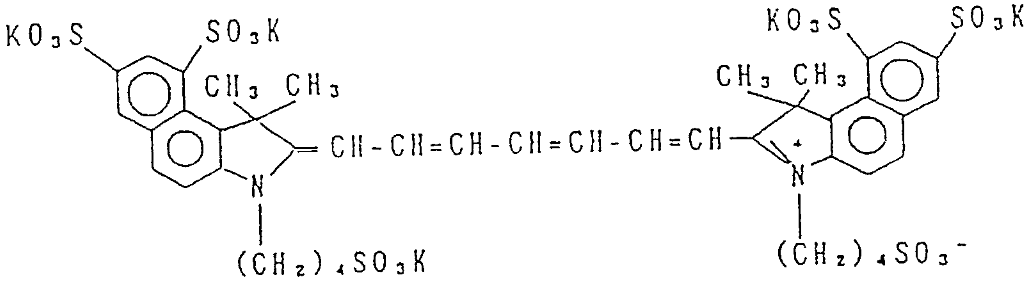
(D－4)



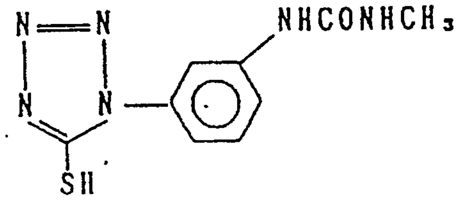
(D－5)



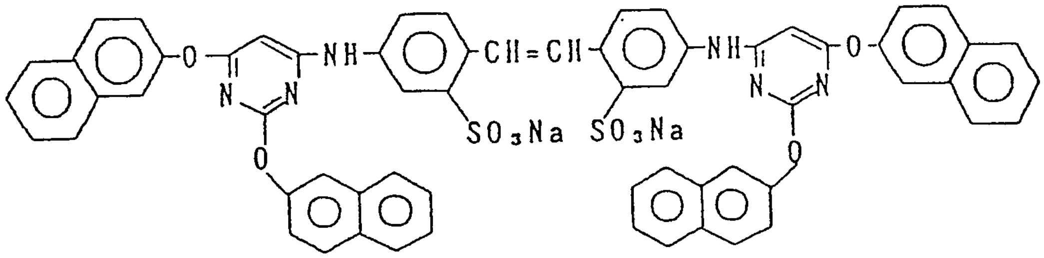
(D－6)



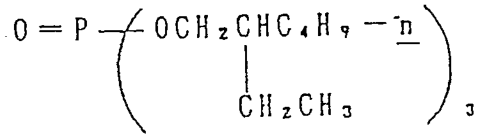
(I－1)



(F－1)

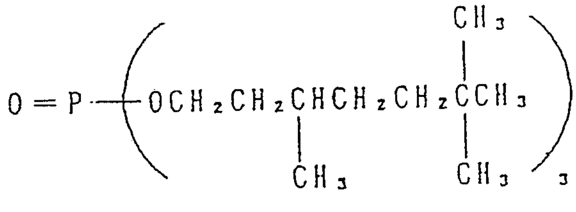


(S－1)



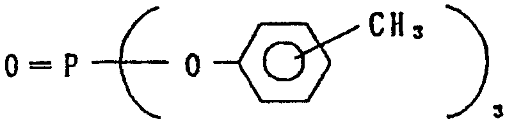
$$O{=}P\left(OCH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HC_4H_9-\underline{n}\right)_3$$

(S－2)

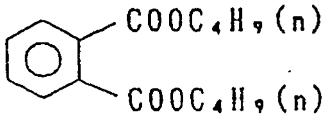


$$O{=}P\left(OCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_3\right)_3$$

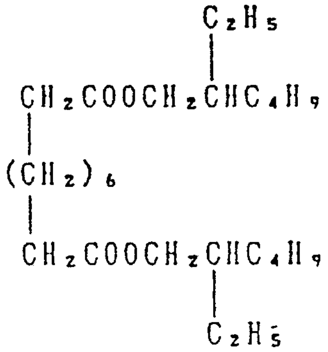
(S － 3)



(S － 4)

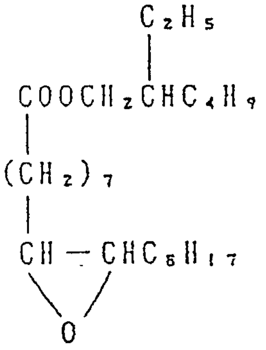


(S － 5)

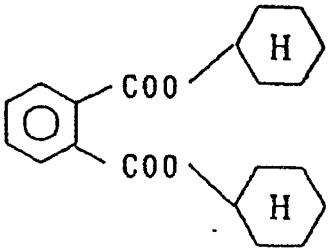


$$CH_2COOCH_2CH(C_2H_5)C_4H_9-(CH_2)_6-CH_2COOCH_2CH(C_2H_5)C_4H_9$$

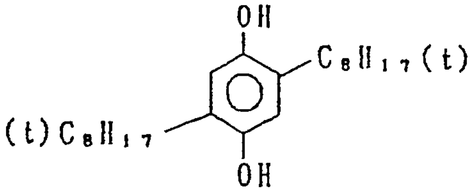
(S － 6)



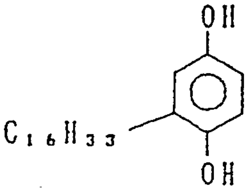
(S－7)



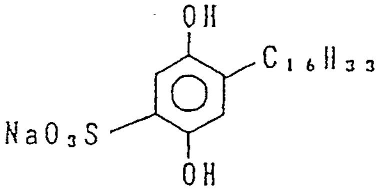
(H－1)



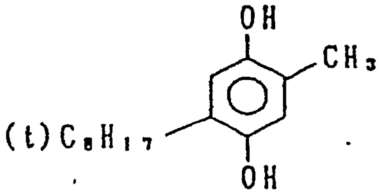
(H－2)



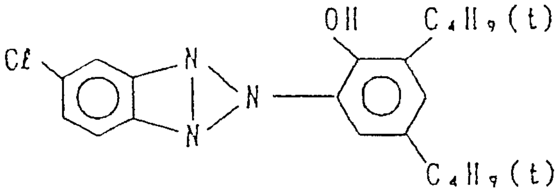
(H－3)



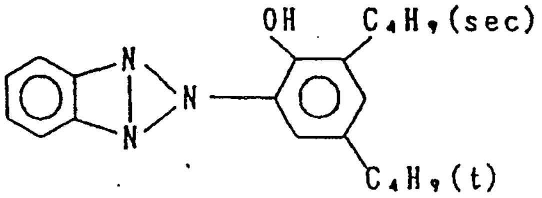
(H - 4)



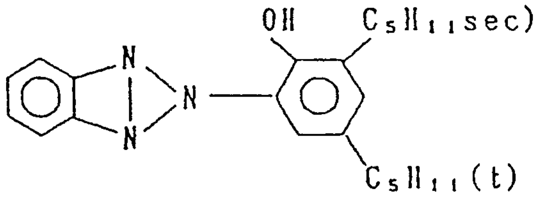
(X - 1)



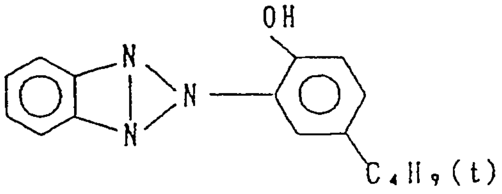
(X－2)


OH
C₄H₉(sec)
N
N
N
C₄H₉(t)

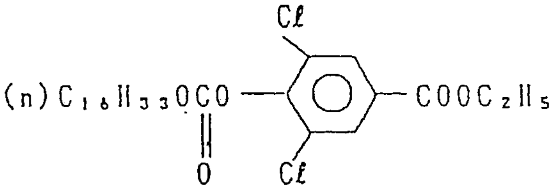
(X－3)


OH
C₅H₁₁sec)
N
N
N
C₅H₁₁(t)

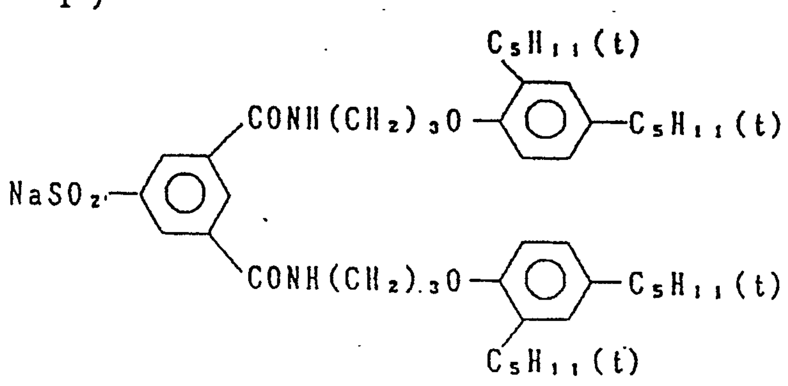
(X－4)


OH
N
N
N
C₄H₉(t)

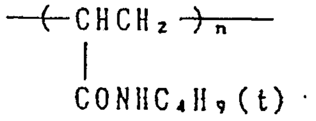
(A－1)


Cℓ
(n)C₁₆H₃₃OCO
O
COOC₂H₅
Cℓ

(B - 1)



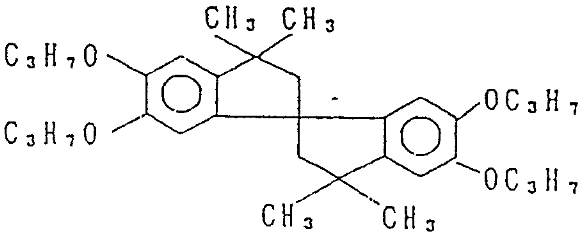
(P - 1)



$$-\!\left(\mathrm{CHCH_2}\right)_n\!- \quad \text{with } \mathrm{CONHC_4H_9(t)} \text{ pendant}$$

Molecular weight:
about 60,000

(E - 1)



The layer structure of Sample A was as follows, wherein the coating amount is shown in g/m^2, and the silver halide emulsion and colloidal silver are calculated in terms of silver.

Support

Paper coated with polyethylene containing 25 g/m^2 of TiO_2.

Layer 1 (Black Antihalation Layer)	Coating Amount (g/m²)
Black colloidal silver	0.04 as Ag
Dye (D-7)	0.02
Dye (D-8)	0.03
Gelatin	1.32
Ultraviolet absorbent (X-1)	0.02
Ultraviolet absorbent (X-2)	0.09
Ultraviolet absorbent (X-3)	0.10
Color mixing inhibitor (H-1)	0.02
Solvent (S-5)	0.11
Layer 2 (Interlayer)	
Gelatin	1.00
Color mixing inhibitor (H-1)	0.09
Solvent (S-3)	0.18
Solvent (S-4)	0.18

Layer 3 (Yellow Coupler-Containing Layer)	Coating Amount (g/m²)
Emulsion for yellow coupler-containing layer	0.30 as Ag
Gelatin	1.44
Polymer (P-1)	0.18
Yellow coupler (Y-4)	0.16
Yellow coupler (Y-6)	0.20
Yellow coupler (Y-1)	0.39
Color image stabilizer (H-4)	0.01
Solvent (S-2)	0.17
Solvent (S-6)	0.16
Layer 4 (Color Mixing Inhibition Layer)	
Gelatin	1.30
Color mixing inhibitor (H-1)	0.12
Solvent (S-3)	0.24
Solvent (S-4)	0.24
Layer 5 (Magenta Coupler-Containing Layer)	
Emulsion for magenta coupler-containing layer	0.13 as Ag
Gelatin	1.36
Magenta coupler (M-13)	0.19
Magenta coupler (M-10)	0.08
Color image stabilizer (E-1)	0.09
Color image stabilizer (A-1)	0.07
Color image stabilizer (B-1)	0.03

	Coating Amount (g/m²)
Color image stabilizer (H-3)	0.01
Solvent (S-1)	0.37
Solvent (S-3)	0.19
Layer 6 (Ultraviolet Absorption Layer)	
Gelatin	1.12
Ultraviolet absorbent (X-1)	0.04
Ultraviolet absorbent (X-2)	0.19
Ultraviolet absorbent (X-3)	0.20
Color mixing inhibitor (H-1)	0.04
Solvent (S-5)	0.18
Layer 7 (Cyan Coupler-Containing Layer)	
Emulsion for cyan coupler-containing layer	0.24 as Ag
Gelatin	1.16
Polymer (P-1)	0.42
Cyan coupler (C-2)	0.07
Cyan coupler (C-5)	0.12
Cyan coupler (C-4)	0.09
Cyan coupler (C-3)	0.07
Color image stabilizer (X-1)	0.04
Color image stabilizer (X-2)	0.05
Color image stabilizer (X-4)	0.05
Color image stabilizer (A-1)	0.01

	Coating Amount (g/m²)
Color image stabilizer (B-1)	0.01
Color image stabilizer (H-4)	0.01
Color image stabilizer (H-2)	0.04
Solvent (S-6)	0.11
Solvent (S-7)	0.11
<u>Layer 8</u> (Ultraviolet Absorption Layer)	
Gelatin	0.65
Ultraviolet absorbent (X-1)	0.02
Ultraviolet absorbent (X-2)	0.09
Ultraviolet absorbent (X-3)	0.10
Color mixing inhibitor (H-1)	0.02
Solvent (S-5)	0.11
<u>Layer 9</u> (Protective Layer)	
Gelatin	1.00
Polyvinyl alcohol-modified polymer (modification degree 17%)	0.12
Liquid paraffin	0.05

TABLE 1

Condition	Oxygen Volume Ratio (%)	Oxygen Concentration Controlling method	Note
1	21	no control	Comparison
2	10.5	Nitrogen mixed	Comparison
3	3	Nitrogen mixed	Comparison
4	1.5	Nitrogen mixed	Invention
5	1.7	Iron powder oxydation	Invention
6	0.1	Iron powder oxydation	Invention
7	0.1	Solid oxygen pump	Invention
8	0.001	Solid oxygen pump	Invention
9	0.021	Vacuum degassing 10-3at	Invention
10	0.021	Vacuum degassing N_2 replacement	Invention

After applying a scanning exposure of 400 dpi at an average exposure time of 2x10^{-7} per one picture element through an optical wedge using a laser diode of light emitting wavelength of 670 nm, 750 nm, or 810 nm, to each of the samples stored under conditions 1 to 10 shown in Table 1, the sample was subjected to the following color development process 1 after 3 seconds.

Processing step	Temperature (°C)	Time
Color Development	50	9 sec.
Blix	50	12 sec.
Rinse 1	40	5 sec.
Rinse 2	40	5 sec.
Rinse 3	40	5 sec.
Drying	90	9 sec.

The compositions of the processing solutions were as follows.

Color Developer	
Ethylenediamine-N,N,N′,N′-tetramethylenesulfonic acid	3.0 g
N,N-Di(carboxymethyl)hydrazine	4.5 g
N,N-Diethylhydroxylamine oxalate	2.0 g
Triethanolamine	8.5 g
Sodium sulfite	0.14 g
Potassium chloride	1.6 g
Potassium bromide	0.01 g
Potassium carbonate	25.0 g
N-Ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g
WHITEX-4 (made by Sumitomo Chemical Company, Limited)	1.4 g
Water to make	1000 ml
pH adjusted to	10.05

Blix Solution	
Ammonium thiosulfate (50 wt%)	100 ml
Sodium sulfite	17.0 g
Ethylenediaminetetraacetic acid iron(III) ammonium	55.0 g
Ethylenediaminetetraacetic acid di-sodium	5.0 g
Ammonium bromide	40.0 g
Glacial acetic acid	9.0 g
Water to make	1,000 ml
pH adjusted to	5.80

Rinse Solution

Ion-exchanged water (calcium ion concentration less than 3 ppm, magnesium ion concentration less than 2 ppm).

Each of the cyan, magenta, and yellow densities of each sample thus processed was measured using a TCD densitometer, made by Fuji Photo Film Co., Ltd., and the sensitivities thus obtained are shown in Table 2.

The sensitivities were determined as relative values with the sensitivity of each coloring layer of the sample stored in a refrigerator for at -16° C being defined as 100.

TABLE 2

Storing Condition	Cyan Sensitivity	Magenta Sensitivity	Yellow Sensitivity	Remark
1	76	85	96	Comparison
2	81	91	96	Comparison
3	91	95	100	Comparison
4	98	100	100	Invention
5	100	102	102	Invention
6	100	102	102	Invention
7	102	100	100	Invention
8	100	100	100	Invention
9	105	105	100	Invention
10	105	105	102	Invention

The samples stored under storage conditions 4 to 10 of this invention had almost the same sensitivity as that of the samples stored in a refrigerator, while the samples stored under comparison conditions 1 to 3 clearly showed loss of sensitivity.

Also, by comparing storage condition 4 of this invention with storage condition 5 of this invention, it is seen that if the oxygen volume ratio is almost the same, the same storage stability improvement was obtained regardless of the manner of obtaining the oxygen volume ratio.

Furthermore, on comparing storage condition 9 of this invention with storage condition 10 of this invention, it is seen that the amount of oxygen present almost completely determined the storage stability of the light-sensitive material.

The improvement in storage stability of this invention was more remarkable in the cyan coloring layer spectrally sensitized by a tricarbocyanine sensitizing dye giving a spectral sensitivity peak at a long wavelength, 835 n.m., than in the yellow coloring layer, spectrally sensitized by a carbocyanine sensitizing dye giving a spectral sensitivity peak at a short wavelength, about 670 n.m.

It is seen that the oxygen volume ratio useful for obtaining the effect of this invention was less than about 2%, by comparing storage conditions 1, 3, and 4.

From the above results it is seen that this invention is effective for stably maintaining the performance of silver halide photographic materials using the infrared spectrally sensitizing dyes specified in this invention.

Also, it was also confirmed that for the samples of this invention, rapid processing, such as process 1 was suitable.

EXAMPLE 2

Samples 1 to 10 prepared in Example 1 were processed by the following processing step 2 in place of the step 1 in Example 1. The exposure was same as in Example 1.

Processing step	Temperature (°C)	Time
Color Development	35	45 sec.
Blix	35	45 sec.
Rinse 1	25	30 sec.
Rinse 2	25	30 sec.
Rinse 3	25	30 sec.
Drying	80	60 sec.

The compositions of the processing solutions were the same as in Example 1.

In the processing step 1 in Example 1, the processing time was 45 seconds and images were very quickly formed, while in processing step 2, 4 minutes were required. In this example as well, the sensitivities obtained under the test storage conditions were almost same as in Example 1.

The sensitivity difference between samples was larger in the processing step in Example 1.

EXAMPLE 3

By following the same procedure for preparing Sample A in Example 1, except that the equimolar amounts of the compounds shown in Table 3 below were used in place of compound (V-23) used for the spectral sensitization of the silver halide emulsion for the cyan coloring layer and compound (V-46) used for the spectral sensitization of the silver halide emulsion for the magenta ooloring layer, light-sensitive materials B to F were prepared.

TABLE 3

	Cyan Coloring Layer		
Sample	Sensitizing Dye	λ_{max}	Magenta Coloring Layer
B	V-18	805	V-5
C	V-20	820	V-5
D	V-19	850	V-15
E	V-26	830	V-15
F	V-49	845	V-48
G	V-51	830	V-48

In the above table, λ_{max} shows the spectral sensitivity peak wavelength in n.m.

For samples B to G, the same test applied to the samples stored under the storage conditions 1 and 6 in Example 1 was applied. The processing was the same as in Example 2.

The results of sensitivity change after storing are shown in Table 4. The sensitivities were determined as relative values, with the sensitivity of each coloring layer of the sample stored in a refrigerator at -16°C being defined as 100.

TABLE 4

	Cyan Coloring Layer		Magenta Coloring Layer	
Sample	Condition 1	Condition 6	Condition 1	Condition 6
B	87	100	93	100
C	83	100	93	100
D	69	100	91	102
E	71	100	91	102
F	72	100	91	102

It is seen that the same stored under storage condition 6 of this invention had almost the same or slightly higher sensitivity than that of the sample stored in the refrigerator, without reducing the sensitivity, as compared with the sample stored under storage condition 1 outside the scope of this invention.

The tricarbocyanine sensitizing dye or the hexamethinemerocyanine sensitizing dye which was used for the cyan coloring layer has a spectral sensitivity of a longer wavelength than the sensitivity dye used for the magenta coloring layer, and it is seen that when using such a sensitizing dye, the improvement in storage stability of this invention was large.

Also, on comparing the sensitivity dyes used for the cyan coloring layer, this improvement was confirmed. Also, it can be seen than in the light-sensitive material having a spectrally sensitized region in the infrared region, the effect of this invention was remarkable.

EXAMPLE 4

By following the same procedure for preparing Sample B in Example 3, except that an equivalent amount of compound (V-31), (V-34), or (V-35) was used in place of the compound (V-18) used for spectral sensitization of the silver halide emulsion for the cyan coloring layer, light-sensitive materials H to J were prepared.

With these samples H to J, the same test as that for the samples stored in storage conditions 1 and 6 in Example 1 was applied. The processing was the same as in Example 2.

The results of the sensitivity change after storage are shown in Table 6. The sensitivities were determined as relative values, with the sensitivity of each coloring layer of a sample stored in a refrigerator at -16° C being defined as 100.

TABLE 6

Sample	Condition 1	Condition 6
H	81	101
I	72	103
J	78	101
Note	Comparison Example	Example of Invention

From the above results, it is seen that the sample stored under storage conditions of this invention had almost the same, or slightly higher sensitivity than the sample stored in the refrigerator, without reducing the sensitivity as compared with the sample stored under storage conditions outside the scope of this invention.

As described above, according to this invention, the change in the photographic properties of a silver halide photographic material spectrally sensitized to the infrared wavelength region can be prevented during storage over a period of time. Thus, the invention provides a photographic light-sensitive material spectrally sensitized to infrared wavelength region having constant high sensitivity.

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 storing an infrared-sensitive silver halide photographic material, comprising storing in a deoxidized state the infrared-sensitive silver halide photographic material comprising a support having thereon at least one silver halide light-sensitive emulsion layer spectrally sensitized with at least one sensitizing dye selected from a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, and a heptamethinerhodacyanine sensitizing dye, said light-sensitive emulsion having a spectral sensitivity peak in the wavelength region of at least 720 n.m.

2. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said silver halide light-sensitive emulsion layer comprises silver chlorobromide containing at least 90 mol% silver chloride.

3. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 2, wherein the silver bromide in said silver chlorobromide is present as a local phase in the interior of the silver halide grains or at the surface of the silver halide grains.

4. The method for storing an infrared-sensitive silver halide photographic material as in claim 3, wherein said local phase has a silver bromide content of at least 15 mol%.

5. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 4, wherein said silver chlorobromide grains have a surface phase containing 15 to 70 mol% silver bromide, said surface phase containing from 0.01 to 20 mol% of the total silver contained in said silver halide grains.

6. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 5, wherein said silver chlorobromide grains have a surface phase containing 20 to 60 mol% silver bromide, said surface phase containing from 0.02 to 7 mol% of the total silver contained in said silver halide grains.

7. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 5, wherein said silver halide emulsion is a monodisperse emulsion and the average grain size of the silver chlorobromide grains is from 0.1 µm to 1.5 µm.

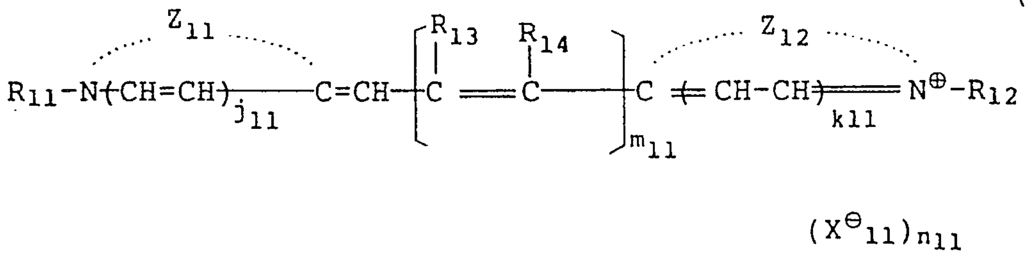
8. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said silver halide light-sensitive emulsion layer has a spectral sensitivity peak in the wavelength region of at least 735 n.m.

9. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 8, wherein said silver halide light-sensitive emulsion layer has a spectral sensitivity peak in the wavelength region of at least 750 n.m.

10. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 9, wherein said silver halide light-sensitive emulsion layer has a spectral sensitivity peak in the wavelength region of at least 770 n.m.

11. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said tricarbocyanine sensitizing dye is represented by formula (I):

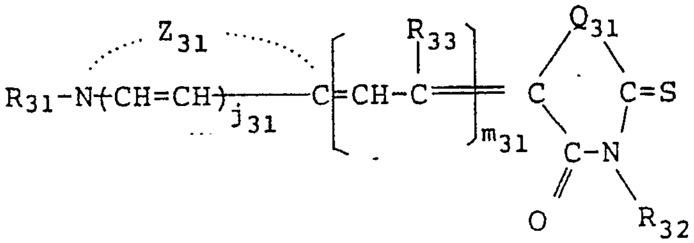
(I)



$$R_{11}-N\left(CH=CH\right)_{j_{11}}\overset{Z_{11}}{\cdots}C=CH-\left[\overset{R_{13}}{\underset{|}{C}}=\overset{R_{14}}{\underset{|}{C}}\right]_{m_{11}}-C\left(=CH-CH\right)_{k_{11}}\overset{Z_{12}}{\cdots}=N^{\oplus}-R_{12}\qquad (X^{\ominus}{}_{11})_{n_{11}}$$

wherein Z_{11} and Z_{12} each represents an atomic group necessary for forming a heterocyclic nucleus; R_{11} and R_{12} each represents an alkyl group, an alkenyl group, an alkynyl group, or an aralkyl group; m_{11} is 3; R_{13} represents hydrogen; R_{14} represents hydrogen, a lower alkyl group or an aralkyl group or when R_{14} is hydrogen and m_{11} is 2 or 3, R_{13} combines with other R_{13} to form a hydrocarbon or a heterocyclic ring; j_{11} and k_{11} each is 0 or 1; X_{11} represents an acid anion; and n_{11} is 0 or 1.

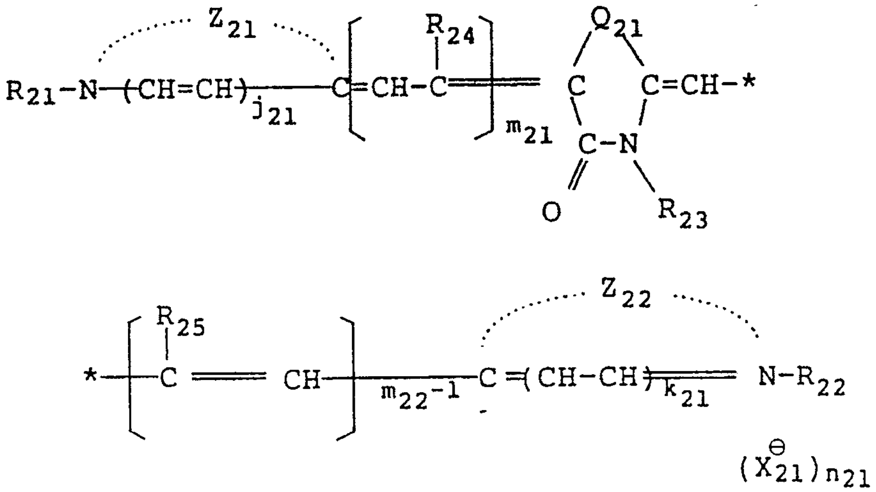
12. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said hexamethinemerocyanine sensitizing dye is represented by formula (III):



(III)

wherein Z_{31} represents an atomic group necessary for forming a heterocyclic ring; Q_{31} represents sulfur, oxygen, selenium or N-R_{26}, wherein R_{26} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; R_{31} represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group; R_{32} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; m_{31} is 3; R_{33} represents hydrogen, a lower alkyl, or an aryl group or R_{33} combines with other R_{33} to form a hydrocarbon ring or a heterocyclic ring; and j_{31} is 0 or 1.

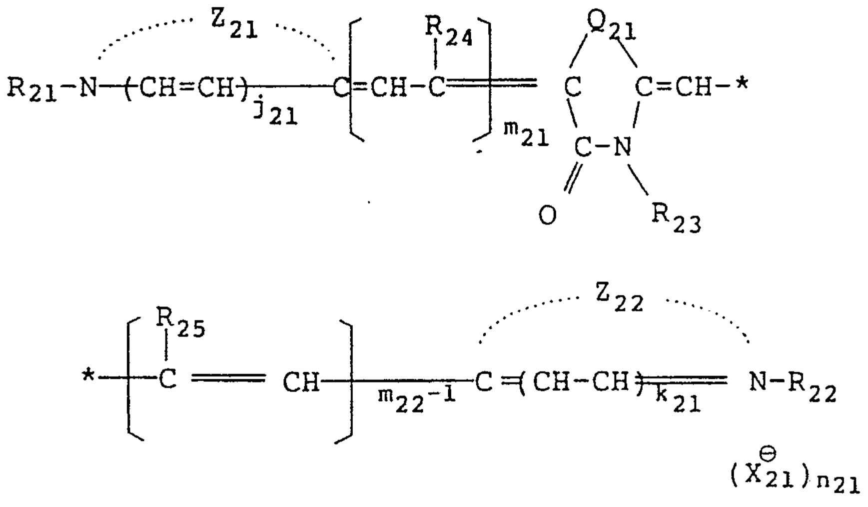
13. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said pentamethinerhodacyanine sensitizing dye is represented by formula (II):



(II)

wherein Z_{21} and Z_{22} each represents an atomic group necessary for forming as heterocyclic nucleus; R_{21} and R_{22} each represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group; R_{23} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; m_{21} and m_{22} each represents 1, 2, or 3, provided that the sum of m_{21} and m_{22} is 3; R_{24} and R_{25} each represents hydrogen, a lower alkyl group, or an aryl group or when m_{21} is 2 or 3, R_{24} combines with other R_{24} or when m_{21} is 3, R_{25} combines with other R_{25}, to form a hydrocarbon ring or a heterocyclic ring; Q_{21} represents sulfur, oxygen, selenium or N-R_{26}, wherein R_{26} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; j_{21} and k_{21} each is 0 or 1; X_{21} represents an acid anion; and n_{21} is 0 or 1.

14. The method for storing an infrared-sensitive silver halide photographic material is claimed in claim 1, wherein said heptamethinerhodacyanine sensitizing dye is represented by formula (II):



(II)

wherein Z_{21} and Z_{22} each represents an atomic group necessary for forming as heterocyclic nucleus; R_{21} and R_{22} each represents an alkyl group, an alkenyl group, an alkynyl group or an aralkyl group; R_{23} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; m_{21} and m_{22} each represents 1, 2, or 3, provided that the sum of m_{21} and m_{22} is 4; R_{24} and R_{25} each represents hydrogen, a lower alkyl group, or an aryl group or when m_{21} is 2 or 3, R_{24} combiens with other R_{24} or when m_{21} is 3, R_{25} combines with other R_{25}, to form a hydrocarbon ring or a heterocyclic ring; Q_{21} represents sulfur, oxygen, selenium or N-R_{26}, wherein R_{26} represents an alkyl group, an alkenyl group, an alkynyl group or an aryl group; j_{21} and k_{21} each is 0 or 1; X_{21} represents an acid anion; and n_{21} is 0 or 1.

15. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said sensitizing dye is present in said silver halide emulsion in an amount from 5×10^{-7} mol to 5×10^{-3} mol per mol of silver therein.

16. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said infrared-sensitive silver halide photographic material is stored at an oxygen volume ratio of at most 2%.

17. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 16, wherein said infrared-sensitive silver halide photographic material is stored at an oxygen volume ratio of at most 1%.

18. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said infrared-sensitive silver halide photographic material is stored at an oxygen volume ratio of at most 0.5%.

19. The method for storing an infrared-sensitive silver halide photographic material as claimed in claim 1, wherein said infrared-sensitive silver halide photographic material is stored in a nitrogen atmosphere.

20. The method for storing an infrared-sensitive silver halide material as in claim 1, wherein the silver halide photographic material has at least two silver haldie light-sensitive layers each having a spectral sensitivity peak in the wavelength region of not shorter than 720 n.m., and each silver halide light-sensitive emulsion layer contains one of a cyan coupler, a magenta coupler, and a yellow coupler.

21. The method for storing an infrared-sensitive silver halide photographic material as in claim 1, wherein the silver halide photographic material has at least three silver halide light-sensitive emulsion layers each containing a silver chlorobromide emulsion having a mean silver chloride content of at least 90 mol% or a silver chloride emulsion, each light-sensitive emulsion layer contains one of a cyan coupler, a magenta coupler, and a yellow coupler, respectively, and the three light-sensitive emulsion layers each has a different spectral sensitivity peak in the wavelength region of from 650 n.m. to 690 n.m., from 720 n.m. to 790 n.m., from 770 n.m. to 850 n.m., respectively.

22. A photographic composite comprising an infrared-sensitive silver halide photographic material enclosed in a packaging material in a deoxidized state, wherein said infrared-sensitive silver halide photographic material comprises an infrared-sensitive silver halide photographic material comprising a support having thereon at least one silver halide light-sensitive emulsion layer spectrally sensitized with at least one sensitizing dye selected from a tricarbocyanine sensitizing dye, a hexamethinemerocyanine sensitizing dye, a pentamethinerhodacyanine sensitizing dye, and a heptamethinerhodacyanine sensitizing dye, said light-sensitive emulsion having a spectral sensitivity peak in the wavelength region of at least 720 n.m.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 9167

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)
Y,D	DE-A-2822524 (KONISHIROKU) * page 27 *compound D-17 * * page 32 *compound D-33 * * page 60, lines 1 - 10 * * page 82, lines 6 - 7; claim 2 * ---	1-22	G03C1/035 G03C1/20 G03C1/26 G03C3/00 G03C5/16
Y	EP-A-0138543 (FUJI) * page 8, line 20 - page 9, line 4 * * page 21 *compound (I-6) * * page 30 *compound (II-1) * ---	1-22	
Y	EP-A-0230100 (MITSUBISHI) * page 30 *compound (III-1) * * page 35 *compound (IV-5) * * page 70, line 14 - page 71, line 3 * ---	1-22	
Y	EP-A-0313021 (FUJI) * page 21, line 52 - page 22, line 28 * * page 23, lines 14 - 20 * ---	1-22	
Y	EP-A-0183528 (3M) * page 22, line 18; claims 1-4 * ---	1-22	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
Y	JP-A-6111736 (FUJI) * abstract * * page 6 *compound I-14 - page 7,compound I-25 * ---	1-22	G03C
A,D	PATENT ABSTRACTS OF JAPAN vol. 12, no. 483 (P-802)(3330) 16 December 1988, & JP-A-63 197947 (FUJI) 16 August 1988, * the whole document * -----	1-22	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 NOVEMBER 1990	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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