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(54) Silver halide color photographic material.

(57) There is disclosed a silver halide color photographic material that has photographic layers comprising a silver halide emulsion layer containing a magenta coupler represented by formula (I) and a nonphotographic layer having a limited coating amount of hydrophilic colloid and containing a compound represented by formula (II) between a yellow-coupler containing silver halide emulsion layer and the magenta coupler-containing silver halide emulsion layer wherein the silver halide emulsion comprises a surface latent image type monodisperse silver chlorobromide grain subjected to a surface halogen conversion. According to the disclosure, a silver halide color photographic material high insensitivity and contrast and excellent in color reproductivity and dye image stability can be attained.

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SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic material, and more particularly, a silver halide color photographic material high in sensitivity and contrast and excellent in color reproduction and dye image stability.

BACKGROUND OF THE INVENTION

In recent years, the demand is high for silver halide photographic materials, in particular photographic materials for prints that can be made highly sensitized or that can be rapidly processed in the developing process, and techniques for shortening the process of processing silver halide photographic materials have been developed and marketed successively. Examples of such techniques include techniques of highly sensitizing photographic materials (shortening the printing time) and techniques of improving the developing speed (shortening the developing process).

In order to make high the sensitivity of silver halide emulsions, there are considered a method wherein the amount of absorption of light is increased per grain of a silver halide, and a method wherein the efficiency of formation of the latent image for the amount of absorbed light is enhanced.

In the former method, for example, it is conceivable that the size of silver halide grains is made large to increase the amount of absorption of light per grain, or that when the emulsion has spectrally been sensitized, for example, the amount of the spectral sensitizing dye is increased to augment the amount of light absorption. However, if the size of silver halide grains is made large, it is known that the developing speed often lowers. It is also known that an increase in a spectral sensitizing dye brings about development obstruction or desilvering obstruction. Consequently, when these methods are used in practice, in many cases problems often arise.

In the latter method, it is effective to use sulfur sensitization, gold sensitization, reduction sensitization, or the like, which is known as chemical sensitization, and these can be used alone or in combination. However, even if these techniques are used, there is a limit to the attainable sensitivity. That is, in many cases excessive chemical sensitization brings about, for example, a rise in fogging or a lowering in contrast in the case of a short-period exposure with a high illuminance.

Therefore, it is an important matter that the sensitivity of emulsions is made high with the size of the silver halide grains kept constant without causing disadvantages, as mentioned above.

On the other hand, concerning the improvement of the developing speed of silver halide emulsions, it is known as effective to make the size of silver halide grains small, to increase the content of silver chloride, in the case of silver chlorobromide substantially free from silver iodide, or to use pure silver chloride. However, if these techniques are used, since the amount of absorption of light per grain of a silver halide lowers, lowering of the sensitivity generally occurs. Consequently, in view of the improvement of the developing speed, it is an important matter to make high the sensitivity of silver halide emulsions.

As an example of the means of obtaining a silver halide emulsion high in sensitivity, a method for forming emulsion grains by halogen conversion is disclosed in JP-B ("JP-B" means examined Japanese patent publication) No. 36978/1975. However, although the emulsion obtained according to this method showed an increase in sensitivity, it was revealed that if pressure was applied to the photographic material, the sensitivity lowered extremely, and the gradation that would be obtained was soft gradation.

As means of obtaining silver halide emulsions that are high in sensitivity and are improved in developing speed, several examples are disclosed concerning layered-type emulsions that have, in the silver halide grains, layers different in silver halide composition.

For example, JP-B No. 18939/1981 describes that an emulsion produced by covering cores of silver bromide with silver chloride, or by depositing a layer of silver bromide on cores of silver chloride, has both the advantages of silver chloride and silver bromide. However, the technique disclosed therein covers generally a wide range of layered-type emulsions consisting of cores of a silver halide covered with different silver halide layers, and according to the test results obtained by the present inventors, the disclosed technique did not necessarily provide emulsions having preferable performance. For instance, when the emulsion prepared according to the above technique was used, in many cases there were such defectives that a reversed image was liable to occur from a relatively low exposure region, and when pressure was applied to the emulsion, desensitization was great. Further, in many cases the resulted gradation was soft, and particularly the foot of the characteristic curve was soft gradation, and the characteristic curve became two-stepped in gradation in some cases.

JP-A ("JP-A" means unexamined published Japanese patent application) No. 9137/1983 describes a technique wherein a layered-type silver bromochloroiodide emulsion with the outermost layer composed of 50 mol% or over of silver bromide is chemically sensitized with an unstable sulfur compound in the presence of particulate silver chloride. However, when the preparation of a layered-type emulsion was attempted according to this technique, it was also found that the gradation of the foot of the characteristic curve was liable to become soft gradation, and when pressure was applied, desensitization was apt to occur.

Further, several techniques of making a layered-type structure have been reported to be effective in order to make high the sensitivity of silver chlorobromide emulsions high in silver chloride content.

For instance, JP-A Nos. 95736/1983 and 108533/1983 disclose techniques concerning high silver chloride emulsions having a layered-type structure. According to the former disclosure, it is stated that by allowing a layer mainly consisting of silver bromide to be present inside the grain, rapid processing becomes possible and an emulsion high in sensitivity can be obtained, but when the technique was tested, it was found that if pressure was applied to the emulsion grains, desensitization was liable to occur, and therefore it was difficult to use the technique in practice. According to the latter disclosure, it is stated that by allowing a layer composed mainly of silver bromide to be present on the grain surface locally, rapid processing becomes possible and an emulsion high in sensitivity as well as having a broad latitude of chemical sensitization can be obtained, but when the technique was carried out in practice, it was found that there were defects that the foot of the characteristic curve was also liable to become soft gradation, and in an extreme case its gradation showed two-stepped gradation, and desensitization was apt to take place due to pressure.

In addition, JP-A Nos. 222844/1985 and 222845/1985 disclose techniques concerning high silver chloride emulsions rendered to have a layered structure. However, even according to these techniques, the defects as described above were not overcome.

As for the formation of a dye image in silver halide color photographic materials, the formation is effected generally in such a manner that an aromatic primary amine color-developing agent is oxidized when silver halide grains in the silver halide color photographic material that has been exposed to light are reduced, and the oxidized product couples with couplers previously included in the silver halide color photographic material. Generally, as the couplers, three kind of couplers are used, which will form three dyes: yellow, magenta, and cyan respectively in order, to effect color reproduction by the subtractive process.

In order to attain better color reproduction, a lot of factors are required to act in concert. That is, the factors include, to begin with, the spectral sensitivity and the interlayer effect of photographic materials for photographing, and, in the case of photographic materials for prints, for example, the matching of its spectral sensitivity with the color-developed dyes of the photographic material for photographing, the overlapping of the spectral sensitivities of the photographic layers different in color sensitivity, the spectral absorption characteristics of the color-developed dyes, and color contamination of the processed photographic layers different in the color-developed dyes, which influence the level of the color reproduction.

Further, basic properties required for couplers include, for example, solubility in high-boiling organic solvents, dispersibility and dispersion stability in silver halide emulsions, photographic characteristics, spectral absorption characteristics of the color-developed dyes, and fastness of dye images to light, heat, and humidity. Among these, in particular, spectral absorption characteristics of the color-developed dyes are important so as to make the color reproduction, quality of color photographics good, and even if couplers capable of forming color-developed dyes having preferable spectral absorption characteristics, the significance will lower considerably if mixing of colors as mentioned above occurs.

In color photographs, dye image fastness has increasingly become an important matter, in particular dye image fastness to light is important, and in current color papers, one big problem is fading of magenta dyes or the occurrence of brown stain attributable to a reaction between color-undeveloped magenta couplers and light.

As means of improving magenta couplers to solve such a problem, a technique is known using, instead of conventionally used 5-pyrazolone four-equivalent couplers, 5-pyrazolone two-equivalent couplers. As regards such magenta couplers, for example, magenta couplers having a nitrogen-linked coupling releasable group described, for example, in U.S. Patent No. 4,310,619, and magenta couplers having a sulfur-linked coupling releasable group described in U.S. Patent No. 4,351,897 are known. Particularly, although magenta couplers having a coupling releasable arylthio group described in the latter U.S. Patent have many practically excellent points, including the stability of the couplers themselves, their levels are still not satisfactory.

As magenta couplers other than 5-pyrazolone couplers, pyrazoloazole magenta couplers are known. In contrast to 5-pyrazolone couplers, for pyrazoloazole magenta couplers it is known that the spectral absorption characteristics of the color-developed dyes are good, the fastness to light is good, and stain due to the color-undeveloped coupler is less, and pyrazoloazole magenta couplers are the most excellent magenta couplers practically.

Couplers of this type are described, for example, in U.S. Patent Nos. 3,369,879 and 3,725,067, Research Disclosure 24220 (June 1984), Research Disclosure 24230 (June 1983), U.S. Patent Nos. 4,500,630 and 4,540,654, JP-A Nos. 65245/1986, 65246/1986, and 20 147254/1986, and European Patent No. 0,226,849.

Of these pyrazoloazole magenta couplers, pyrazolo[5,1-c][1,2,4]triazoles and pyrazolo[1,5-b][1,2,4]-triazoles are preferable in view of the combined performance of color-forming properties, the spectral absorption characteristics of the color-developed dye, and dye image fastness, and in particular pyrazolo-[1,5,-b][1,2,4]triazoles described in U.S. Patent No. 4,540,654 can preferably be used.

Further, those wherein such couplers as mentioned above are combined with, as a substituent, a branched alkyl group, as described in JP-A No. 65245/1986, those wherein a sulfonamido group is introduced in the molecule, as described in JP-A No. 65246/1986, those wherein an alkoxyphenylsulfonamido group is introduced, as described in JP-A No. 147254/1986, or those wherein an alkoxy group or an aryloxy group is introduced to the 6-position, as described in European Patent Nos. 0,226,849 and 0,294,785, are more preferable. However, it was found that although they had preferable points, when so-called two-equivalent couplers, i.e. those couplers having a releasable group other than a hydrogen atom in the coupling position, were used in a green-sensitive silver halide emulsion layer, the above-described color contamination of the color, with the color of other photographic layers different in color-developed dyes, is liable to take place in the processing. In order to prevent such mixing of colors, it is conceivable to increase the amount of the color contamination preventive agent in the nonphotographic layer between the particular layers, but when this technique was used there arose such problems that changes in the sensitivity and in the gradation during storage increased, and the progress of the development of the blue-sensitive silver halide emulsion layer nearest the base got slower in the initial stage.

BRIEF SUMMARY OF THE INVENTION

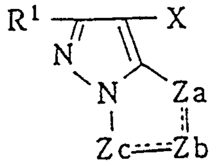
Therefore, the object of the present invention is to provide a silver halide color photographic material high in sensitivity and contrast and excellent in color reproduction and dye image stability. In particular, the object of the present invention is to prevent processing color contamination that is apt to occur in silver halide color photographic materials excellent in color reproduction and dye image stability, thereby providing a silver halide color photographic material whose quality is made markedly high and is stabilized.

Other and further objects, features, and advantages of the invention will become apparent more fully from the following description.

DETAILED DESCRIPTION OF THE INVENTION

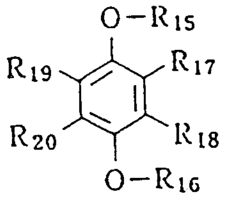
The objects of the present invention have been fulfilled by providing a silver halide color photographic material that has photographic layers that include at least one silver halide emulsion layer containing a yellow coupler, at least one silver halide emulsion layer containing a magenta coupler, and at least one silver halide emulsion layer containing a cyan coupler, on a support in the stated order, with said yellow coupler-containing silver halide emulsion layer nearest the support, characterized in that (a) said magenta coupler is a compound represented by the below-given formula (I), (b) the coating amount of the hydrophilic colloid in the nonphotosensitive layer positioned between said yellow coupler-containing silver halide emulsion layer and said magenta coupler-containing silver halide emulsion layer is 1.1 g/m^2 or over, (c) said nonphotographic layer contains a compound represented by the below-given formula (II) in an amount between 7.75 x 10^{-5} mol/m^2 and 9.00 x 10^{-4} mol/m^2, and (d) at least one silver halide emulsion layer on the support contains a surface latent image-type monodisperse silver chlorobromide emulsion that comprises silver chlorobromide substantially free from silver iodide, and is obtained by subjecting the surface of silver halide grains having plural partial structures different in halogen composition to halogen conversion:

Formula (I)



wherein R^1 represents a hydrogen atom or a substituent, X represents a group capable of being released upon coupling reaction with the oxidized product of an aromatic primary amine developing agent, Za, Zb, and Zc each represent a 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; if the Zb-Zc is a carbon-carbon double bond, it may be part of the aromatic ring; a dimer or higher polymer may be formed through R^1 or X; or if Za, Zb, or Zc is a substituted methine, a dimer or higher polymer may be formed through the substituted methine;

Formula (II)



wherein R_{15} and R_{16} each represent a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an acyl group, a cycloalkyl group, or a nitrogen-containing heterocyclic group, R_{17}, R_{18}, R_{19}, and R_{20} each represent a hydrogen atom, a halogen atom, an alkyl group, an alkenyl group, an aryl group, a cycloalkyl group, an alkoxy group, an alkylthio group, an arylthio group, a nitrogen-containing heterocyclic thio group, an aryloxy group, an acyl group, an acylamino group, an alkylamino group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, or a sulfonic acid group, provided that when R_{17}, R_{18}, R_{19}, and R_{20} are hydrogen atoms at the same time, R_{15} and R_{16} are not hydrogen atoms at the same time, and R_{18} and R_{20} may bond together to form a 5-membered ring or a 6-membered ring.

In this specification and claims, methine represented by Za, Zb, or Zc in formula (I) include substituted and unsubstituted methine. As the substituents of methine can be mentioned a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonyl group, or an aryloxycarbonyl group. The examples of R^1 are the same as those of R^{11}, R^{12}, and R^{13} enumerated later.

The present invention will now be described in more detail.

The silver halide emulsion used in the present silver halide color photographic material is silver chlorobromide substantially free from silver iodide. The term "substantially free from silver iodide" means that the silver iodide content is 1 mol% or below, preferably 0.5 mol% or below, and most preferably silver iodide is not contained at all. In the silver halide emulsion used in the present invention, although the content ratio of silver chloride to silver bromide may take any value ranging from a value indicating nearly pure silver to a value indicating nearly pure silver bromide, it is desirable that the silver bromide content is between 0.3 mol% and 97 mol%.

In order to obtain a photographic material stable in fogging, sensitivity, and gradation in accordance with the present invention, it is desirable that the silver bromide content of the emulsion is made high, and a silver bromide content of 45 % or over is good, with 60 % or over preferred.

In such a silver chlorobromide emulsion of the present invention, it is needed that the crystalline grains contained therein have at least two partial structures, wherein the difference of the silver bromide content is 10 mol% or over. Herein the term "partial structures" refers to a structure wherein the inside and the surface of the crystal grain are different in halogen composition, and which may be a so-called core-shell structure or a layered structure having plural layers. Herein, the layered structure may not necessarily be continuous, and it may be a structure wherein discontinuous layers have been grown, for example, on the corners or planes of the crystal grain epitaxially.

In the thus formed partial structures, for example, the core section of crystalline grains having a core-shell structure may have a high silver bromide content, and the shell section may have a low silver bromide content, or conversely the core section may have a low silver bromide content and the shell section may have a high silver bromide content. The boundary between the partial structures of such a crystalline grain that are different in halogen composition may be a distinct boundary with respect to the composition, or a boundary where the composition continuously changes due to the formation of a mixed crystal due to the difference of the composition.

Although there is no particular limit on the constitutional ratio in the crystalline grain having two or more partial structures different in halogen composition, for example in the case of crystalline grains having a core/shell structure, the constitutional silver halide molar ratio of the core to the shell is preferably in the range of 2 : 98 to 98 : 2, more preferably 10 : 90 to 95 : 10, further more preferably 40 : 60 to 90 : 10, and most preferably 67 : 33 to 90 : 10.

Although the difference of the silver bromide content between the core section and the shell section may vary depending on the constitutional silver halide molar ratio between the core section and the shell section, it is required that the difference is at least 10 mol% or over, but less than 100 mol%, more preferably between 10 mol% and 50 mol%, and most preferably between 15 mol% and 35 mol%. If the difference of the silver bromide content between two or more partial structures is not large, the effect of the grain is not so different from a grain having a uniform structure, whereas if the composition difference is too large, it is not preferable because a problem concerning the performance, such as pressure desensitization, is liable to occur. The suitable composition difference is dependent on the constitutional ratio of the partial structures, and the nearer the constitutional ratio is to 0 : 100 or 100 : 0, the more preferable it is to make greater the composition difference, and the nearer the constitutional ratio is to 1 : 1, the more preferable it is to make the composition difference reduce to a certain range of 10 mol% or over.

The term "halogen conversion" used in the present invention is defined as "conversion of the composition of already formed silver halide crystals by the addition of a material containing a halide ion capable of forming a more sparingly soluble silver salt." As a typical example thereof, the reaction wherein silver chloride is converted to silver bromide, when potassium bromide is added to pure silver chloride grains, can be mentioned. Generally halogen conversion includes such a reaction as will occur when a silver halide crystal that will undergo halogen conversion which is a mixed crystal of silver chlorobromide, is treated in the solution containing bromide ions in an amount exceeding the equilibrium concentration of bromide ions, thereby allowing the composition of the surface silver halide to be converted to be rich in silver bromide.

To subject the surface of such grains to halogen conversion, it is convenient to add a required amount of bromide ions in the form of a soluble bromide, but a donor that can control the supply or the supply speed of bromide ions can also be used. As such a donor, for example, an organic bromide, an inorganic bromide having a suitable solubility for water, and a bromide wherein the capsule membrane is coated with a semipermeable film can be used. A fine grain silver halide having a silver bromide content higher than the silver bromide content of the grain surface before the halogen conversion can also be used.

In the present invention, it is preferable that the amount of halogen conversion is between 0.5 mol% and to 15 mol% for the total silver halide. If the amount of halogen conversion is 0.5 mol% or below, the effect of the present invention is barely exhibited, whereas if the amount exceeds 20 mol%, it is not preferable because desensitization due to pressure, as mentioned above, becomes great.

As is generally well known, the step of preparing the silver halide emulsion is made up of a step of forming silver halide grains by the reaction of a water soluble silver salt and a water-soluble halide, a step of desalting, and a step of chemically ripening. The time when halogen conversion is effected in the present invention is preferably before the chemical ripening step, more preferably before the desalting step, of the above steps, and particularly preferably halogen conversion is effected after the grain formation step.

In the present invention, the silver halide emulsions in the silver halide emulsion layers are chemically sensitized. In this case, as the chemical sensitization, sulfur sensitization is preferable, but sulfur sensitization may be carried out together with reduction sensitization or gold sensitization.

The chemical sensitization with sulfur used in the present invention is carried out by using active gelatin or a compound containing sulfur capable of reacting with silver (e.g., thiosulfates, thioureas, mercapto compounds, and rhodanines), and specific examples thereof are described, for example, in U.S. Patent Nos. 1,574,944, 2,278,947, 2,410,689, 2,728,668, and 3,656,955.

In the present invention, the silver halide emulsions in the silver halide emulsion layers may be subjected to a chemical sensitization process in the presence of a nucleic acid or its dispersion before the completion of the chemical sensitization.

The nucleic acid used includes deoxyribonucleic acids (DNA) and ribonucleic acids (RNA), and, as nucleic acid degradation products, degradation intermediates, and adenine, guanine, uracil, cytosine, and thymine, which may be used alone or in combination.

Although the chemical sensitization process in the present invention can be carried out in any pH range, if it is carried out at a pH in the range of 7.0 to 9.0, more preferable results will be obtained.

The silver chlorobromide emulsion grains used in the present invention are ones that have a regular crystal shape, such as a cubic shape and an octahedral shape, or an irregular crystal shape, such as a spherical shape and a tabular shape, or a composite of these. A mixture of grains having various crystal shapes can be used, with grains having a regular shape preferably used.

Preferably the silver halide emulsion used in the present invention is a tabular grain emulsion wherein grains having a thickness of 0.5 microns or below, preferably 0.3 microns or below, a diameter of 0.6 microns or over, and an average aspect ratio of 5 or over, account for 50 % or over of the total projective area, or a monodisperse emulsion having a statistical deviation coefficient (the value $S/\bar{d}$ obtained by dividing the standard deviation S by the diameter $\bar{d}$ with the projective area approximated to a circle) of 20 % or below. A mixture of two or more tabular grain emulsions and monodisperse emulsions may be used.

The photographic emulsion used in the present invention can be put in due condition by processes described, for example, by P. Glafkides in Chimie et Physique Photographeque (published by Paul Montel in 1967), by G.F. Duffin in Photographic Emulsion Chemistry (published by Focal Press in 1966), and by V.L. Zelikman et at. in Making and Coating Photographic Emulsion (published by Focal Press in 1964).

Further, in order to control the growth of the silver halide grains at the time when the silver halide grains are formed, use can be made of, as a silver halide solvent, for example, ammonia, potassium thiocyanate, ammonium thiocyanate, a thioether compound (e.g., those described in U.S. Patent Nos. 3,271,157, 3,574,628, 3,704,130, 4,297,439, and 4,276,374), a thion compound (e.g., those described in JP-A Nos. 144319/1978, 82408/1978, and 77737/1980), and an amine compound (e.g., those described in JP-A No. 100717/1979).

In the process wherein the silver halide grains are formed or physically ripened, for example, a cadmium salt, a zinc salt, a thallium salt, an iridium salt or its complex salt, a rhodium salt or its complex salt, or an iron salt or its complex salt may also be present.

The silver halide emulsion is generally sensitized spectrally. In the spectral sensitization, use can be made of a common methine dye, and details thereof are described in JP-A No. 215272/1987, page 22, lines 3 to 38 in the right upper column, and in the Attached Paper B of Amendment thereof dated March 16, 1987.

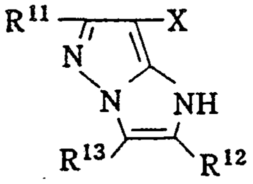
The silver halide photographic emulsion used in the present invention can contain various compounds for the purpose of preventing fogging in the process of the production of photographic materials, or fogging during the storage or photographic processing of photographic materials, or for the purpose of stabilizing the photographic performance. That is, various compounds known as antifoggants or stabilizers can be added, such as azoles, for example benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles, and benzimidazoles (particularly nitro- or halogen-substituted benzimidazoles); heterocyclic mercapto compounds, for example mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiazoles, mercaptotetrazoles (particularly 1-phenyl-5-mercaptotetrazole and phenyl-substituted 1-phenyl-5-mercaptotetrazole), and mercaptopyrimidines; heterocyclic mercapto compounds (e.g., mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiazoles, mercaptotetrazoles (particularly 1-phenyl-5-mercaptotetrazole and phenyl-substituted 1-phenyl-5-mercaptotetrazole), and mercaptopyrimidines) having a water-soluble group, such as a carboxyl group or a sulfone group; thioketo compounds, for example oxazolinethion; azaindenes, for example tetraazaindenes (particularly 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes); benzenethiosulfonic acids; and benzenesulfinic acids.

Specific examples of particularly preferable compounds are described in the above-mentioned JP-A No. 215272/1987, pages 40 to 72.

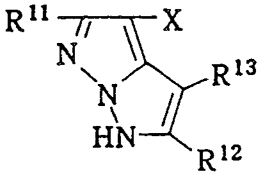
Next the magenta couplers represented by formula (I) in the present invention are described in detail.

In the magenta dye-forming couplers represented by formula (I), the term "polymer" means one having two or more groups represented by formula (I) in the molecule, which includes bis-forms and polymer couplers. Herein the polymer coupler may be a homopolymer consisting only of a monomer (preferably one having a vinyl group, which is referred hereinafter to as vinyl monomer) having a moiety represented by formula (I), or it may be a copolymer of such a monomer with a non-color-forming ethylenically-unsaturated monomer that will not couple with the oxidized product of an aromatic primary amine developing agent.

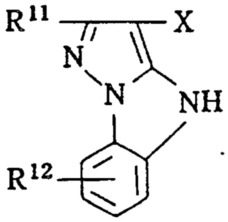
Of the magenta dye-forming couplers represented by formula (I), preferable ones are those represented by the following formulae (Ia), (Ib), (Ic), (Id), (Ie), (If), and (Ig):



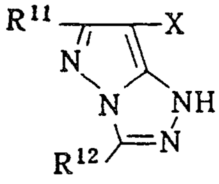
(Ia)



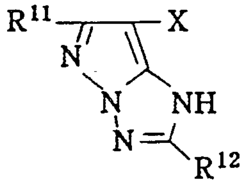
(Ib)



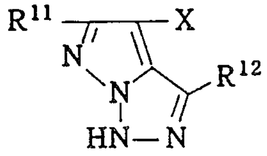
(Ic)



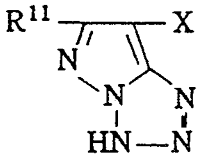
(Id)



(Ie)



(If)



(Ig)

Of the couplers represented by formulae (Ia) to (Ig), preferable ones for the objects of the present invention are those represented by formulae (Ia), (Id), and (Ie), and more preferably those represented by formula (Ie).

In formulae (Ia) to (Ig), R^{11}, R^{12}, and R^{13}, which may be the same or different, each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonyl group, or an aryloxycarbonyl group, X represents a halogen atom, a carboxyl group, or a group that bonds to the carbon atom in the coupling position through an oxygen atom, a nitrogen atom, or a sulfur atom, and which is capable of being released upon coupling reaction, and preferably a halogen atom or a group capable of being released through a sulfur atom, and R^{11}, R^{12}, R^{13}, or X may become a bivalent group to form a bis-form.

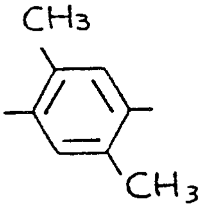
It is also possible to use a polymer coupler having in its main chain or side chains coupler residues represented by one of formulae (Ia) to (Ig), and in particular a polymer derived from a vinyl monomer having a moiety represented by formula is preferable, wherein R^{11}, R^{12}, R^{13} or X represents a vinyl group or a linking group.

More particularly, R^{11}, R^{12}, and R^{13} each represent a hydrogen atom, a halogen atom (e.g., a chlorine atom or a bromine atom), an alkyl group (e.g., methyl, propyl, t-butyl, trifluoromethyl, tridecyl, 3-(2,4-di-t-amylphenoxy)propyl, allyl, 2-dodecyloxyethyl, 3-phenoxypropyl, 2-hexylsulfonyl-ethyl, cyclopentyl, and benzyl), an aryl group (e.g., phenyl, 4-t-butylphenyl, 2,4-di-t-amylphenyl and 4-tetradecaneamidophenyl), a heterocyclic group (e.g., 2-furyl, 2-thienyl, 2-pyrimidyl, and 2-benzothiazolyl), a cyano group, an alkoxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-dodecyloxyethoxy, and 2-methanesulfonylethoxy), an aryloxy group (e.g., phenoxy, 2-methylphenoxy, and 4-t-butylphenoxy), a heterocyclic oxy group (e.g., 2-benzimidazolyloxy), an acyloxy group (e.g., acetoxy and hexadecanoyloxy), a carbamoyloxy group (e.g., N-phenylcarbamoyloxy and N-ethylcarbamoyloxy), a silyloxy group (e.g., trimethylsilyloxy), a sulfonyloxy group (e.g., dodecylsulfonyloxy), an acylamino group (e.g., acetamido, benzamido, tetradecaneamido, α-(2,4-di-t-amylphenoxy)butyramido, γ-(3-t-butyl-4-hydroxyphenoxy)butyramido, and α-{4-(4-hydroxyphenylsulfonyl)phenoxy}decaneamido), an anilino group (e.g., phenylamino, 2-chloroanilino, 2-chloro-5-tetradecaneamidoanilino, 2-chloro-5-dodecyloxycarbonylanilino, N-acetylanilino, and 2-chloro-5-{α-(3-t-butyl-4-hydroxyphenoxy)dodecaneamido}anilino), a ureido group (e.g. phenylureido, methylureido, and N,N-dibutylureido), an imido group (e.g., N-succinimido, 3-benzylhydantoinyl, and 4-(2-ethylhexanoylamino)-phthalamido), a sulfamoylamino group (e.g., N,N-dipropylsulfamoylamino and N-methyldecylsulfamoylamino), an alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, and 3-(4-t-butylphenoxy)propylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, and 4-tetradecaneamidophenylthio), a heterocyclic thio group (e.g., 2-benzothiazolylthio), an alkoxycarbonylamino group (e.g., methoxycarbonylamino and tetradecyloxycarbonylamino), an aryloxycarbonylamino group (e.g., phenoxycarbonylamino and 2,4-di-t-butylphenoxycarbonylamino), a sulfonamido group (e.g., methanesulfonamido, hexadecanesulfonamido, benzenesulfonamido, p-toluenesulfonamido, octadecanesulfonamido, and 2-methyloxy-5-t-butylbenzenesulfonamido), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-dodecyloxyethyl)-carbamoyl, N-methyl-N-dodecylcarbamoyl, and N-{3-(2,4-di-t-amylphenoxy)propyl}carbamoyl, an acyl group (e..g, acetyl, (2,4-di-t-aminophenoxy)acetyl, and benzoyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-(2-dodecyloxyethyl)sulfamoyl, N-ethyl-N-dodecylsulfamoyl, and N,N-diethylsulfamoyl), a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, and toluenesulfonyl), a sulfinyl group (e.g., octanesulfinyl, dodecylsulfinyl, and phenylsulfinyl), an alkoxycarbonyl group (e.g., methoxycarbonyl, butyloxycarbonyl, dodecylcarbonyl, and octadecylcarbonyl), or an aryloxycarbonyl group (e.g., phenyloxycarbonyl and 3-pentadecyloxy-carbonyl), and X represents a halogen atom (e.g., chlorine, bromine, and iodine), a carboxyl group, a group that bonds through an oxygen atom (e.g., acetoxy, propanoyloxy, benzoyloxy, 2,4-dichlorobenzoyloxy, ethoxyoxazolyloxy, pyruvinyloxy, cinnamoyloxy, phenoxy, 4-cyanophenoxy, 4-methanesulfonamidophenoxy, 4-methanesulfonylphenoxy, α-naphthoxy, 3-pentadecylphenoxy, benzyloxycarbonyloxy, ethoxy, 2-cyanoethoxy, benzyloxy, 2-phenetyloxy, 2-phenoxyethoxy, 5-phenyltetrazolyloxy, and 2-benzothiazolyloxy), a group that bonds through a nitrogen atom (e.g., benzenesulfonamido, N-ethyltoluenesulfonamido, heptafuluorobutaneamido, 2,3,4,5,6-pentafluorobenzamido, octanesulfonamido, p-cyanophenylureido, N,N-diethylsulfamoylamino, 1-piperidyl, 5,5-dimethyl-2,4-dioxo-3-oxazolidinyl, 1-benzyl-ethoxy-3-hydantoinyl, 2N-1,1-dioxy-3(2H)-oxo-1,2-benzoisothiazolyl, 2-oxo-1,2-dihydro-1-pyridinyl, imidazolyl, pyrazolyl, 3,5-diethyl-1,2,4-triazol-1-yl, 5- or 6-bromo-benzotriazol-1-yl, 5-methyl-1,2,3,4-triazol-1-yl, benzimidazolyl, 3-benzyl-1-hydantoinyl, 1-benzyl-5-hexadecyloxy-3-hydantoinyl, and 5-methyl-1-tetrazolyl), an arylazo group (e.g., 4-methoxyphenylazo, 4-pivaloylaminophenylazo, 2-naphthylazo, and 3-methyl-4-hydroxyphenylazo), or a group that bonds through a sulfur atom (e.g., phenylthio, 2-

carboxyphenylthio, 2-methoxy-5-t-octylphenylthio, 4-methanesulfonylphenylthio, 4-octanesulfonamidophenylthio, 2-butoxyphenylthio, 2-(2-hexasulfonylethyl)-5-t-octylphenylthio, benzylthio, 2-cyanoethylthio, 1-ethoxycarbonyltridecylthio, 5-phenyl-2,3,4,5-tetrazolylthio, 2-benzothiazolylthio, 2-dodecylthio-5-thiophenylthio, and 2-phenyl-3-dodecyl-1,2,4-triazolyl-5- thio).

In the coupler represented by formulae (Ia) and (Ib), R^{12} and R^{13} may bond together to form a 5- to 6-membered ring.

When R^{11}, R^{12}, R^{13}, or X becomes a bivalent group to form a bis-form, preferably R^{11}, R^{12}, and R^{13} each represent a substituted or unsubstituted alkylene group (e.g., methylene, ethylene, 1,10-decylene, or $-CH_2CH_2-O-CH_2CH_2-$), a substituted or unsubstituted phenylene group (e.g., 1,4-phenylene, 1,3-phenylene,



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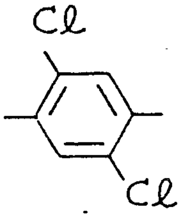
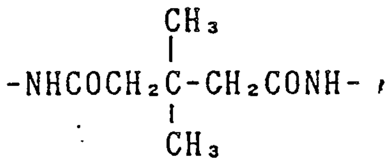


),

a group $-NHCO-R^{14}-CONH-$ (wherein R^{14} represents a substituted or unsubstituted alkylene group or phenylene group, such as

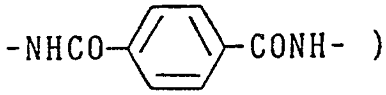
$-NHCOCH_2CH_2CONH-$,



$$-NHCOCH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2CONH-$$

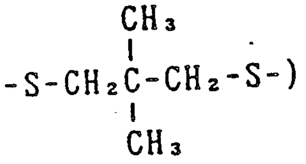
,

or



or a group $S-R^{14}-S-$ (wherein R^{14} represents a substituted or unsubstituted alkylene group, such as

$-S-CH_2CH_2-S$ or

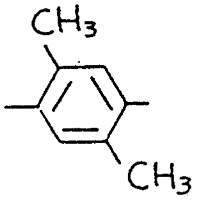


$$-S-CH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2-S-)$$

),

and X represents a bivalent group that is formed suitably from the above monovalent group.

The linking group represented by R^{11}, R^{12}, R^{13} or X, when the coupler represented one of formulae (Ia), (Ib), (Ic), (Id), (Ie), (If), and (Ig) is contained in a vinyl monomer includes groups formed by combining groups selected from substituted or unsubstituted alkylene groups (e.g., methylene, ethylene, 1,10-decylene, and $-CH_2CH_2OCH_2CH_2-$), substituted or unsubstituted phenylene groups (e.g., 1,4-phenylene, 1,3-phenylene,



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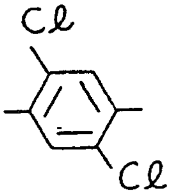
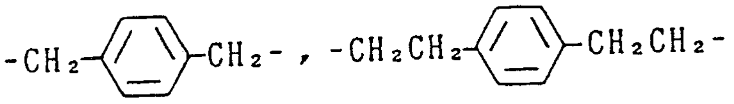


),

-NHCO-, -CONH-, -O-, -OCO-, and aralkylene groups (e.g.,



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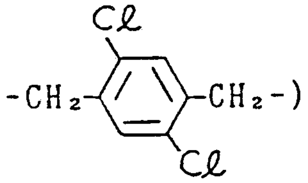
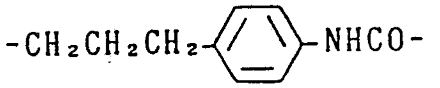


.

Preferable linking groups are

$-NHCO-$, $-CH_2CH_2-$,



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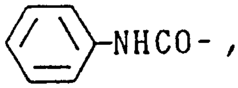
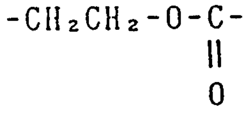


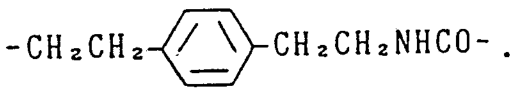
, $-CH_2CH_2NHCO-$,



$-CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-$,

$-CONH-CH_2CH_2NHCO-$, $-CH_2CH_2O-CH_2CH_2-NHCO-$,

and



.

The vinyl group may have substituents other than one represented by formulae (Ia), (Ib), (Ic), (Id), (Ie), (If), or (Ig), and a preferable substituent is a chlorine atom or a lower alkyl group having 1 to 4 carbon atoms (e.g., methyl and ethyl).

The monomer that contains coupler represented by one of formulae (Ia), (Ib), (Ic), (Id), (Ie), (If), and (Ig) may form a copolymer with a non-color-forming ethylenically-unsaturated monomer that will not couple with the oxidized product of aromatic primary amine developing agents.

As the non-color-forming ethylenically-unsaturated monomer that will not couple with the oxidized product of aromatic primary amine developing agents can be mentioned, for example, acrylic acid, α-chloroacrylic acid, α-alkylacrylic acids (e.g., methacrylic acid) and esters and amides derived from these acrylic acids (e.g., acrylamide, n-butylacrylamide, t-butylacrylamide, diacetoneacrylamide, methacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, iso-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, and β-hydroxy methacrylate), methylenebisacrylamide, vinyl esters (e.g., vinyl acetate, vinyl propionate, and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (e.g., styrene and its derivatives, vinyl toluene, divinyl benzene, vinylacetophenone, and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (e.g., vinyl ethyl ether), maleic acid, maleic anhydride, maleates, N-vinyl-2-pyrrolidone, N-vinylpyridine, and 2- and 4-vinylpyridine. Two or more of such non-color-forming ethylenically-unsaturated monomers can be used together. For example, n-butyl acrylate and methyl acrylate, styrene and methacrylic acid, methacrylic acid and acrylamide, or methyl acrylate and diacetoneacrylamide may be used together.

As is well known in the field of polymer color couplers, the non-color-forming ethylenically-unsaturated monomer to be copolymerized with a water-insoluble solid monomer coupler can be selected in such a manner that the physical properties and/or chemical properties of the copolymer, such as the solubility of the copolymer, the compatibility with the binder (such as gelatin) of the photographic colloid composition, and the flexibility and heat stability of the photographic colloid composition, are influenced favorably.

The polymer couplers used in the present invention may be water-soluble ones or water-insoluble ones, and of these, polymer coupler latices are particularly preferable.

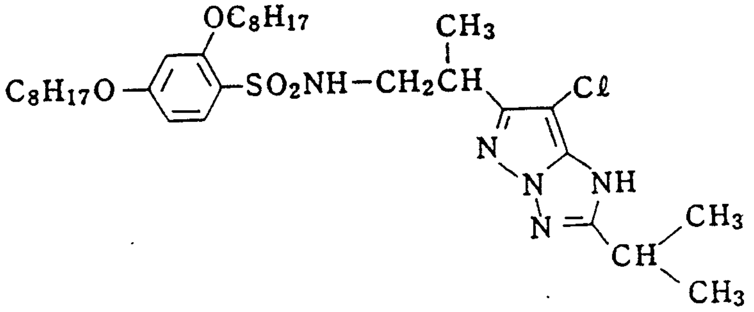
Specific examples of pyrazoloazole magenta couplers represented by formula (I) used in the present invention and methods for synthesizing them are described for example in JP-A Nos. 162548/1984, 43659/1985, 171956/1984, 172982/1985, and 33552/1985, and U.S. Patent No. 3,061,432.

Of the pyrazoloazole magenta couplers represented by formula (I), pyrazolotriazole couplers are preferable, and particularly preferable pyrazolotriazole couplers are those wherein the 2-, 3-, or 6-position has a branched alkyl group (which may be substituted) and the split-off group is a halogen atom, or the 2- or 3-position has an alkoxy group or an aryl group, the 6-position has an alkoxy group or an aryloxy group, and the split-off group is a split-off group through a sulfur atom.

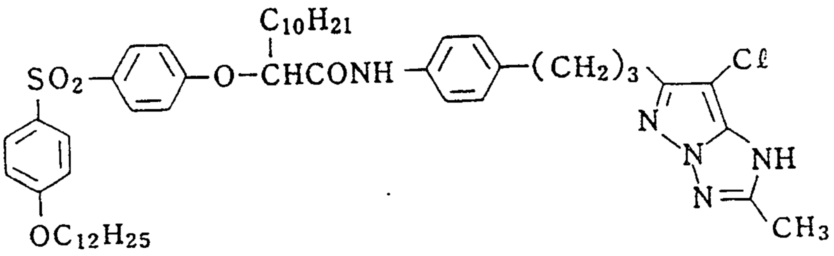
The magenta coupler represented by formula (I) used in the present invention is contained generally in an amount of 0.005 to 4 mol, preferably 0.05 to 2 mol, in the silver halide emulsion layer.

Specific examples of typical magenta couplers and their vinyl monomers related to the present invention are given below, although the present invention is not intended to be limited to them only.

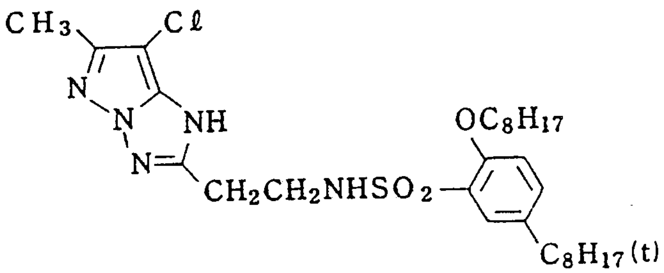
(I-1)



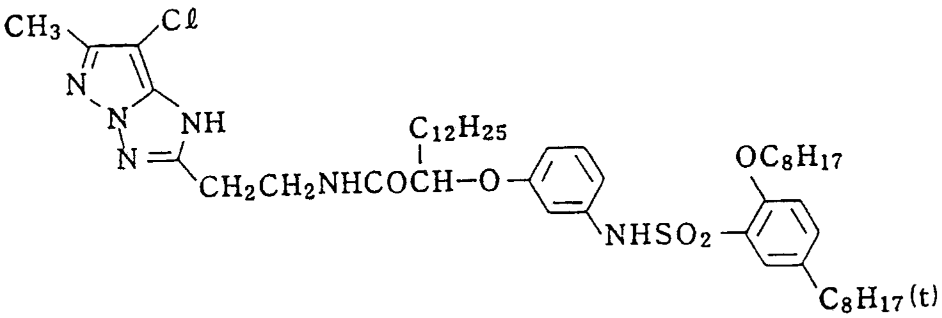
(I-2)



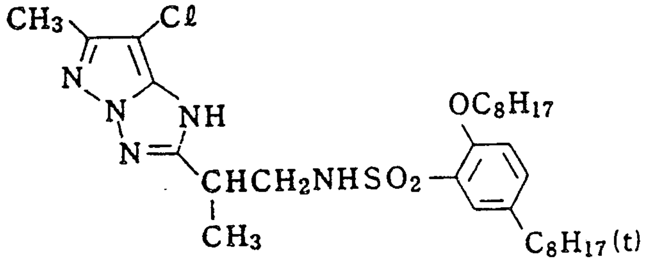
(I-3)



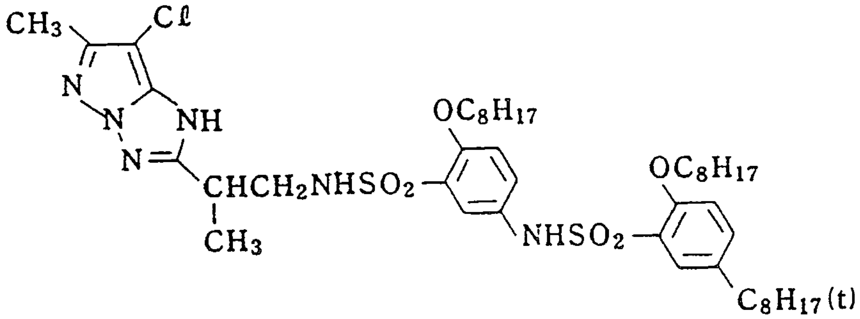
(I-4)



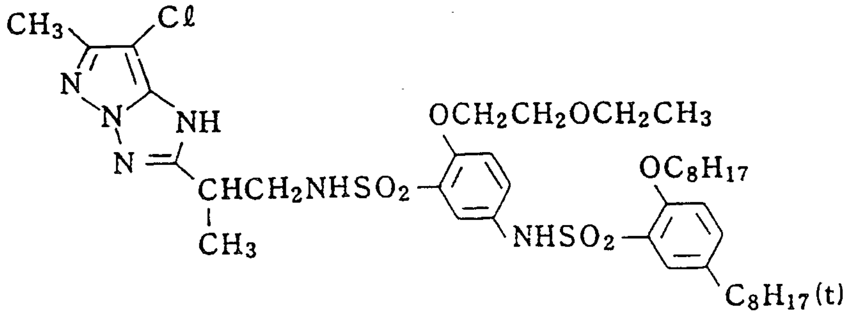
(I-5)



(I-6)



(I-7)



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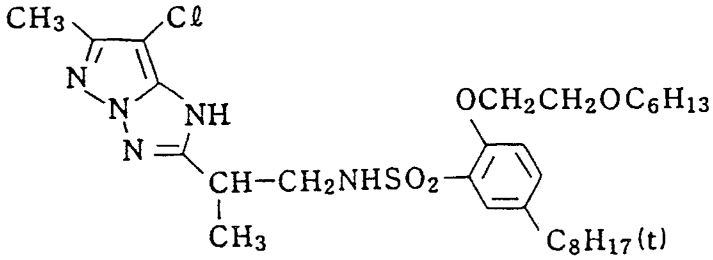

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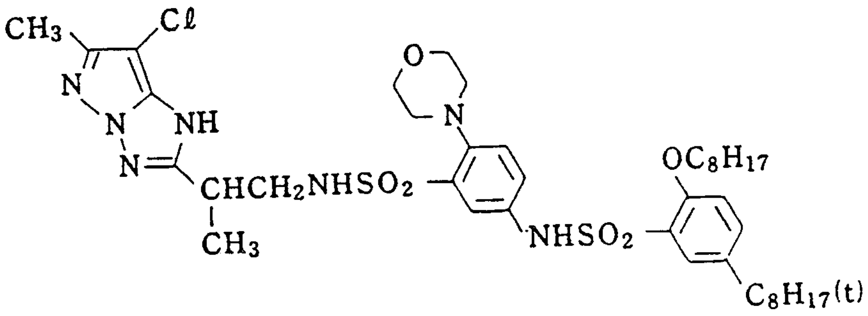

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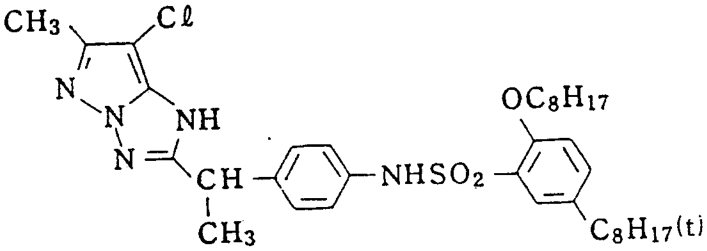
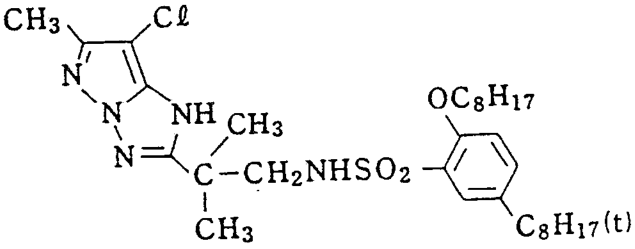


(I-11)



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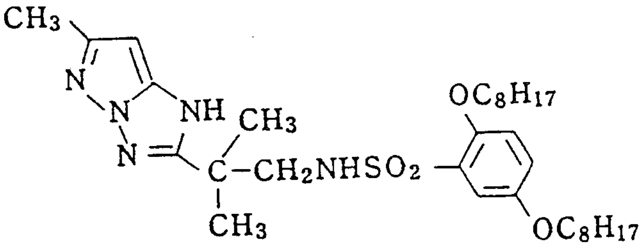

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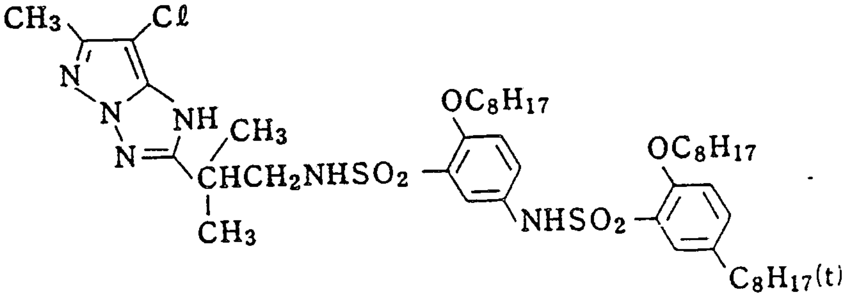

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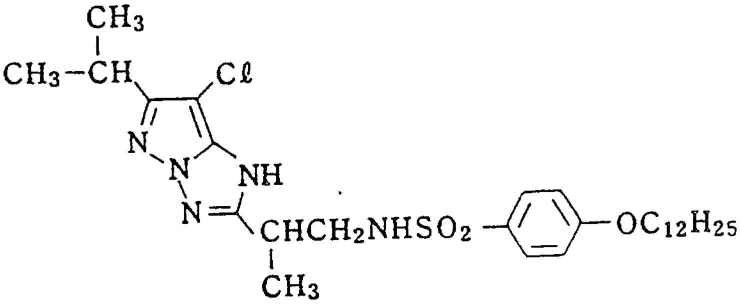

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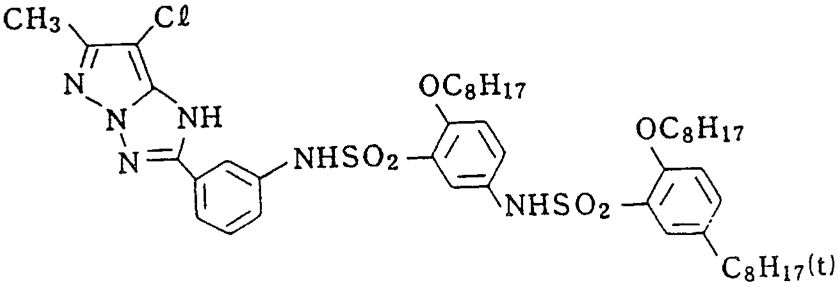

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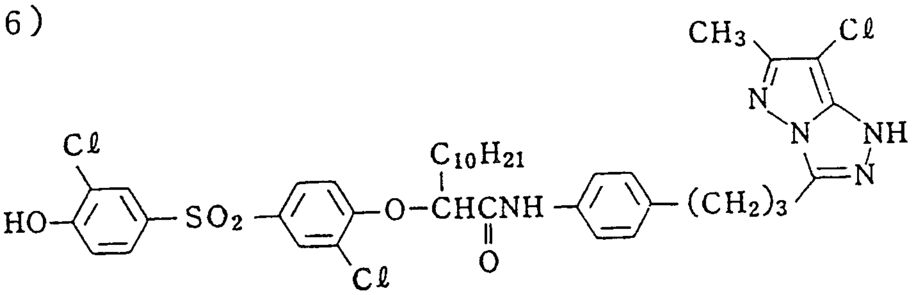

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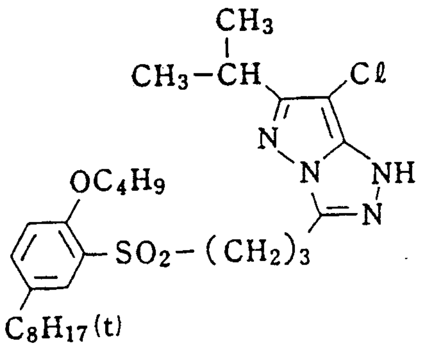

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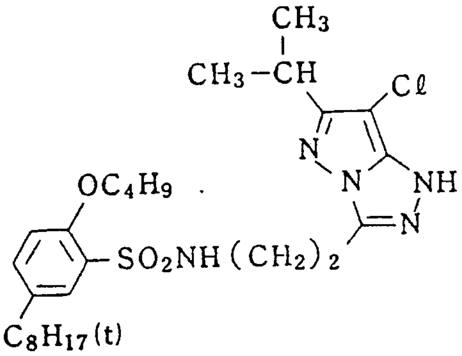

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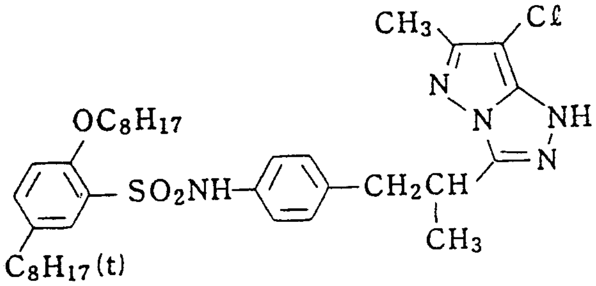
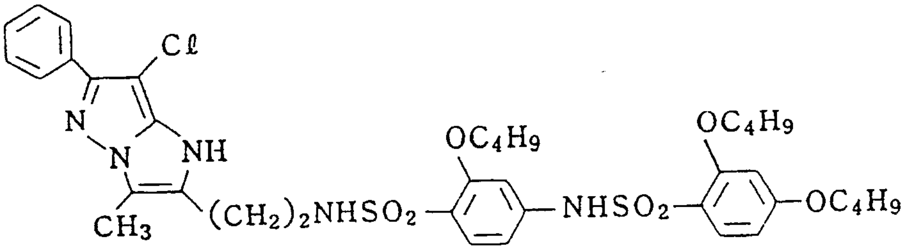


(I-20)



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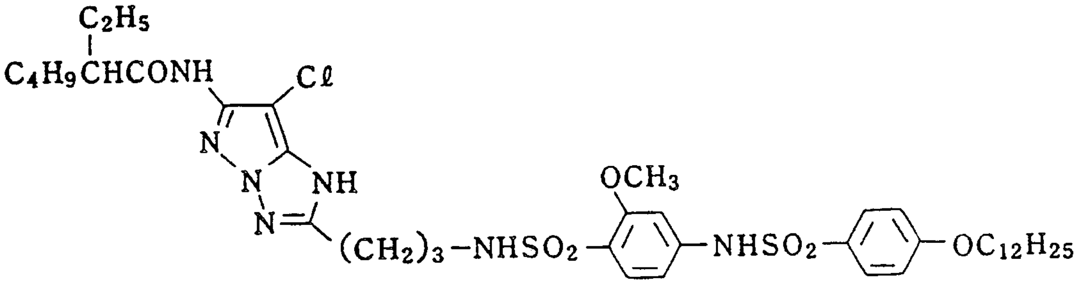

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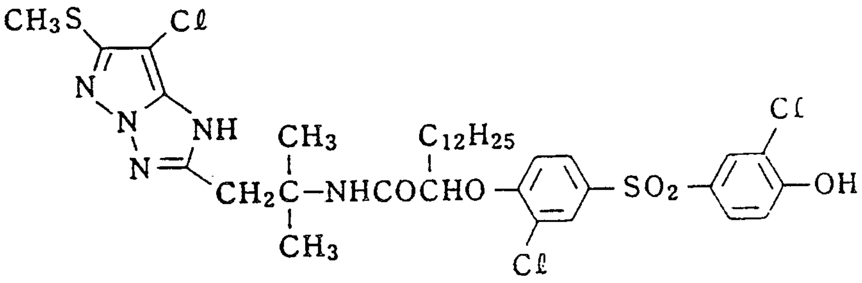

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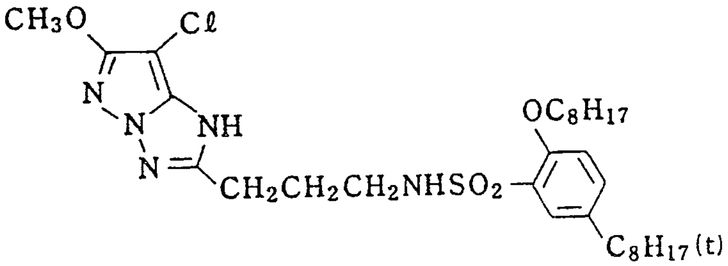

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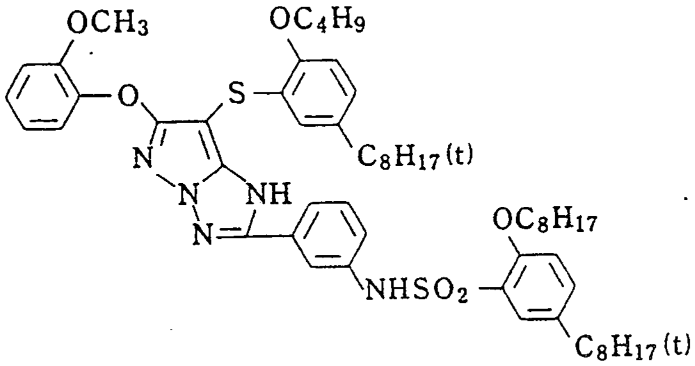
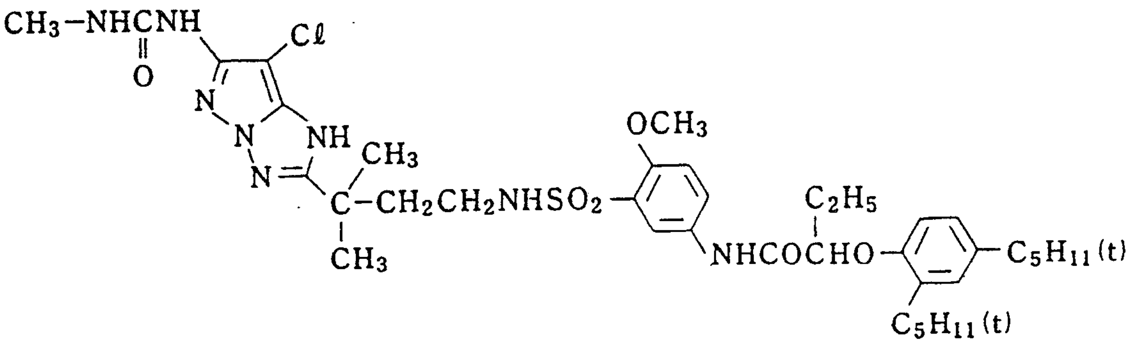


(I-25)



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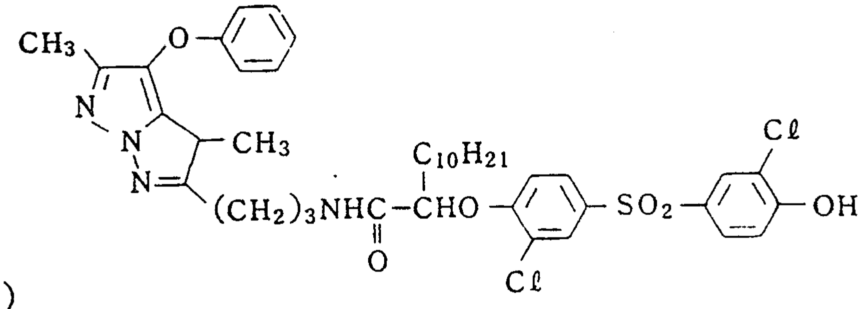

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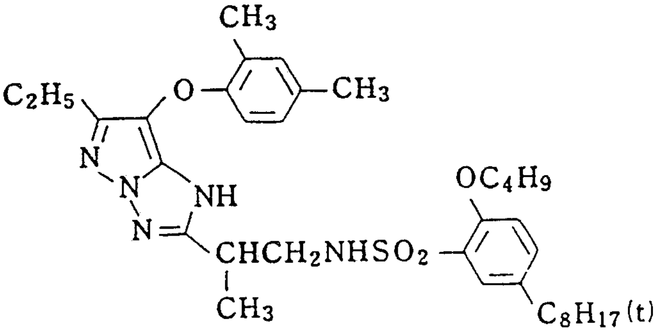

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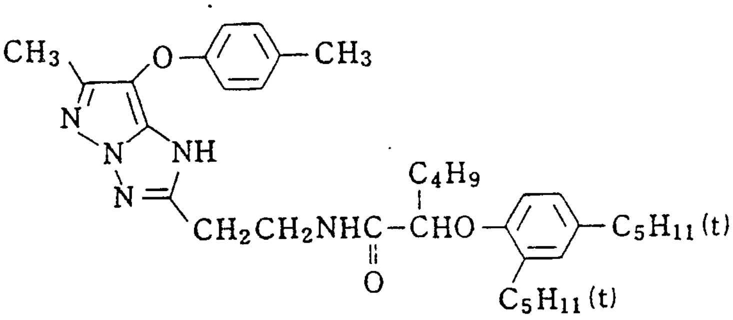

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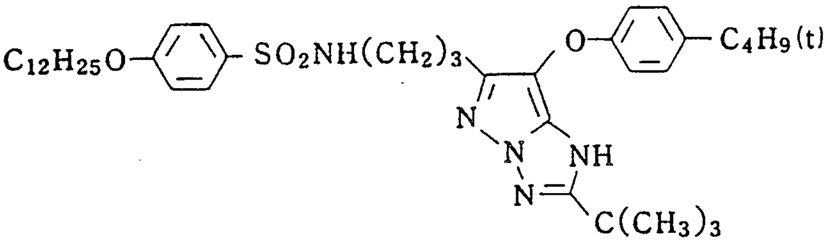

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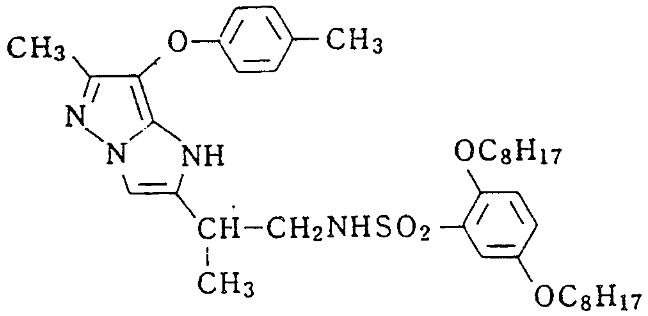

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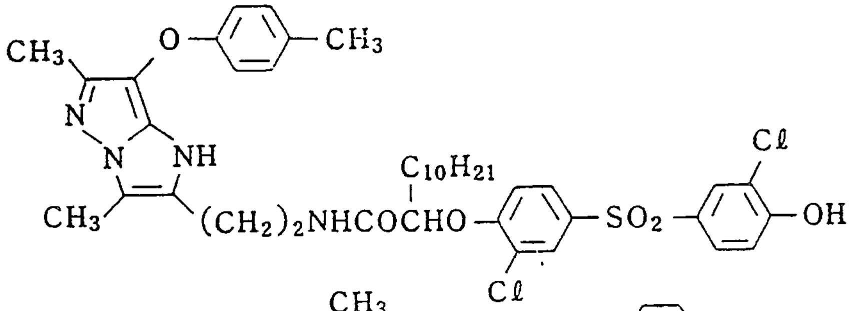

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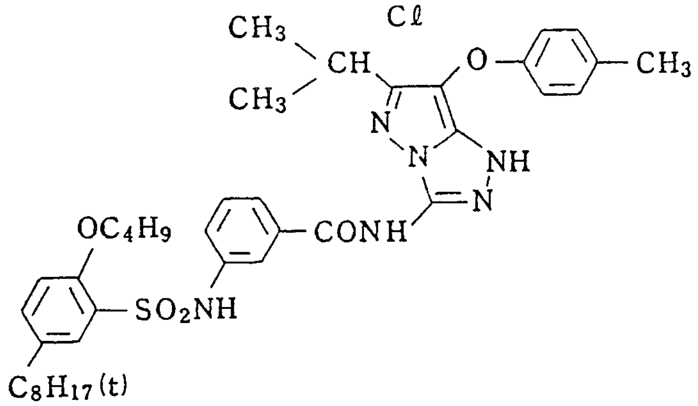

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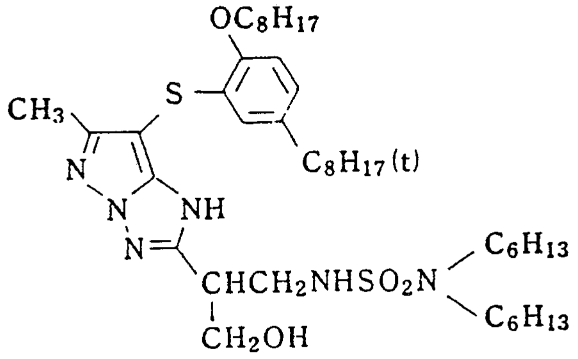
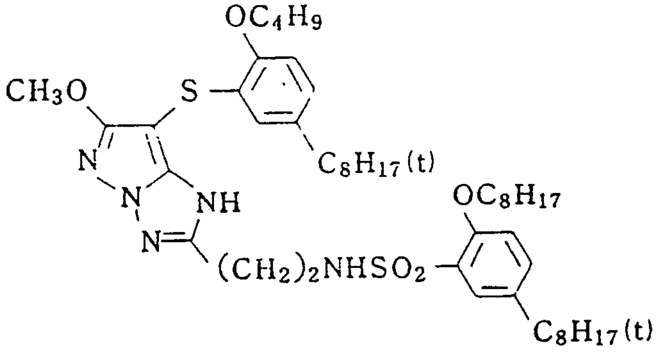
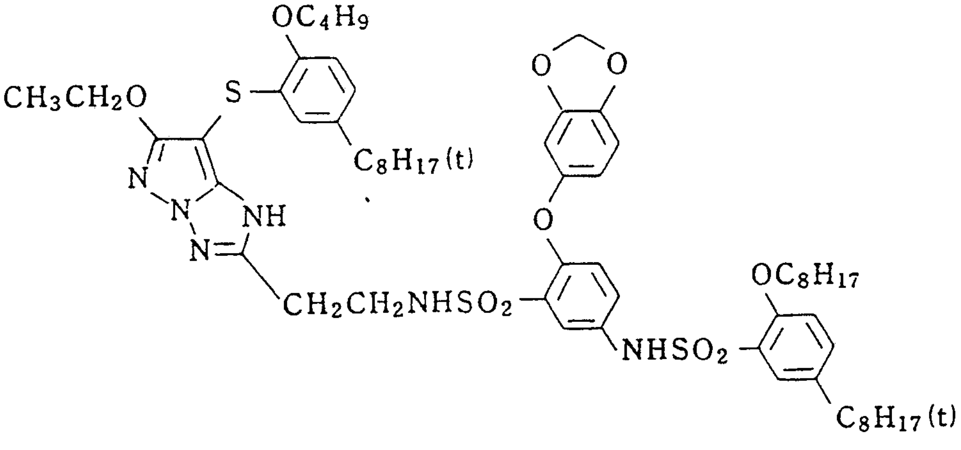

OC8H17
S
CH3
C8H17(t)
N
N
NH
N
C6H13
CHCH2NHSO2N
C6H13
CH2OH

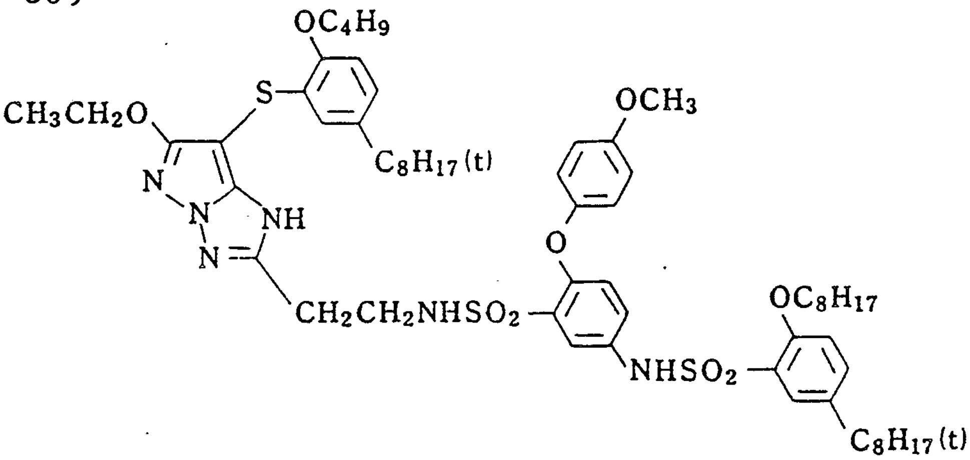
(I-34)


OC4H9
CH3O
S
C8H17(t)
N
N
NH
OC8H17
N
(CH2)2NHSO2
C8H17(t)

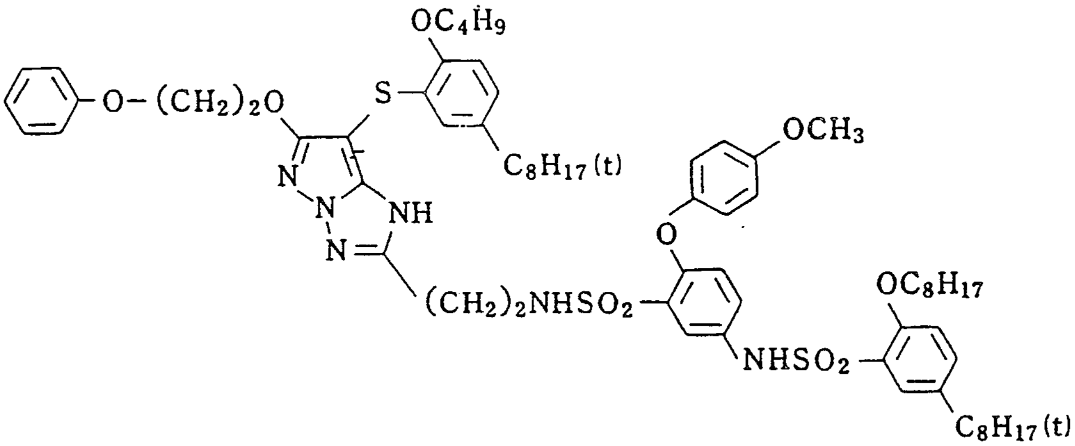
(I-35)


OC4H9
O
O
CH3CH2O
S
C8H17(t)
N
N
NH
O
N
OC8H17
CH2CH2NHSO2
NHSO2
C8H17(t)

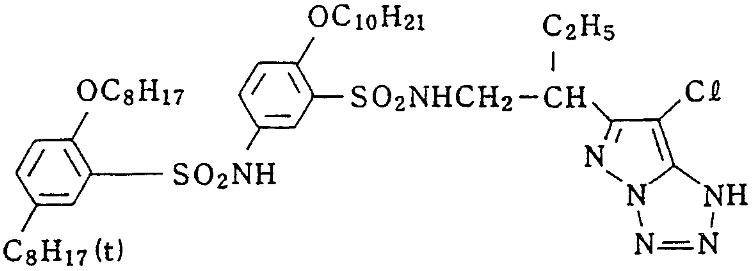
(I-36)



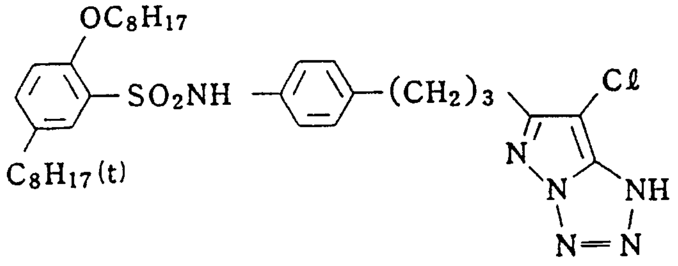
(I-37)



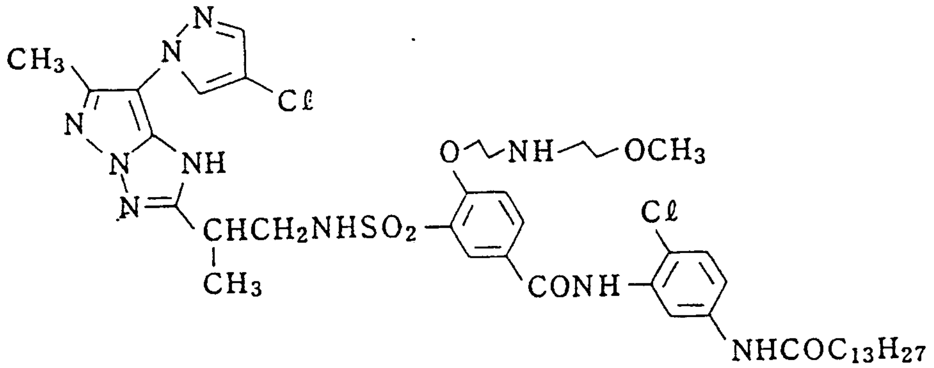
(I-38)



(I-39)



(I-40)



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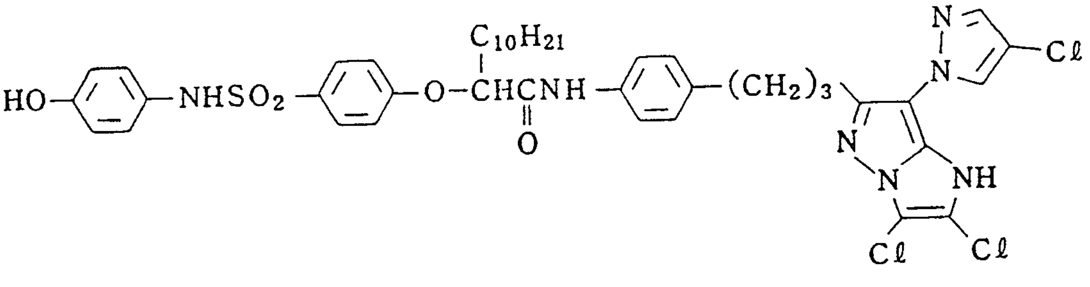
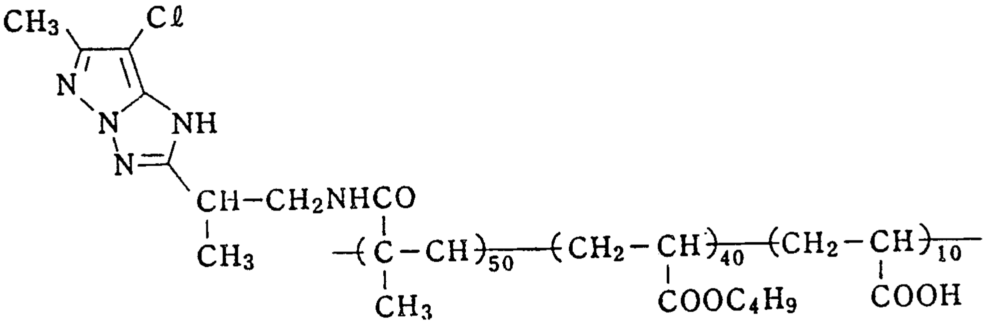
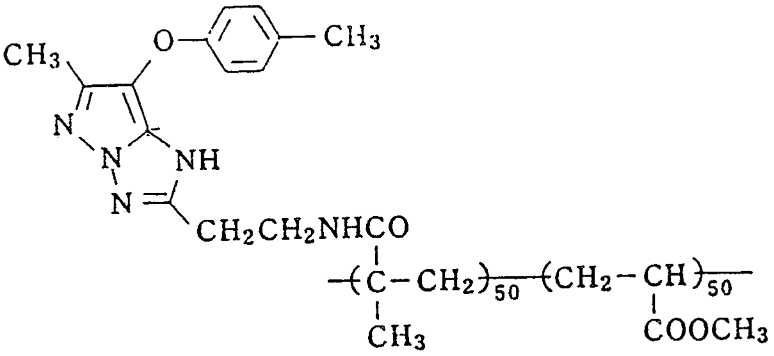


(I-42)



(I-43)



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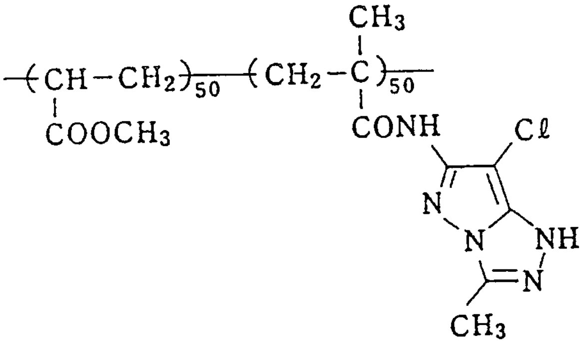

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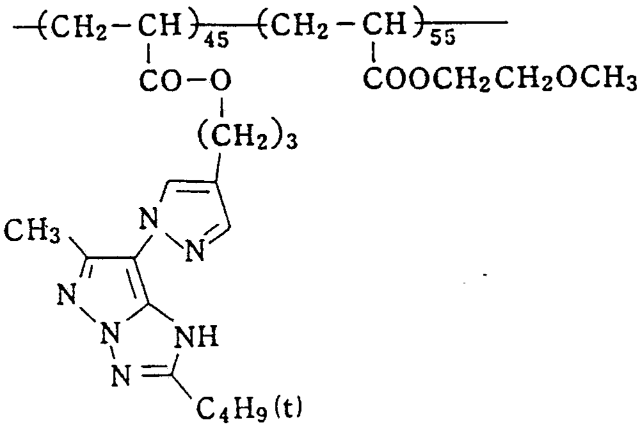
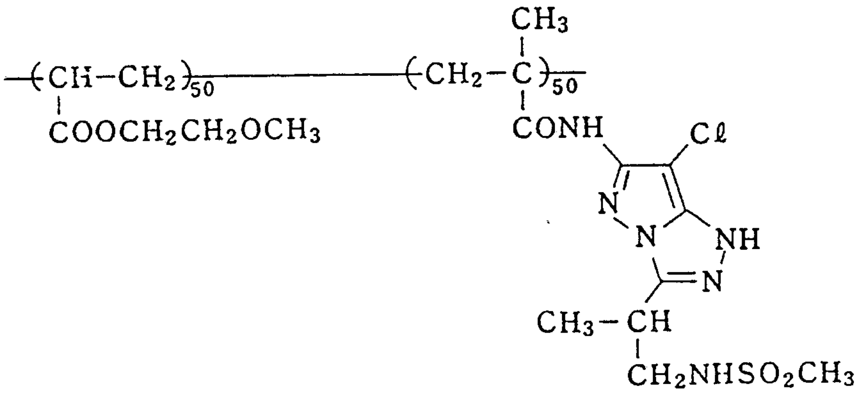


(I-46)



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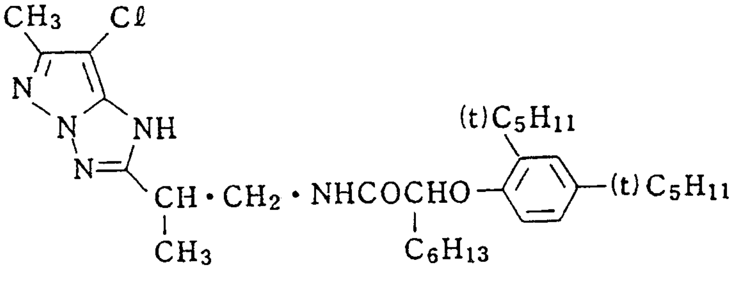
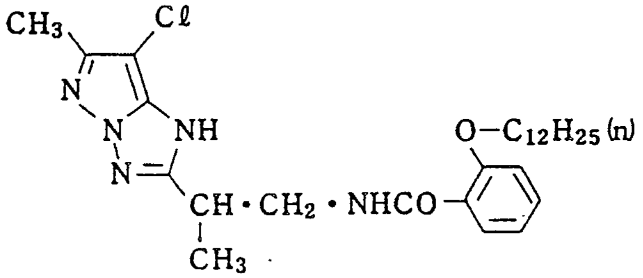
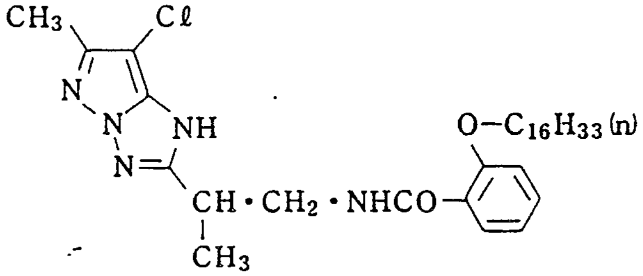


(I-48)



(I-49)



Now compounds represented by formula (II) are described in detail.

Substituents in formula (II) are as follows:

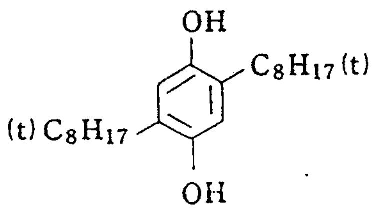
R_{15} and R_{16} each represent a hydrogen atom, a substituted or unsubstituted alkyl group (preferably having 1 to 24 carbon atoms, e.g., methyl, ethyl, n-butyl, n-amyl, t-amyl, n-octyl, t-octyl, n-dodecyl, n-octadecyl, 2-methoxyethyl, 2-ethoxyethyl, 2-phenylethyl, benzyl, and 3-cyanopropyl), a substituted or unsubstituted alkenyl group (preferably having 2 to 24 carbon atoms, e.g., ally, octenyl, and oleyl), a substituted or unsubstituted aryl group (preferably having 6 to 24 carbon atoms, e.g., phenyl, tolyl, 4-t-butylphenyl, and naphthyl), a substituted or unsubstituted acyl group (preferably having 1 to 24 carbon atoms, e.g., acetyl and octanoyl), a substituted or unsubstituted cycloalkyl group (preferably having 3 to 24 carbon atoms, e.g., cyclohexyl and cyclopentyl), or a substituted or unsubstituted nitrogen-containing heterocyclic group (preferably having 1 to 24 carbon atoms e.g., imidazolyl, furyl, pyridyl, triazinyl, thiazolyl, and 3,5-didodecyl-4-butoxyphenyl).

R_{17}, R_{18}, R_{19}, and R_{20} each represent a hydrogen atom, a halogen atom (e.g., fluorine, chlorine, or bromine), a substituted or unsubstituted alkyl group (preferably having 1 to 24 carbon atoms, e.g., methyl, ethyl, n-propyl, i-propyl, n-butyl, t-butyl, n-amyl, i-amyl, n-octyl, t-octyl, n-dodecyl, n-octadecyl, 2-methoxyethyl, 2-ethoxyethyl, 2-phenylethyl, benzyl, and 3-cyanopropyl), a substituted or unsubstituted alkenyl group (preferably having 2 to 24 carbon atoms, e.g., ally and octenyl), a substituted or unsubstituted aryl group (preferably having 6 to 24 carbon atoms e.g., phenyl, tolyl, naphthyl, and methoxyphenyl), a substituted or unsubstituted cycloalkyl group (preferably having 3 to 24 carbon atoms e.g., cyclohexyl and cyclopentyl), a substituted or unsubstituted alkoxy group (preferably having 1 to 24 carbon atoms e.g., methoxy, ethoxy, dodecyloxy, ethoxyethoxy, and phenoxymethoxy), a substituted or unsubstituted alkylthio group (preferably having 1 to 24 carbon atoms e.g., methylthio, n-butylthio, and n-dodecylthio), a substituted or unsubstituted arylthio group (preferably having 6 to 24 carbon atoms e.g., phenylthio and dimethylphenylthio), a substituted or unsubstituted heterocyclic thio group (e.g., tetrazolyl, thiazolyl, and oxazolyl), a substituted or unsubstituted aryloxy group (preferably having 6 to 24 carbon atoms e.g., phenoxy and methylphenoxy), a substituted or unsubstituted acyl group (preferably having 1 to 24 carbon atoms e.g., acetyl and octanoyl), a substituted or unsubstituted acylamino group (preferably having 1 to 24 carbon atoms e.g., acetylamino, octanoylamino and benzoylamino), a substituted or unsubstituted alkylamino group (preferably having 1 to 24 carbon atoms e.g., methylamino, diethylamino, n-octylamino and dodecylamino), a substituted or unsubstituted alkoxycarbonyl group (preferably having 2 to 24 carbon atoms e.g., methoxycarbonyl and benzyloxycarbonyl), a substituted or unsubstituted aryloxycarbonyl group (preferably having 7 to 24 carbon atoms e.g., phenoxycarbonyl and ethylphenoxycarbonyl), a carbamoyl group (preferably having 1 to 24 carbon atoms e.g., methylcarbamoyl, octadecylcarbamoyl and phenylcarbamoyl), a sulfamoyl group (e.g., methylsulfamoyl and octadecylsulfamoyl), or a sulfonic acid group, provided that when R_{17}, R_{18}, R_{19}, and R_{20} are simultaneously hydrogen atoms, R_{15} and R_{16} are not hydrogen atoms simultaneously. R_{18} and R_{20} may bond together to form a substituted or unsubstituted 5- or 6-membered ring.

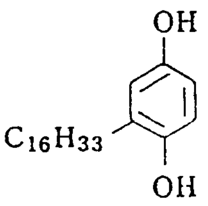
The number of carbon atom is preferably 1 to 24 when the substituent contains carbon atom. Of the above mentioned substituents, R_{15} and R_{16} each are preferably a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, more preferably R_{15} and R_{16} are both hydrogen atoms, and R_{17}, R_{18}, R_{19}, and R_{20} each are preferably a hydrogen atom or an alkyl group having 1 to 18 carbon atoms, more preferably sum of carbon atom numbers of R_{17}, R_{18}, R_{19}, and R_{20} is 24 or below. The number of carbon atom above-mentioned means a total number of carbon atoms.

Specific examples of compounds represented by formula (II) are shown below.

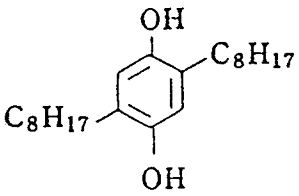
(H−1)



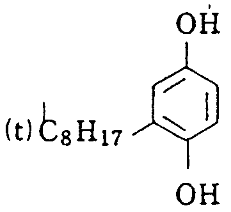
(H−2)



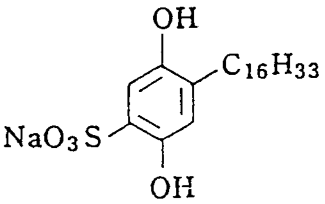
(H−3)



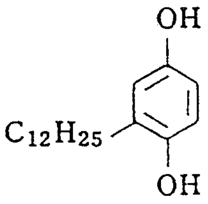
(H−4)



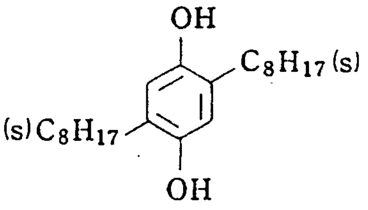
(H−5)



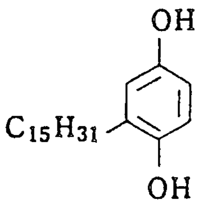
(H−6)



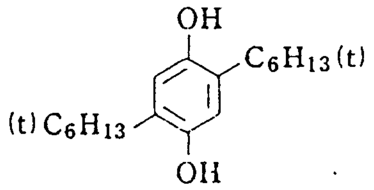
(H-7)



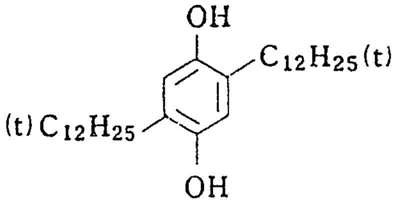
(H-8)



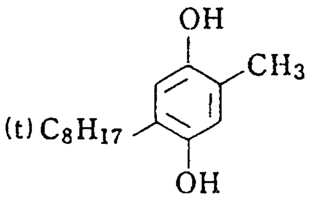
(H-9)



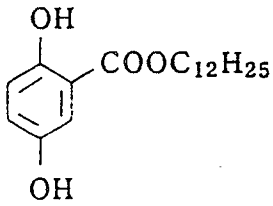
(H-10)



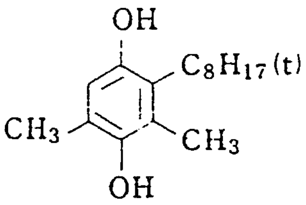
(H-11)



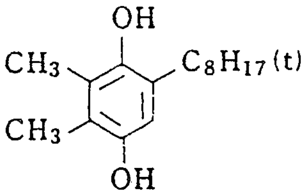
(H-12)



(H-13)



(H-14)



These compounds are added together with a hydrophilic colloid to the nonphotosensitive layer situated between the yellow coupler-containing silver halide emulsion layer and the magenta coupler-containing silver halide emulsion layer, in an amount between 7.75 x 10^{-5} mol/m^2 and 9.00 x 10^{-4} mol/m^2, with the coating amount of the hydrophilic colloid being 1.1 g/m^2 or over. If the amount of the compounds is less than 7.75 x 10^{-5} mol/m^2, the effect of the present invention will not be exhibited sufficiently, whereas if the amount exceeds 9.00 x 10^{-4} mol/m^2, it will bring about such adverse effects that not only the color density of the adjacent yellow coupler-containing silver halide emulsion layer or magenta coupler-containing silver halide emulsion layer lowers, and the development of the silver halide emulsion layer situated nearer the support is made slow, but also the fastness of the color-developed dye of the adjacent yellow coupler-containing silver halide emulsion layer, and in some cases the magenta coupler-containing silver halide emulsion layer, is hampered. By "the coating amount of the hydrophilic colloid" is meant the solid content of the hydrophilic colloid used in the particular nonphotosensitive layer.

If the amount of the hydrophilic colloid in the nonphotosensitive layer is less than 1.1 g/m^2, the effect of the present invention will not be sufficiently exhibited, and although the greater the amount thereof is, the more highly the effect thereof is exhibited, a highly greater amount will result in such an adverse effect that the development of the silver halide emulsion layer situated nearer the support is made slow. The coating amounts of the hydrophilic colloid to be contained in the particular nonphotosensitive layer and the compound represented by formula (II) are about 1.0 g/m^2 or below and about 1.0 x 10^{-4} mol/m^2 or below respectively, even, for example, in commercially available color papers or in known literature, including JP-A No. 267050/1986, whereas in the present invention their coating amounts are greater than those, which is one of features of the present invention.

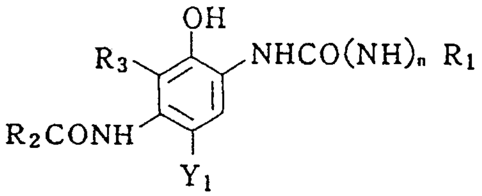
In the present invention, although it is enough if the coating amount of the hydrophilic colloid is 1.1 g/m^2 or over, preferably the coating amount is in the range of 1.1 to 3.0 g/m^2, and more preferably in the range of 1.1 to 2.2 g/m^2. The coating amount of the compound represented by formula (II) is between 7.75 x 10^{-5} mol/m^2 and 9.00 x 10^{-4} mol/m^2, preferably between 1.00 x 10^{-4} mol/m^2 and 8.00 x 10^{-4} mol/m^2, and more preferably between 1.00 x 10^{-4} mol/m^2 and 4.0 x 10^{-4} mol/m^2.

As the hydrophilic colloid that can be used in the intermediate layer and the emulsion layers of the photographic material of the present invention, gelatin is preferably used, although other hydrophilic colloids can be used. For instance, proteins, such as gelatin derivatives, graft polymers of gelatin and other polymer, albumin, and case in; cellulose derivatives, such as hydroxyethyl cellulose, carboxymethylcellulose, and cellulose sulfate; saccharide derivatives, such as starch derivatives and sodium alginate; and various synthetic hydrophilic polymers, such as homopolymers and copolymers, for example polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole, and polyvinylpyrazole, can be used.

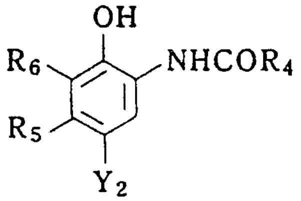
As the gelatin, general-purpose lime-treated gelatin as well as acid-processed gelatins and enzyme-processed gelatins, as described in Bull. Soc. Sci. Phot. Japan, No. 16, page 30 (1966), can be used, and hydrolyzates of gelatin can also be used.

Cyan couplers and yellow couplers preferably used in the present invention are those represented by the following formulae (III), (IV) and (V):

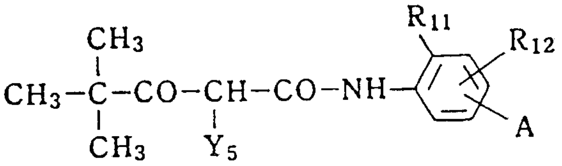
Formula (III)



Formula (IV)



Formula (V)



wherein R_1, R_2, and R_4 each represent a substituted or unsubstituted aliphatic, aromatic, or heterocyclic group, R_3, R_5, and R_6 each represent a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, or an acylamino group, R_3 may represent, together with R_4, a non-metal atom group forming a nitrogen-containing 5-membered ring or 6-membered ring, and Y_1 and Y_2 each represent a hydrogen atom or a group that can split off when the compound couples with the oxidized product of developing agents.

R_5 in formula (IV) is preferably an aliphatic group, such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentadecyl group, a t-butyl group, a cyclohexyl group, a cyclohexylmethyl group, a phenylthiomethyl group, a dodecyloxyphenylthiomethyl group, a butaneamidomethyl group, and a methoxymethyl group.

Preferable examples of cyan couplers represented by formula (III) or (IV) are as follows:

R_1 in formula (III) is preferably an aryl group or a heterocyclic group, and more preferably an aryl group that is 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 oxycarbonyl group, or a cyano group.

If R_3 and R_2 in formula (III) do not together from a ring, preferably R_2 represents a substituted or unsubstituted alkyl group or aryl group, and particularly preferably an alkyl group substituted by a substituted aryloxy group, and R_3 represents preferably a hydrogen atom.

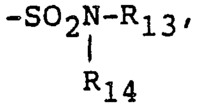
Preferably R_4 in formula (IV) represents a substituted or unsubstituted alkyl group or aryl group, and particularly preferably an alkyl group that is substituted by a substituted aryloxy group.

Preferably R_5 in formula (IV) represents an alkyl group having 2 to 15 carbon atoms or a methyl group having a substituent with 1 or more carbon atoms, the substituent preferably being an arylthio group, an alkylthio group, an acylamino group, an aryloxy group, or an alkyloxy group.

More preferably R_5 in formula (IV) represents an alkyl group having 2 to 15 carbon atoms, and particularly preferably an alkyl group having 2 to 4 carbon atoms.

Preferably R_6 in formula (IV) represents a hydrogen atom or a halogen atom, with a chlorine atom or a fluorine atom being particularly preferable. Preferably Y_1 and Y_2 in formula (III) and (IV) each represent a hydrogen atom, a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, or a sulfonamido group.

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

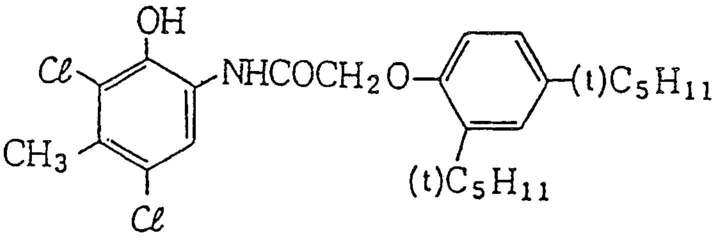


$$-SO_2\underset{\displaystyle R_{14}}{\underset{|}{N}}-R_{13},$$

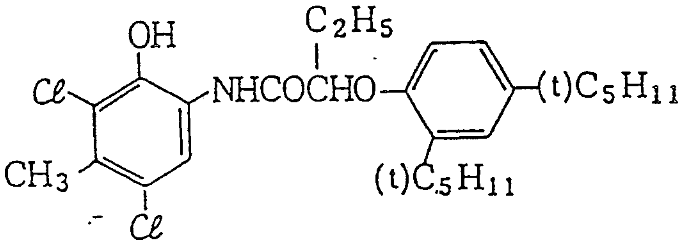
in which R_{13} and R_{14} each represent an alkyl group, and Y_5 represents a split-off group. The substituents of R_{12}, R_{13}, and R_4 are the same as those allowed for R_1, and preferably the split-off group Y_5 is of a type wherein the split-off will occur at the oxygen atom or the nitrogen atom, with particular preference given to the latter.

Specific examples of couplers represented by formulae (III) to (V) are:

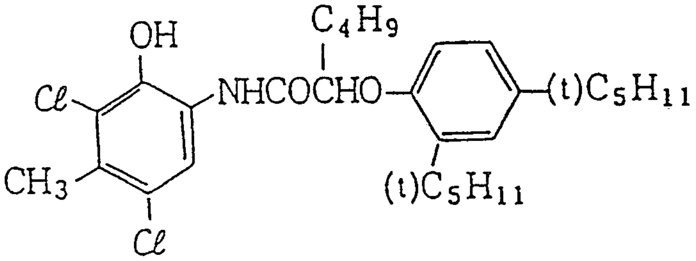
(C − 1)



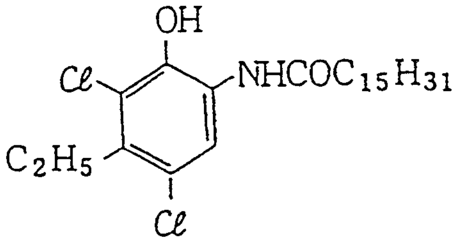
(C − 2)



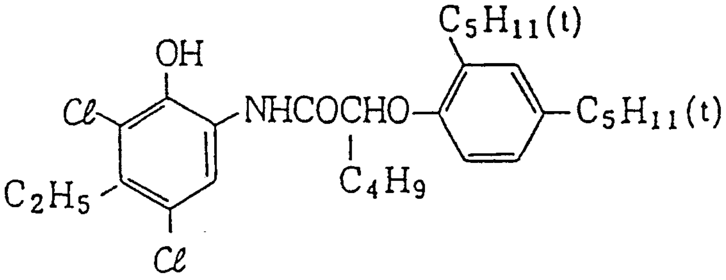
(C − 3)



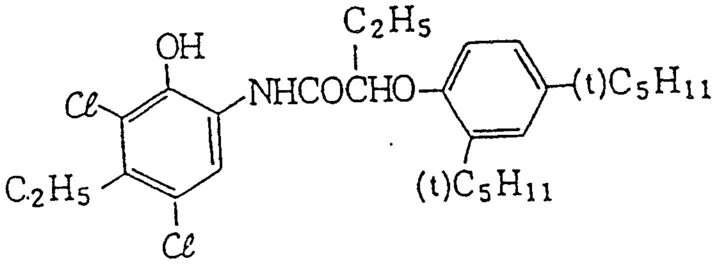
(C − 4)



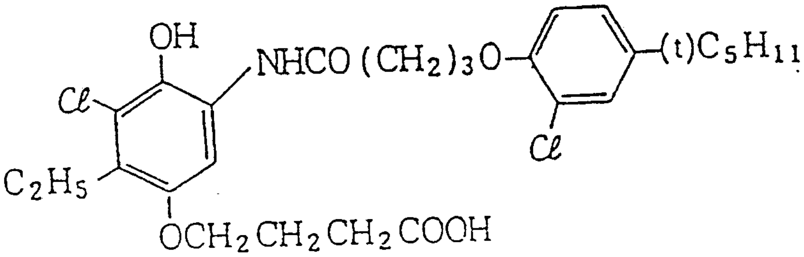
(C − 5)



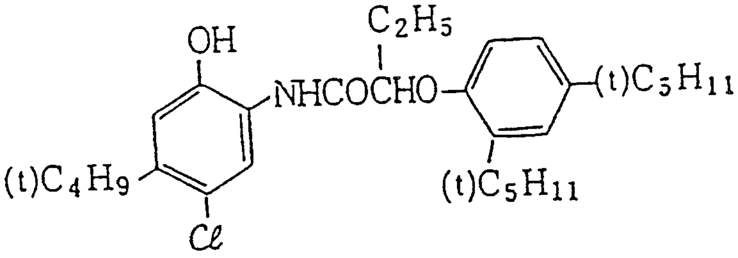
(C − 6)



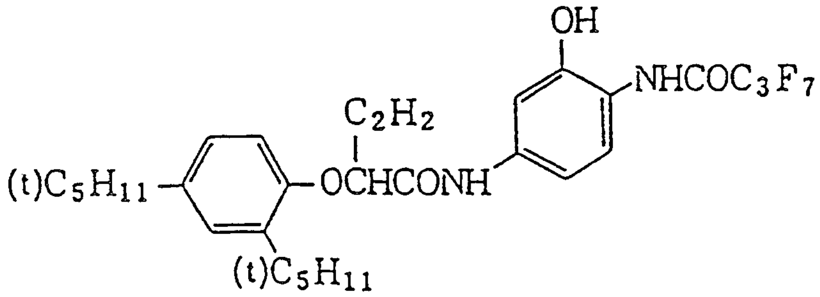
(C − 7)



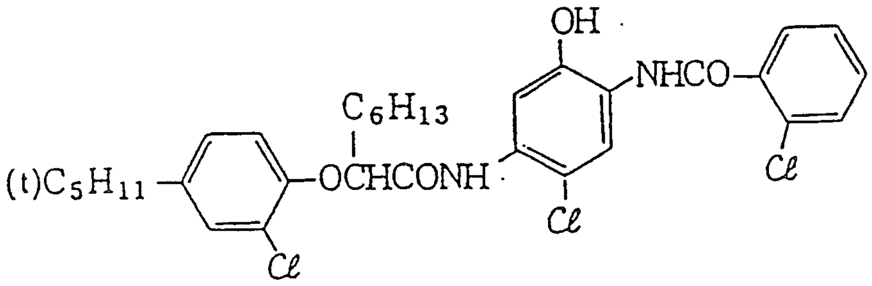
(C − 8)



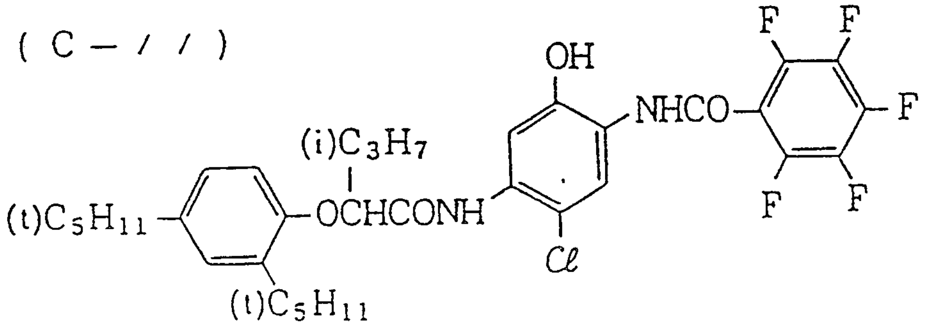
(C-9)



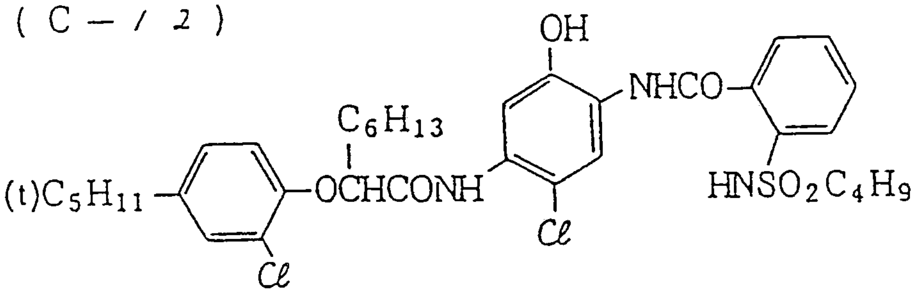
(C-10)



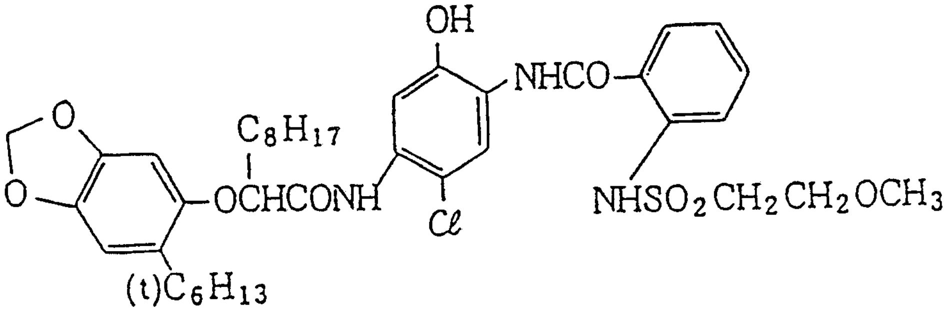
(C-11)



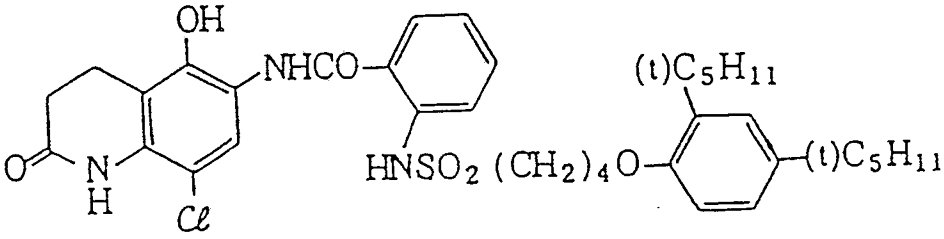
(C-12)



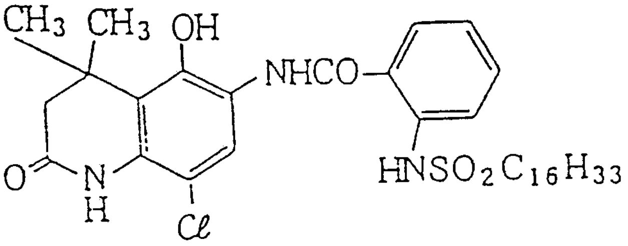
(C-13)



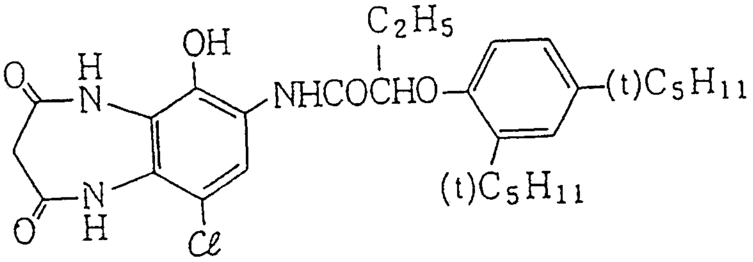
(C-14)



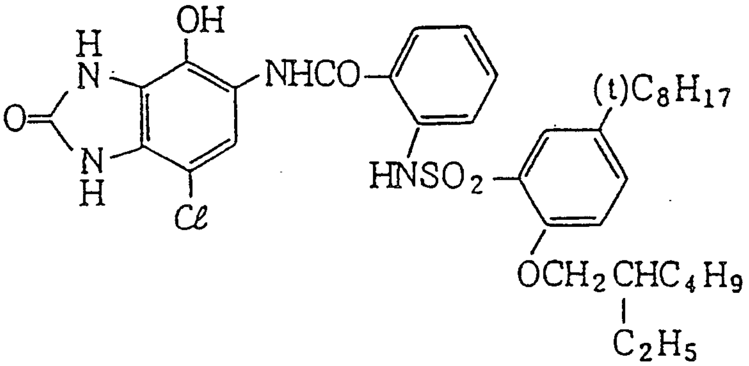
(C-15)



(C-16)

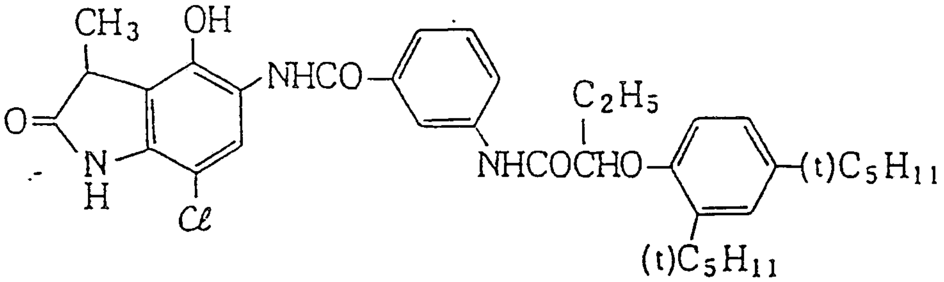


(C－17)



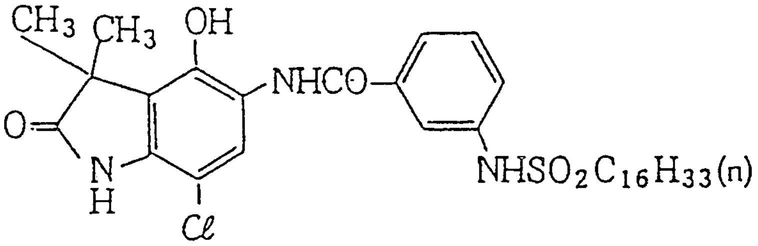
OH
H
N
O
N
H
Cl
NHCO
HNSO2
(t)C8H17
OCH2CHC4H9
C2H5

(C－18)



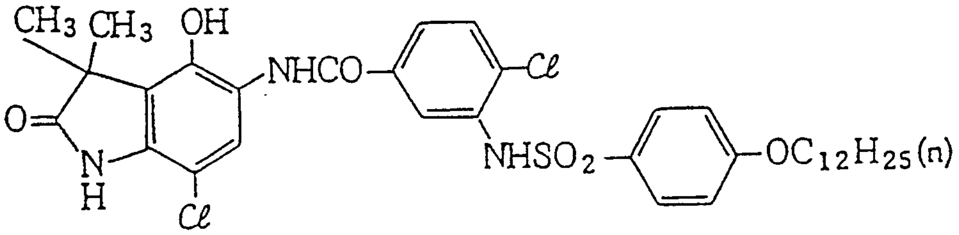
CH3
OH
O
N
H
Cl
NHCO
C2H5
NHCOCHO
(t)C5H11
(t)C5H11

(C－19)

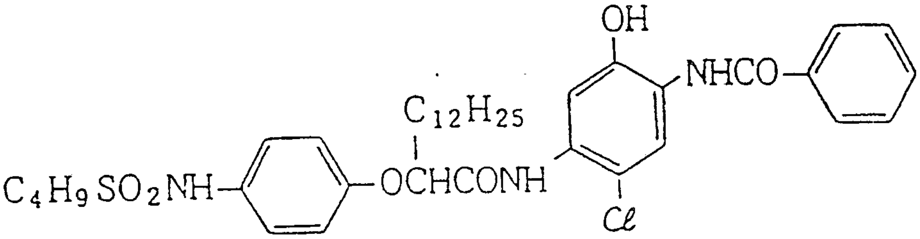


CH3
CH3
OH
O
N
H
Cl
NHCO
NHSO2C16H33(n)

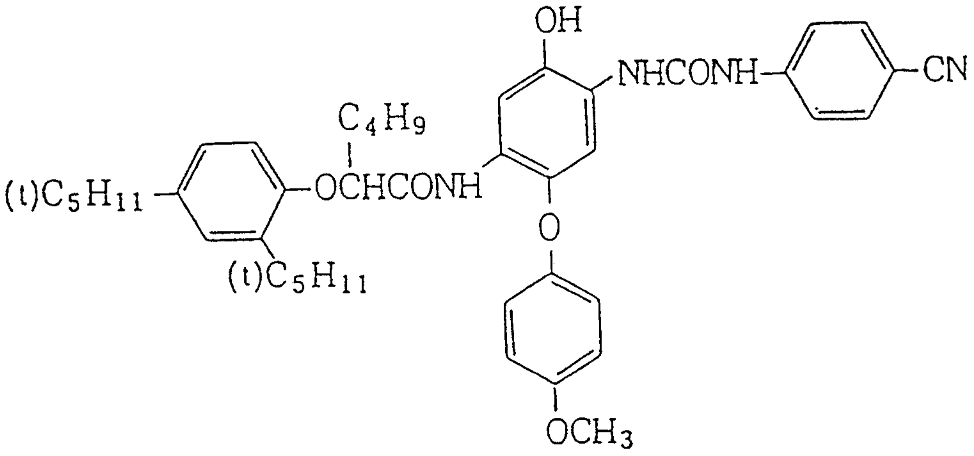
(C－20)



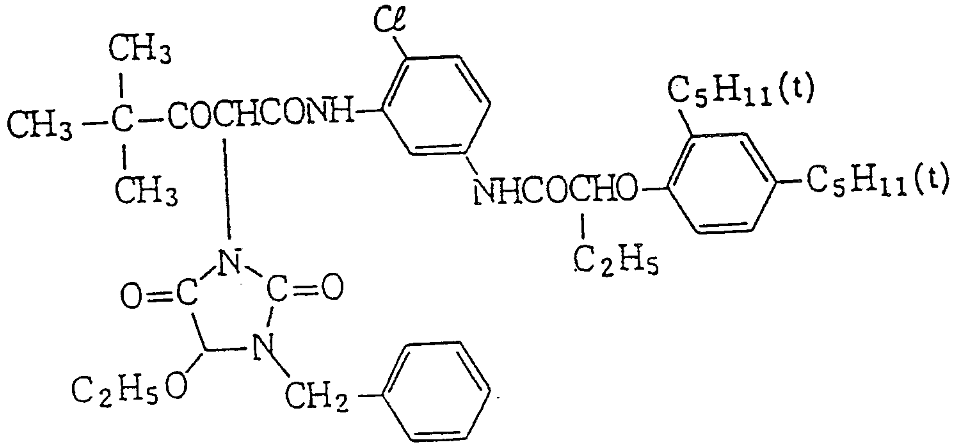
(C－21)



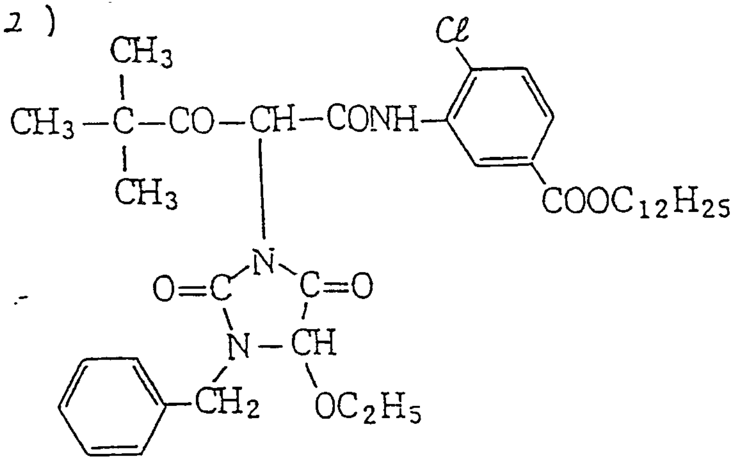
(C－22)



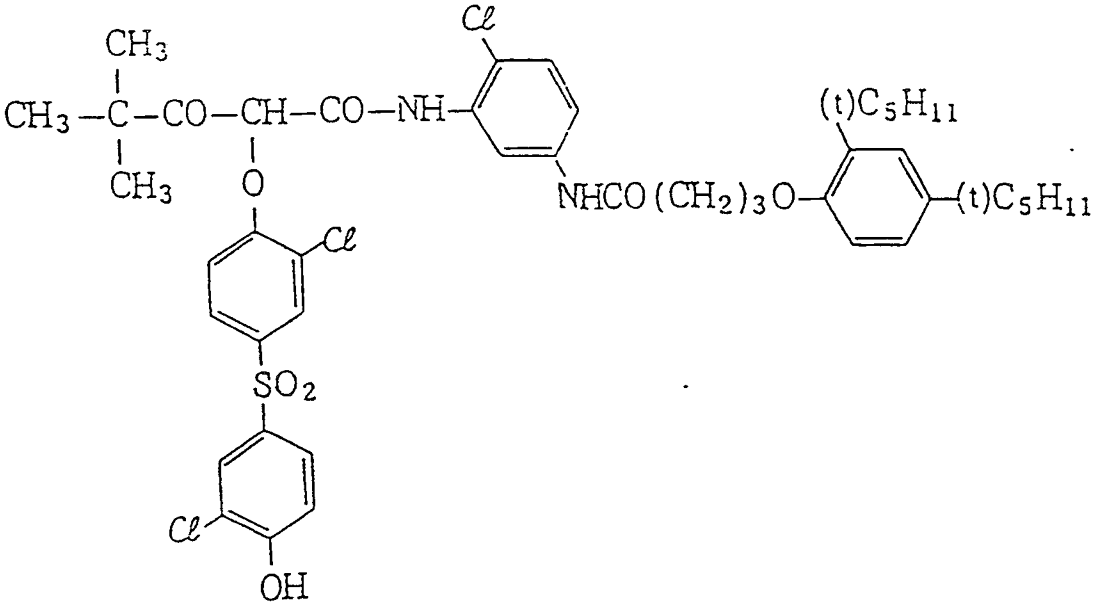
(Y — 1)



(Y — 2)



(Y — 3)



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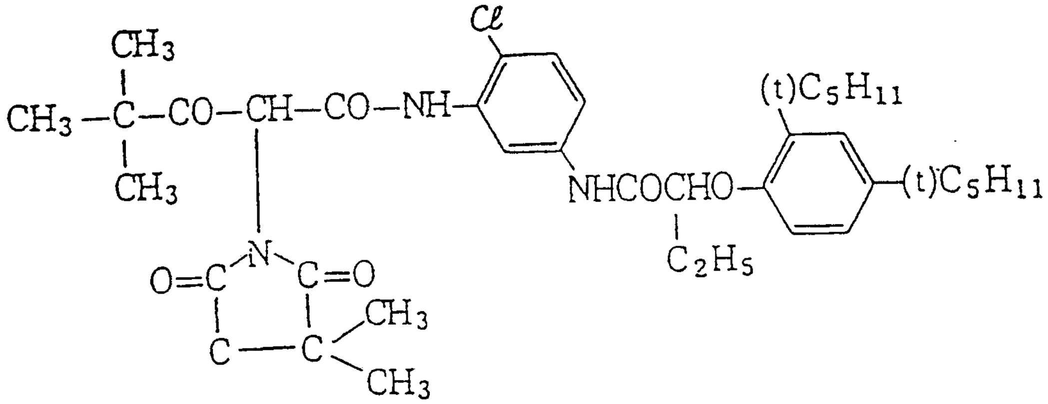
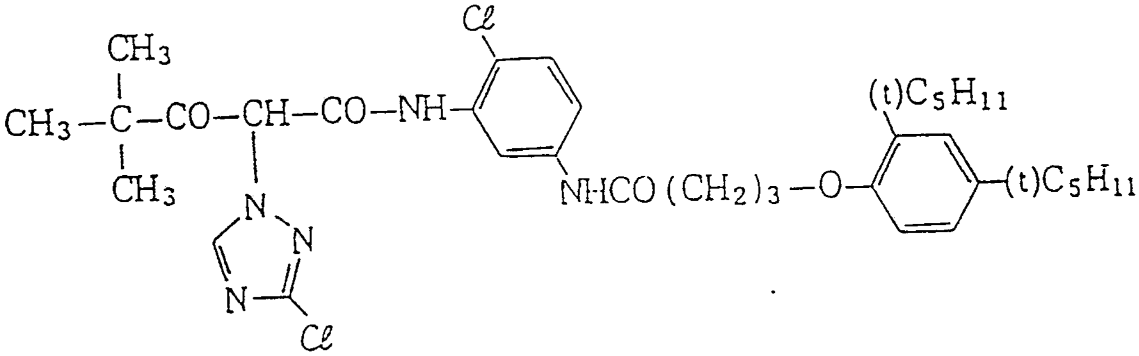
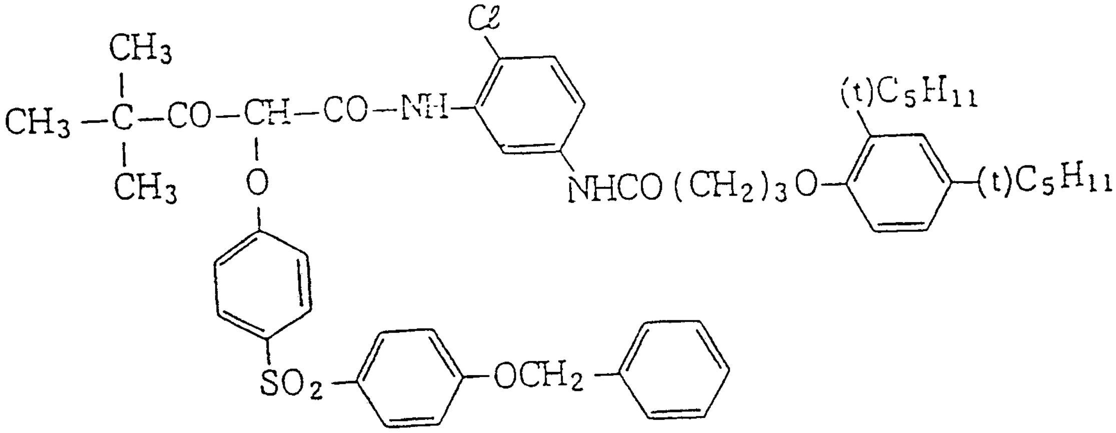


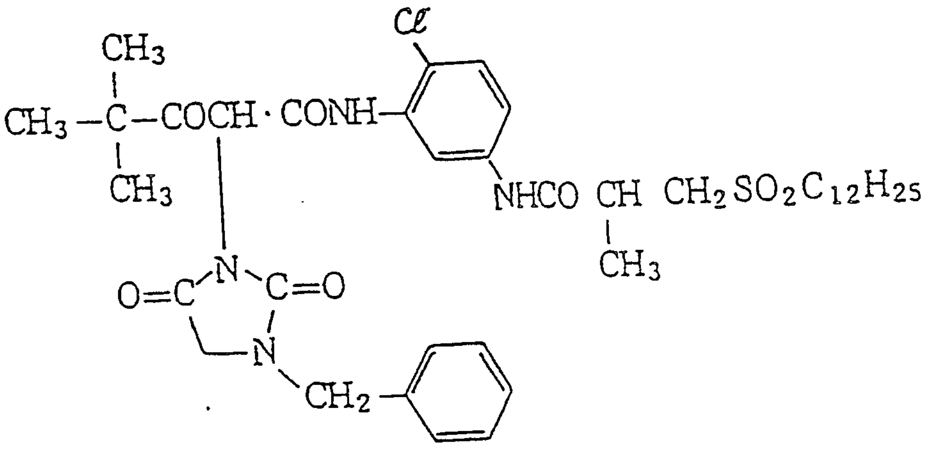
(Y − 5)



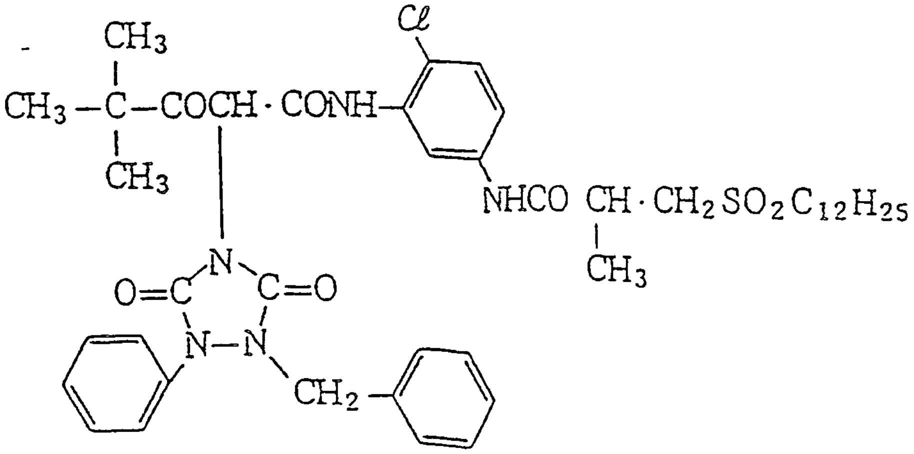
(Y − 6)



(Y－7)



(Y－8)

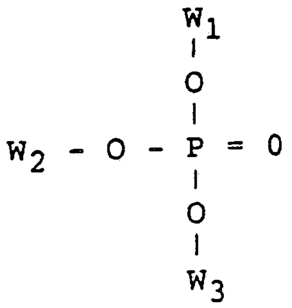


In the present invention, in order to add the above couplers to the photographic layers, various known techniques can be applied. Generally the addition can be carried out by the oil-in-water dispersion method, known as the oil protect method, wherein the coupler is dissolved in a solvent and the solution is emulsified and dispersed into an aqueous gelatin solution containing a surface-active agent. Alternatively water or an aqueous gelatin solution may be added to a coupler solution containing a surface-active agent, to obtain an oil-in-water dispersion with phase inversion of emulsion being accompanied. Couplers soluble in alkalis can be dispersed by the so-called Fischer dispersion method. The low-boiling organic solvent may be removed from the coupler dispersion, for example, by distillation, noodle washing, or ultrafiltration, and the resulting mixture may be mixed with a photographic emulsion.

As the dispersant for the couplers, water-insoluble polymer compounds and/or high-boiling organic solvents having a dielectric constant of 2 to 20 (25°C) and a refractive index of 1.3 to 1.7 (25°C) are preferably used.

As the high-boiling organic solvents, preferably high-boiling organic solvents represented by the following formulae (A) to (E) are used.

Formula (A)

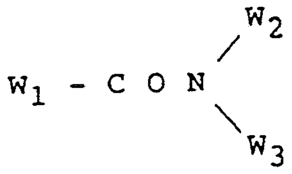


$$W_2-O-\overset{\overset{\displaystyle W_1}{|}}{\underset{\underset{\displaystyle W_3}{|}}{\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{\overset{|}{\underset{|}{P}}}}}}=O$$

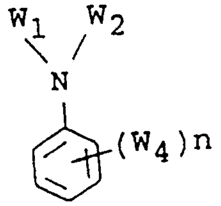
Formula (B)

$$W_1-COO-W_2$$

Formula (C)



Formula (D)



Formula (E)

$$W_1-O-W_2$$

wherein W_1, W_2, and W_3 each represent a substituted or unsubstituted alkyl group, cycloalkyl group, alkenyl group, aryl group or heterocyclic group, W_4 represents W_1, OW_1, or S-W_1, n is an integer of 1 to 5, W_4 groups may be the same or different when n is 2 or over, and in formula (E), W_1, and W_2 may together form a condensed ring.

In addition to the high-boiling organic solvents represented by formula (A) to (E), other high-boiling organic solvents can be used in the present invention if they are compounds which have a melting point of 100° C or below and a boiling point of 140° C, are incompatible with water, and are good solvents for the coupler. Preferably the melting point of the high-boiling organic solvents is 80° C or below. Preferably the boiling point of the high-boiling organic solvents is 160° C or over, and more preferably 170° C or over.

Details of these high-boiling organic solvents are described in JP-A No. 215272/1987, in the right lower column on page 137 to the right upper column on page 144.

The couplers can also be emulsified and dispersed into a hydrophilic colloid aqueous solution by impregnating them into a loadable latex polymer (e.g., see U.S. Patent No. 4,203,716) in the presence or absence of the above-mentioned high-boiling point organic solvent, or by dissolving it in a water-insoluble and organic-solvent-soluble polymer.

Preferably monopolymers or copolymers described on pages 12 to 30 of International Publication No. WO 88/00723 are used, and more preferably acrylamide polymers are used because, for example, the dye image is stabilized.

The photographic material that is prepared according to the present invention may contain, as a color antifoggant, for example, a hydroquinone derivative, an aminophenol derivative, a gallic acid derivative, or an ascorbic acid derivative.

In the photographic material of the present invention, various discoloration inhibitors can be used. As organic discoloration inhibitors for cyan, magenta, and/or yellow images, typical examples are hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols, hindered phenols, including bisphenols, gallic acid derivatives, methylenedioxybenzenes, aminophenols, and hindered amines, and ether or ester derivatives thereof, obtained by silylating or alkylating the phenolic hydroxyl group of these compounds. Metal complexes such as (bissalicylaldoxymato)nickel complexes and (bis-N,N-dialkyldithiocarbamato)nickel complexes can also be used.

Specific examples of organic discoloration inhibitors are described in the following patent specifications.

Hydroquinones are described, for example, in U.S. Patent Nos. 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 No. 1,363,921, and U.S. Patent Nos. 2,710,801 and 2,816,028; 6-hydroxychromans, 5-hydroxycoumarans, and spirochromans are described, for example, in U.S. Patent Nos. 3,432,300, 3,573,050, 3,574,627, 3,698,909, and 3,764,337, and JP-A No. 152225/1987; spiroindanes are described, for example, in U.S. Patent No. 4,360,589; p-alkoxyphenols are described, for example, in U.S. Patent No. 2,735,765, British Patent No. 2,066,975, JP-A No. 10539/1984, and JP-B No. 19765/1982; hindered phenols are described, for example, in U.S. Patent No. 3,700,455, JP-A No. 72224/1977, U.S. Patent No. 4,228,235, and JP-B No. 6623/1977; gallic acid derivatives, methylenedioxybenzenes, and aminophenols are described, for example, in U.S. Patent Nos. 3,457,079 and 4,332,886 and JP-B No. 21144/1981, respectively; hindered amines are described, for example, in U.S. Patent Nos. 3,336,135 and 4,268,563, British Patent Nos. 1,32889, 1,354,313, and 1,410,846, JP-B No. 1420/1976, and JP-A Nos. 114036/1983, 53846/1984, and 78344/1984; ether and ester derivatives obtained by silylating or alkylating their phenolic hydroxyl group are described, for example, in U.S. Patent Nos. 4,155,765, 4,174,220, 4,254,216, and 4,264,720, JP-A No. 145530/1979, 6321/1980, 105147/1983, and 10539/1984, JP-B No. 37856/1982, U.S. Patent No. 4,279,990, and JP-B No. 3263/1978; and metal complexes are described, for example, in U.S. Patent No. 4,050,938 and 4,241,155 and British Patent No. 2,027,731 (A). These compounds are coemulsified with respective couplers generally in amounts of 5 to 100 wt.% for respective couplers, and are added to photosensitive layers to attain the purpose. For the purpose of preventing the cyan dye image from being deteriorated by heat and light, it is more effective to introduce an ultraviolet-absorbing agent into the cyan color-forming layer and the layers opposite the cyan color-forming layer.

As the ultraviolet-absorbing agent, benzotriazoles substituted by a aryl group (e.g., those described in U.S. Patent No. 3,533,794), 4-thiazolidone compounds (e.g., those described in U.S. Patent Nos. 3,314,794 and 3,352,681), benzophenone compounds (e.g., those described in JP-A No. 2784/1971), cinnamate compounds (e.g., those described in U.S. Patent No. 3,705,805 and 3,707,375), butadiene compounds (e.g., those described in U.S. Patent No. 4,045,229), or benzooxidol compounds (e.g., those described in U.S. Patent No. 3,700,455) can be used. Ultraviolet-absorbing couplers (e.g., α-naphthol-type cyan dye-forming couplers), ultraviolet-absorbing polymers, etc., can also be used. These ultraviolet-absorbing agents may be mordanted to a particular layer.

Of these ultraviolet absorbing agents, benzotriazoles substituted by an aryl group are particularly preferable.

In the present invention, together with the above couplers, the following compounds are preferably used. The use in combination with a pyrazoloazole coupler is, in particular, preferable.

That is, it is preferred that a compound (F), which will chemically bond to the aromatic amine developing agent remaining after the color-developing process, to form a chemically inactive and substantially colorless compound, and/or a compound (G), which will chemically bond to the oxidized product of the aromatic amine color developing agent remaining after the color-developing process, to form a chemically inactive and substantially colorless compound, are used simultaneously or separately, for example, to prevent the occurrence of stain due to the formation of a color-developed dye by the reaction of the couplers with the color-developing agent remaining in the layer during storage after the processing or with the oxidized product of the color-developing agent, and to prevent other side effects.

Preferable as compound (F) are those that can react with p-anisidine at the second-order reaction-specific rate k_2 (in trioctyl phosphate at 80° C) in the range of 1.0 ℓ/mol•sec to 1 x 10^{-5} ℓ/mol•sec. The second-order reaction-specific rate can be determined by the method described in JP-A No. 158545/1983.

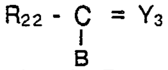
If k_2 is over this range, the compound itself becomes unstable, and in some cases the compound reacts with gelatin or water to decompose. On the other hand, if k_2 is below this range, the reaction with the remaining aromatic amine developing agent becomes slow, resulting, in some cases, in the failure to prevent the side effects of the remaining aromatic amine developing agent.

More preferable as compound (F) are those that can be represented by the following formula (FI) or (FII):

Formula (FI)

$R_{21} - (A)_n - X_3$

Formula (FII)



$$R_{22} - \underset{\displaystyle B}{\underset{|}{C}} = Y_3$$

wherein R_{21} and R_{22} each represent an aliphatic group, an aromatic group, or a heterocyclic group, n is 1 or 0, A represents a group that will react with an aromatic amine developing agent to form a chemical bond therewith, X_3 represents a group that will react with the aromatic amine developing agent and split off, B represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, or a sulfonyl group, Y_3 represents a group that will facilitate the addition of the aromatic amine developing agent to the compound represented by formula (FII), and R_{21} and X_3, or Y_3 and R_{22} or B, may bond together to form a ring structure.

Of the processes wherein compound (F) bonds chemically to the remaining aromatic amine developing agent, typical processes are a substitution reaction and an addition reaction.

Preferable examples of the compounds represented by formulae (FI) and (FII) include those described, for example, in JP-A Nos. 158545/1988, 283338/1987, and 2042/1989, and European Published Patent No. 277589.

On the other hand, more preferable examples of compound (G), which will chemically bond to the oxidized product of the aromatic amine developing agent remaining after color development processing, to form a chemically inactive and colorless compound, can be represented by the following formula (GI):

Formula (GI)

R - Z

wherein R represents an aliphatic group, an aromatic group, or a heterocyclic group, Z represents a nucleophilic group or a group that will decompose in the photographic material to release a nucleophilic group. Preferably the compounds represented by formula (GI) are ones wherein Z represents a group whose Pearson's nucleophilic $^{n}CH_3I$ value (R.G. Pearson, et al., J. Am. Chem. Soc., 90, 319 (1968)) is 5 or over, or a group derived therefrom.

Specific examples of compounds represented by formula (GI) described, for example, in European Published Patent No. 255722, JP-A Nos. 143048/1987 and 229145/1987, Japanese Patent Application No. 136724/1988, JP-A Nos. 57259/1989 and 2042/1989, and European Published Patent No. 277589 are preferable.

Details of combinations of compound (G) and compound (F) are described in European Published Patent No. 277,589.

The photographic material prepared in accordance with the present invention may contain, in the hydrophilic colloid layer, water-soluble dyes as filter dyes or to prevent irradiation and for other various purposes. Such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Among others, oxonol dyes, hemioxonol dyes, and merocyanine dyes are useful.

As a binder or a protective colloid that can be used in the emulsion layers of the present photographic material, gelatin is advantageously used, but other hydrophilic colloids can be used alone or in combination with gelatin.

In the present invention, gelatin may be lime-treated gelatin or acid-processed gelatin. Details of the manufacture of gelatin is described by Arthur Veis in The Macromolecular Chemistry of Gelatin (published by Academic Press, 1964).

As a base to be used in the present invention, a transparent film, such as cellulose nitrate film, and polyethylene terephthalate film or a reflection-type base that is generally used in photographic materials can be used. For the objects of the present invention, the use of a reflection-type base is more preferable.

The "reflection base" to be used in the present invention is one that enhances reflectivity, thereby making sharper the dye image formed in the silver halide emulsion layer, and it includes one having a base coated with a hydrophobic resin containing a dispersed light-reflective substance, such as titanium oxide, zinc oxide, calcium carbonate, and calcium sulfate, and also a base made of a hydrophobic resin containing a dispersed light-reflective substance. For example, there can be mentioned baryta paper, polyethylene-coated paper, polypropylene-type synthetic paper, a transparent base having a reflective layer, or additionally using a reflective substance, such as glass plate, polyester films of polyethylene terephthalate, cellulose triacetate, or cellulose nitrate, polyamide film, polycarbonate film, polystyrene film, and vinyl chloride resin, which may be suitably selected in accordance with the purpose of the application.

It is advantageous that, as the light-reflective substance, a white pigment is kneaded well in the presence of a surface-active agent, and it is preferable that the surface of the pigment particles has been treated with a divalent to tetravalent alcohol.

The occupied area ratio (%) per unit area prescribed for the white pigments finely divided particles can be obtained most typically by dividing the observed area into contiguous unit areas of 6 μm x 6 μm, and measuring the occupied area ratio (%) (Ri) of the finely divided particles projected onto the unit areas. The deviation coefficient of the occupied area ratio (%) can be obtained based on the ratio s/R, wherein s stands for the standard deviation of Ri, and R stands for the average value of Ri. Preferably, the number (n) of the unit areas to be subjected is 6 or over. Therefore, the deviation coefficient s/R can be obtained by

$$\sqrt{\frac{\sum_{i=1}^{n}(R_i-\bar{R})^2}{n-1}} \Bigg/ \frac{\sum_{i=1}^{n}R_i}{n}$$

In the present invention, preferably the deviation coefficient of the occupied area ratio (%) of the finely divided particles of a pigment is 0.15 or below, and particularly 0.12 or below. If the deviation coefficient is 0.08 or below, it can be considered that the substantial dispersibility of the particles is substantially "uniform."

The color developer to be used in the developing process for the photographic material of the present invention is preferably an aqueous alkali solution whose major component is an aromatic primary amine color-developing agent. As this color-developing agent, aminophenol compounds are useful, but preferably p-phenylenediamine compounds are used. Typical examples thereof include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesufonamidoethylaniline, and 3-methyl-4-amino-N-ethyl-N-β-methoxyaniline, and their sulfates, hydrochlorides, and p-toluenesulfonates. Two or more of them may be combined to achieve the purpose.

The color developer generally contains, for example, pH buffers, such as carbonates, borates, or phosphates of alkali metals, development restrainers, such as bromides, iodides, benzimidazoles, benzothiazoles, or mercapto compounds, or antifoggants. If necessary the color developer contains various preservatives, such as hydroxyamine, diethylhydroxylamine, sulfites, hydrazines, phenylsemicarbazides, triethanolamine, catecholsulfonates, and triethylenediamine(1,4-diazabicyclo[2,2,2]octane), organic solvents, such as ethylene glycol and diethylene glycol, development accelerators, such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts, and amines, dye forming couplers, competing couplers, fogging agents, such as sodium boron hydride, auxiliary developers, such as 1-phenyl-3-pyrazolidone, viscosity increasers, and various chelate agents, such as aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids, and phosphonocarboxylic acids, for example ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodinoacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′,N′-tetramethylenephosphonic acid, and ethylenediamine-di(o-hydroxyphenylacetic acid), and their salts.

If a reversal process is effected, generally black-and-white development is first carried out, and then color development is carried out. In this black-and-white developing solution, use is made of a known black-and-white developing agent, such as hydroxybenzenes such as hydroquinone, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, and aminophenols such as N-methyl-p-aminophenol, which may be used alone or in combination.

Generally the pH of this color developer and black-and-white developing solution is 9 to 12. The replenishing amount of these developing solutions is generally 3 or below per square meter of the color photographic material to be processed, though the replenishing amount changes depending on the type of color photographic material, and if the concentration of bromide ions in the replenishing solution is lowered previously, the replenishing amount can be lowered to 500 m or below per square meter of the color photographic material. If it is intended to lower the replenishing amount, it is preferable to prevent the evaporation of the solution and oxidation of the solution with air by reducing the area of the processing tank that is in contact with the air.

It is also possible to reduce the replenishing amount by using means of suppressing the accumulation of bromide ions in the developer.

The photographic emulsion layer are generally subjected to a bleaching process after color development.

The bleaching process can be carried out together with the fixing process (bleach-fixing process), or it can be carried out separately from the fixing process. Further, to quicken the process bleach-fixing may be carried out after the bleaching process. In accordance with the purpose, the process may be arbitrarily carried out using a bleach-fixing bath having two successive tanks, or a fixing process may be carried out before the bleach-fixing process, or a bleaching process.

As the bleaching agent, use can be made of, for example, compounds of polyvalent metals, such as iron (III), cobalt (III), chromium (VI), and copper (II), peracids, quinones, and nitro compounds. As typical bleaching agents, use can be made of ferricyanides; dichromates; organic complex salts of iron (II) or cobalt

(III), such as complex salts of aminopolycarboxylic acids, for example ethylenediaminetetraacetic acid, diethylenetriaminetetraacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid, citric acid, tartaric acid, and malic acid; persulfates; bromates; permanganates; and nitrobenzenes. Of these, aminopolycarboxylic acid iron (III) complex salts, including ethylenediaminetetraacetic acid iron (III) complex salts are particularly useful in a bleaching solution as well as a bleach-fix solution. The pH of the bleaching solution or the leach-fix solution using these aminopolycarboxylic acid iron (III) complex salts is generally 5.5 to 8, but if it is required to quicken the process, the process can be effected at a lower pH.

In the bleaching solution, the bleach-fix solution, and the baths preceding them a bleach-accelerating solution may be used if necessary. Examples of useful bleach-accelerating agents are compounds having a mercapto group or a disulfide linkage, described in U.S. Patent No. 3,893,858, West German Patent Nos. 1,290,812, JP-A No. 95630/1978, and Research Disclosure No. 17129 (July, 1978); thiazolidine derivatives, described in JP-A No. 140129/1975 thiourea derivatives, described in U.S. Patent No. 3,706,561; iodide salts, described in JP-A No. 16235/1983; polyoxyethylene compounds, described in West German Patent No. 2,748,430; polyamine compounds, described in JP-B No. 8836/1970; and bromide ions. Of these, compounds having a mercapto group or a disulfide group are preferable in view of higher acceleration effect, and in particular, compounds described in U.S. Patent No. 3,893,858, West German Patent No. 1,290,812, and JP-A No. 95630/1978 are preferable. Compounds described in U.S. Patent No. 4,552,834 are preferable. These bleach-accelerating agents may be added into the photographic material. When the color photographic materials for photographing are to be bleach-fixed, these bleach-accelerating agents are particularly effective.

As a fixing agent can be mentioned thiosulfates, thiocyanates, thioether-type compounds, thioureas, and large amounts of iodide salts, although thiosulfate is used usually, and in particular ammonium thiosulfate is widely used. As the preservative for bleach-fix solution sulfite salt, bisulfite salt, or carbonyl-bisulfite adduct is preferable.

It is common for the silver halide color photographic material of the present invention to undergo, after a desilvering process such as fixing or bleach-fix, a washing step and/or a stabilizing step. The amount of washing water may be set within a wide range depending on the characteristics (e.g., due to the materials used, such as couplers), the application of the photographic material, the washing temperature, the number of washing tanks (the number of steps), the type of replenishing system, including, for example, the counter-current system and the direct flow system, and other various conditions. Of these, the relationship between the number of water-washing tanks and the amount of washing water in the multi-stage counter-current system can be found according to the method described in Journal of Society of Motion Picture and Television Engineers, Vol. 64, pages 248 to 253 (May, 1955).

According to the multi-stage-counter-current system described in the literature mentioned above, thiocyanates, thioether-type compounds, thioureas, and large amounts of iodide salts, although thiosulfate is used usually, and in particular ammonium thiosulfate is widely used. As the preservative for bleach-fix solution sulfite salt, bisulfite salt, or carbonyl-bisulfite adduct is preferable.

It is common for the silver halide color photographic material of the present invention to undergo, after a desilvering process such as fixing or bleach-fix, a washing step and/or a stabilizing step. The amount of washing water may be set within a wide range depending on the characteristics (e.g., due to the materials used, such as couplers), the application of the photographic material, the washing temperature, the number of washing tanks (the number of steps), the type of replenishing system, including, for example, the counter-current system and the direct flow system, and other various conditions. Of these, the relationship between the number of water-washing tanks and the amount of washing water in the multi-stage counter-current system can be found according to the method described in Journal of Society of Motion Picture and Television Engineers, Vol. 64, pages 248 to 253 (May, 1955).

According to the multi-stage-counter-current system described in the literature mentioned above, although the amount of washing water can be considerably reduced, bacteria propagate with an increase of retention time of the washing water in the tanks, leading to a problem with the resulting suspend matter adhering to the photographic material. In processing the present color photographic material, as a measure to solve this problem, the method of reducing calcium and magnesium described in JP-A No. 288838/1987 can be used quite effectively. Also chlorine-type bactericides such as sodium chlorinated isocyanurate, cyabendazoles, isothiazolone compounds described in JP-A No. 8542/1982, benzotriazoles, and other bactericides described in Hiroshi Horiguchi "Bokin Bobaizai no Kagaku" in "Biseibutsu no Mekkin, Sakkin, Bobaigijutsu" edited by Eiseigijutsu-kai, and in "Bokin Bobaizai Jiten", edited by Nihon Bokin Bobai-Gakkai, can be used.

The pH of the washing water used in processing the present photographic material is 4 to 9, preferably

5 to 8. The washing water temperature and the washing time to be set may vary depending, for example, on the characteristics and the application of the photographic material, and they are generally selected in the range of 15 to 45°C for 20 sec. to 10 min., and preferably in the range of 25 to 40°C for 30 sec. to 5 min. Further, the photographic material of the present invention can be processed directly with a stabilizing solution instead of the above washing. In such a stabilizing process, any of known processes, for example, a multi-step counter-current stabilizing process or its low-replenishing-amount process, described in JP-A Nos. 8543/1982, 14834/1983, and 220345/1985.

In some cases, the above washing process is further followed by a stabilizing process, and as an example thereof can be mentioned a stabilizing bath that is used as a final bath for color photographic materials for photography, which contains formalin and a surface-active agent. In this stabilizing bath, each kind of the chelating agents and bactericides may be added.

The over-flowed solution due to the replenishing of washing solution and/or stabilizing solution may be reused in other steps, such as a desilvering step.

The silver halide color photographic material of the present invention may contain therein a color-developing agent for the purpose of simplifying and quickening the process. To contain such a color-developing agent, it is preferable to use a precursor for a color-developing agent. For example, indoaniline-type compounds described in U.S. Patent No. 3,342,597, Schiff base-type compounds described in U.S. Patent No. 3,342,599 and Research Disclosure Nos. 14850 and 15159, aldol compounds described in Research Disclosure No. 13924, metal salt complexes described in U.S. Patent No. 3,719,492, and urethane-type compounds described in JP-A No. 135628/1978 can be mentioned.

For the purpose of accelerating the color development, the present silver halide color photographic material may contain, if necessary, various 1-phenyl-3-pyrazolidones. Typical compounds are described in JP-A No. 64339/1981, 144547/1982, and 115438/1983.

The various processing solutions used for the present invention are used at 10 to 50°C. Although generally a temperature of 33 to 38°C is standard, a higher temperature can be used to accelerate the process to reduce the processing time, or a lower temperature can be used to improve the image quality or the stability of the processing solutions. Also, to save the silver of the photographic material, a process using hydrogen peroxide intensification or cobalt intensification described in West German Patent No. 2,226,770 and U.S. Patent No. 3,674,499 may be carried out.

The silver halide color photographic material of the present invention is high in sensitivity and contrast, and excellent in color reproduction and dye image stability. According to the present invention, processing color contamination, which is liable to occur in silver halide color photographic materials excellent in color reproduction and dye image stability, can be prevented, thereby permitting a silver halide color photographic material to be provided wherein the quality is made fairly high, and which is stabilized.

Next, the present invention will be described in detail in accordance with examples, but the invention is not limited to these embodiments.

Example 1

A photographic material was prepared by multi-coatings composed of the following layer composition on a two-side polyethylene laminated paper support.

Composition of Layers

Composition of layers:

The composition of each layer is shown below. Each ingredient is indicated in a coating amount (g/m^2), but the coating amount of the silver halide emulsion is indicated in terms of silver.
Support:
Polyethylene-laminated paper support [the polyethylene of the first layer side contained a white pigment (TiO_2) and a bluish dye (ultramarine)]

First layer (Blue-sensitive emulsion layer):	
Monodisperse silver chlorobromide emulsion (EM-1) added spectral-sensitizing agent (Sen-1)	0.09
Monodisperse silver chlorobromide emulsion (EM-2) added spectral-sensitizing agent (Sen-1)	0.21
Fogging inhibitor (Cpd-1)	0.004
Gelatin	1.28
Yellow coupler (ExY)	0.68
Fogging inhibitor (Cpd-2)	0.006
Solvent (mixture of Solv-1 and Solv-2 in a volume ratio of 1 : 1)	0.24

Second layer (Color-mix preventing layer):	
Gelatin	0.89
Color-mix inhibitor (H-1)	0.024
Solvent (mixture of Solv-3 and Solv-4 in a volume ratio of 1 : 1)	0.20

Third Layer (Green-sensitive emulsion layer):	
Monodisperse silver chlorobromide emulsion added spectral-sensitizing agent (Sen-2 and -3)	0.125
Fogging inhibitor (Cpd-1)	0.002
Fogging inhibitor (Cpd-5)	0.001
Gelatin	1.47
Magenta coupler (ExM)	0.26
Image-dye stabilizer (Cpd-6)	0.10
Image-dye stabilizer (Cpd-7)	0.08
Image-dye stabilizer (Cpd-8)	0.03
Image-dye stabilizer (Cpd-9)	0.004
Solvent (mixture of Solv-3 and Solv-5 in a volume ratio of 1 : 2)	0.65

Fourth Layer (Ultraviolet ray absorbing layer):	
Gelatin	1.43
Ultraviolet adsorbent (mixture of UV-1, -2, and -3 in a molar ratio of 1 : 4 : 4)	0.47
Color-mix inhibitor (Cpd-4)	0.05
Solvent (Solv-6)	0.24

Fifth Layer (Red-sensitive emulsion layer):	
Monodisperse silver chlorobromide emulsion (EM-3) added spectral-sensitizing agent (Sen-4 and -5)	0.06
Monodisperse silver chlorobromide emulsion (EM-4) added spectral-sensitizing agent (Sen-4 and -5)	0.14
Fogging inhibitor (Cpd-2)	0.008
Fogging inhibitor (Cpd-10)	0.0001
Fogging inhibitor (Cpd-11)	0.0001
Gelatin	0.85
Cyan coupler (ExC-1)	0.13
Cyan coupler (ExC-2)	0.15
Image-dye stabilizer (mixture of UV-1, -2, and -3 in a molar ratio of 1 : 3 : 3)	0.067
Image-dye stabilizer (Cpd-3)	0.25
Image-dye stabilizer (Cpd-7)	0.004
Image-dye stabilizer (Cpd-8)	0.007
Solvent (Solv-1)	0.16

Sixth Layer (Ultraviolet ray absorbing layer):	
Gelatin	0.38
Ultraviolet absorbent (mixture of UV-1, -2, and -3 in a molar ratio of 1 : 4 : 4)	0.13
Solvent (Solv-6)	0.06

Seventh layer (Protective layer)	
Gelatin	1.25
Acryl-modified copolymer of polyvinyl alcohol (modification degree : 17%)	0.05
Liquid paraffin	0.02

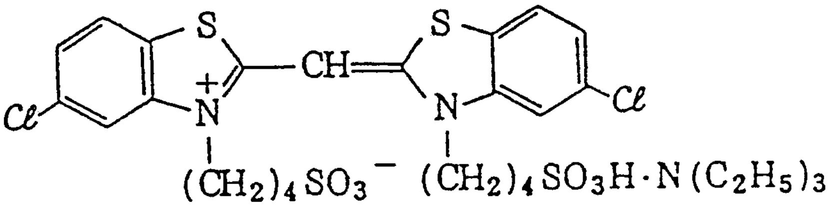
Details of silver halide emulsions used in the above sample are shown in Table 1.

Table 1

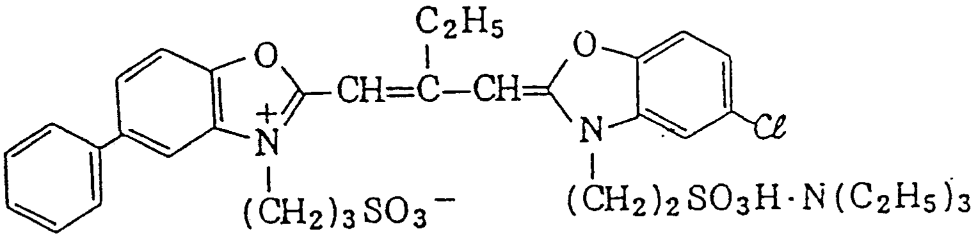
Emulsion	Shape	Average grain size (µm)	Br-content (mol%)	Deviation coefficient*
EM-1	Cubic	0.88	79	0.06
EM-2	Cubic	0.65	80	0.06
EM-3	Cubic	0.48	74	0.10
EM-4	Cubic	0.34	74	0.10
Note :				

* Deviation coefficient = Standard deviation/Average grain size

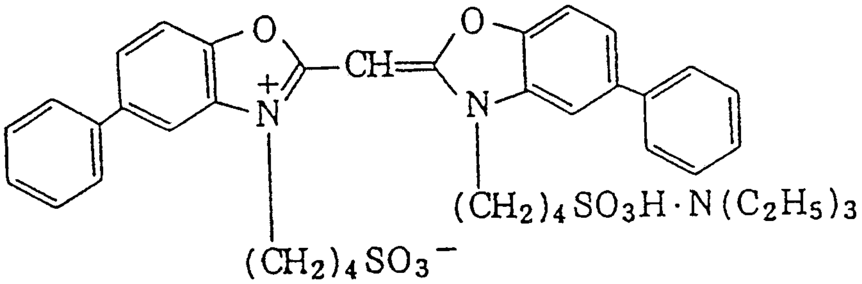
(Sen - 1) 3.8 x 10^{-4} mol/Ag•mol



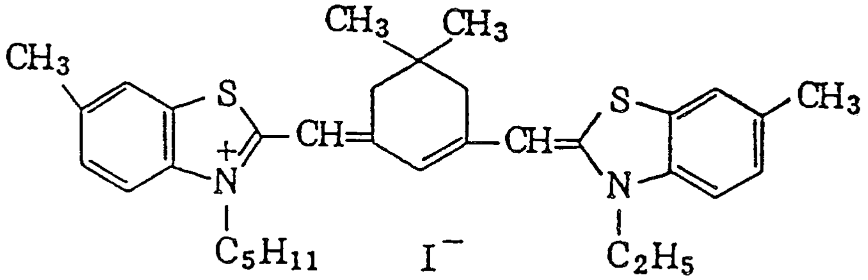
(Sen - 2) 2.1 x 10^{-4} mol/Ag•mol



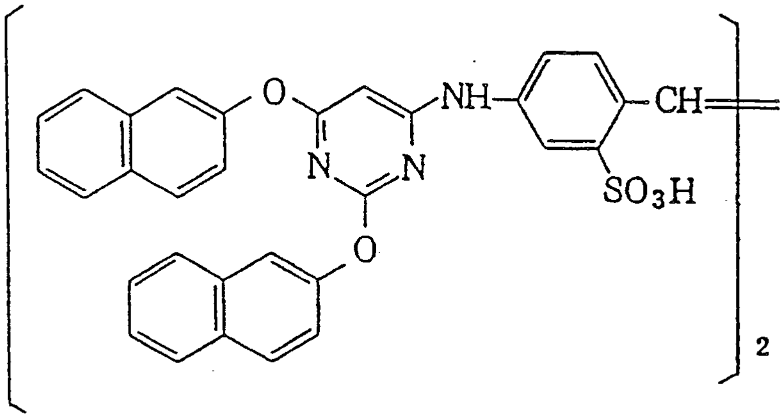
(Sen - 3) 4.2 x 10^{-5} mol/Ag•mol



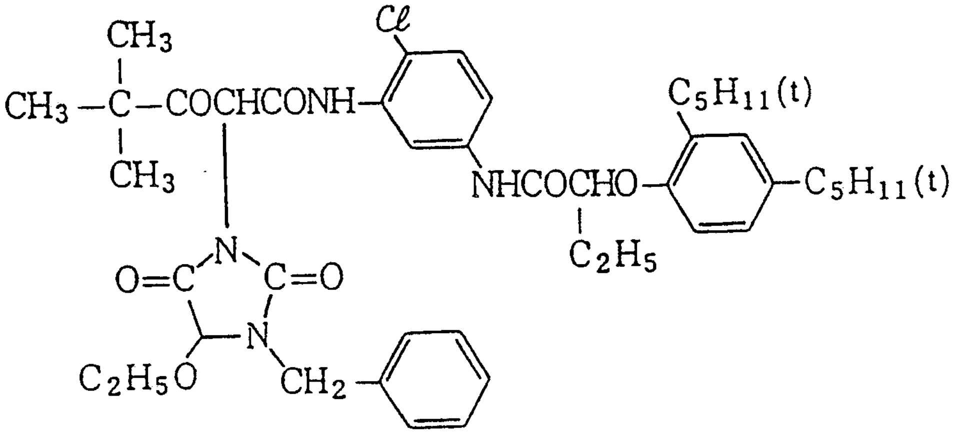
(Sen - 4) 6.1 x 10^{-5} mol/Ag•mol



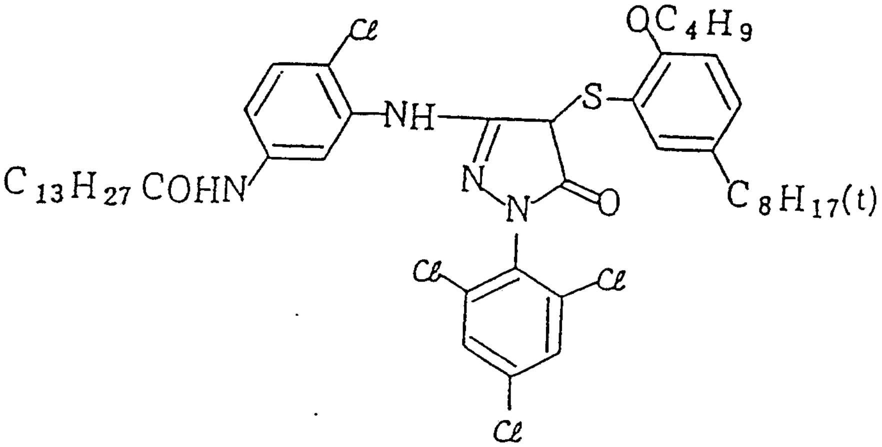
(Sen - 5) 2.3 x 10^{-3} mol/Ag•mol



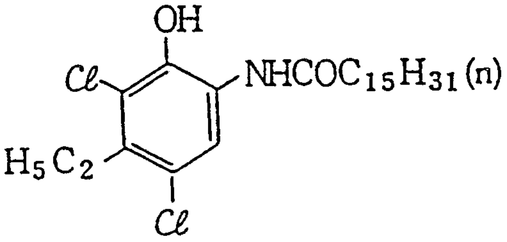
(E x Y)


CH3
CH3—C—COCHCONH—
CH3
Cl
C5H11(t)
NHCOCHO—
C2H5
—C5H11(t)
O=C N C=O
N
C2H5O
CH2—

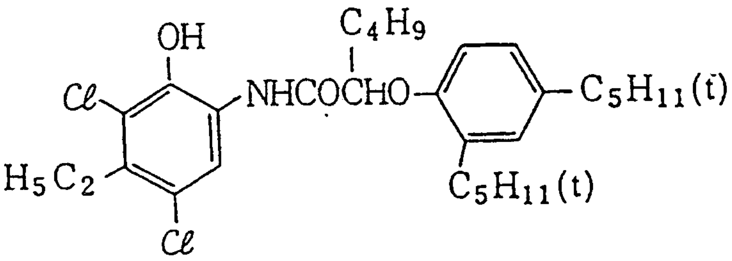
(E x M)


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

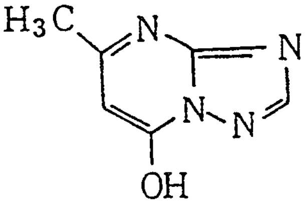
(ExC－1)



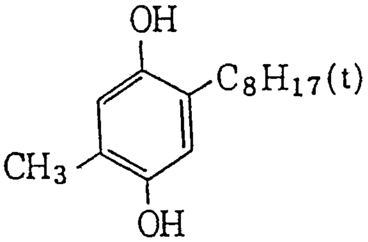
(ExC－2)



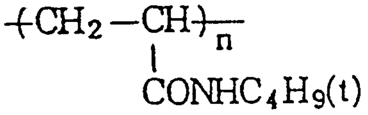
(Cpd－1)



(Cpd－2)



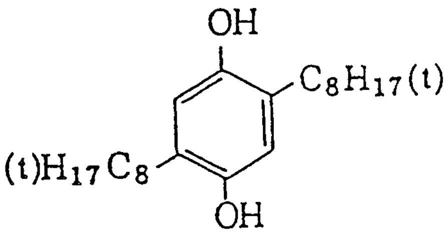
(Cpd-3)



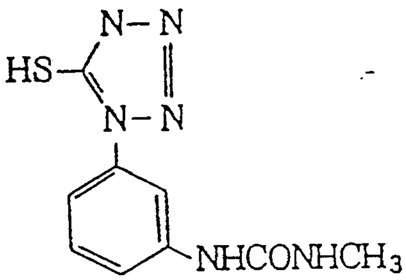
$$-\!\left(CH_2-\underset{\displaystyle CONHC_4H_9(t)}{\underset{|}{CH}}\right)_{\!n}\!-$$

Molecular weight : about 60,000

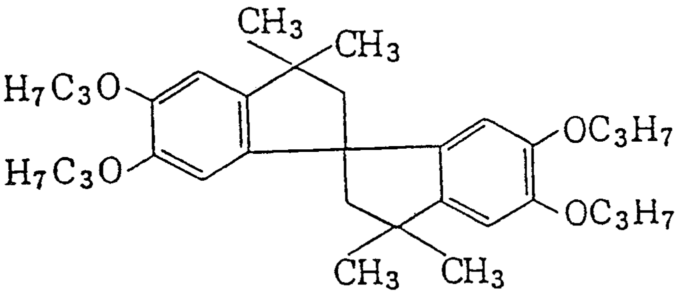
(Cpd-4)



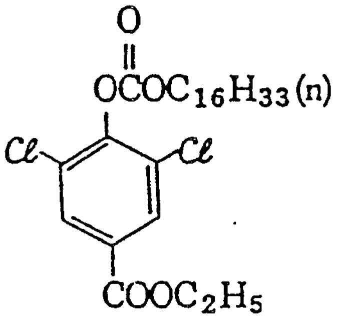
(Cpd-5)



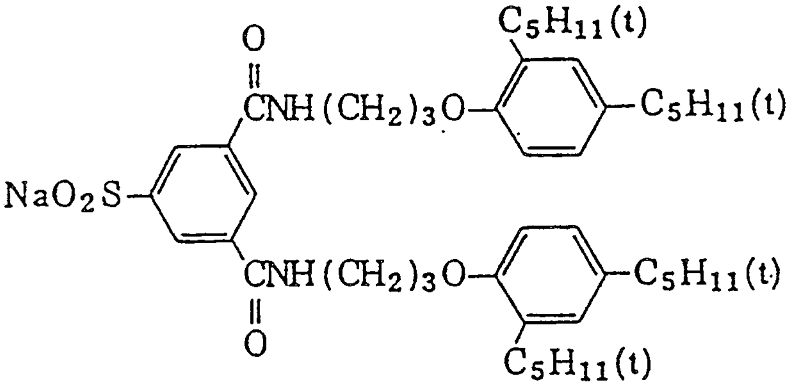
(Cpd-6)



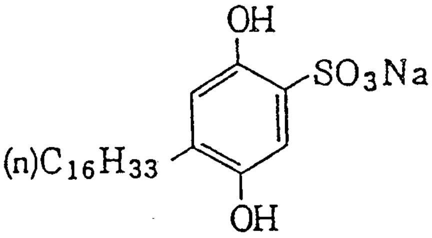
(Cpd-7)



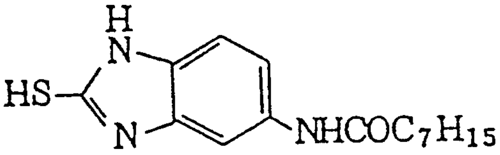
(Cpd-8)



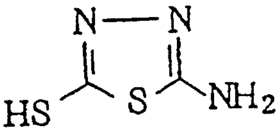
(Cpd-9) Image-dye stabilizer



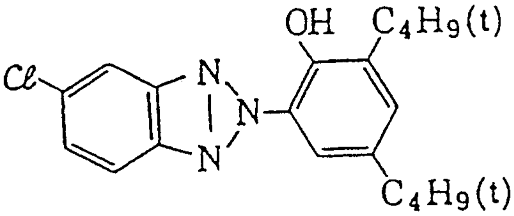
(Cpd−10)



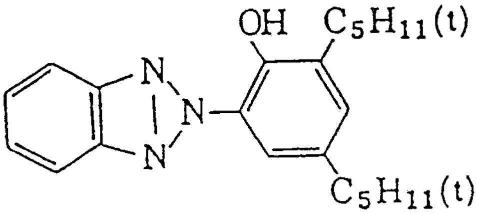
(Cpd−11)



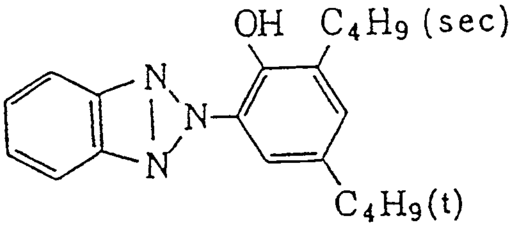
(UV−1)



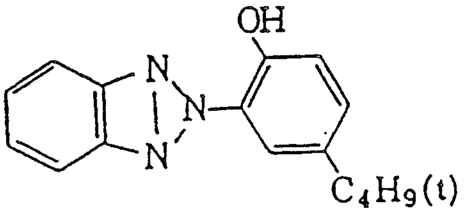
(UV−2)



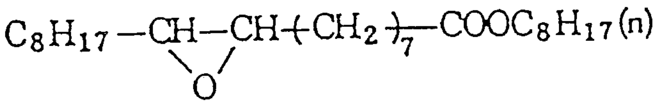
(UV−3)



(UV-4)



(Solv-1)

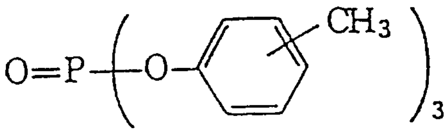


$C_8H_{17}-\underset{\diagdown O \diagup}{CH-CH}-(CH_2)_7-COOC_8H_{17}(n)$

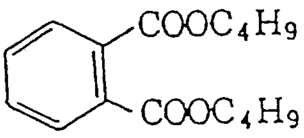
(Solv-2)

$O=P(OC_9H_{19}(iso))_3$

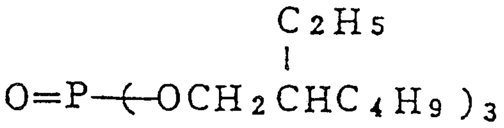
(Solv-3)



(Solv-4)

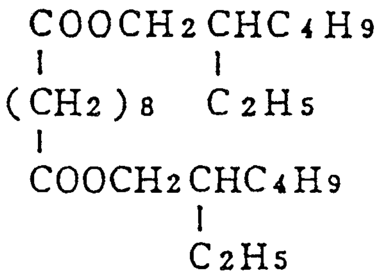


(Solv-5)

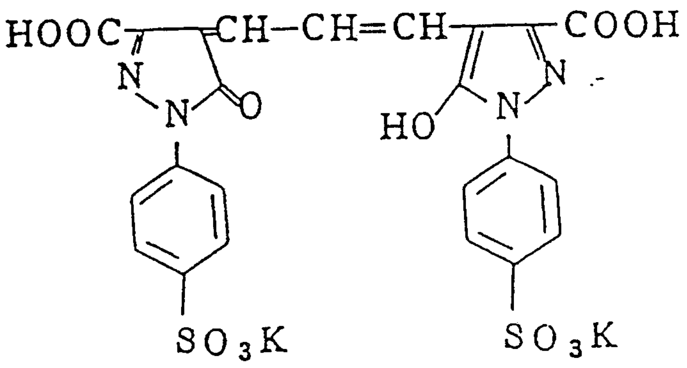


$O=P-(OCH_2\overset{C_2H_5}{\overset{|}{C}}HC_4H_9)_3$

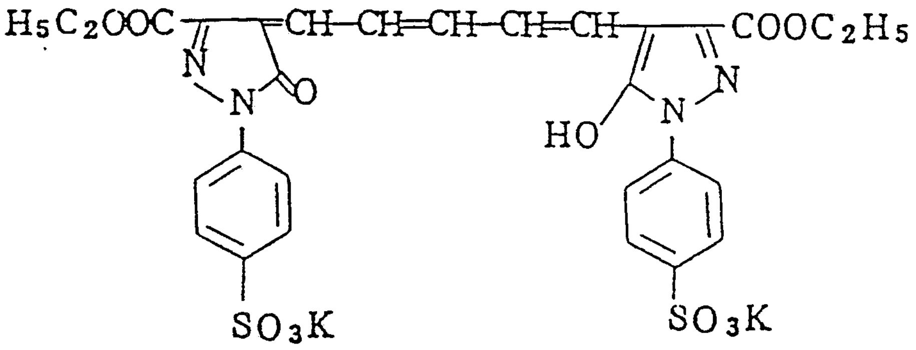
(Solv-6) Solvent



The sodium salt of 1-oxy-3,5-dichloro-s-triazine was used as a hardener of gelatin for each layer. Two dyes shown below were used as irradiation preventing dye.



and



Samples 101 to 117 having layers based on the above-described composition in which the silver halide emulsion and magenta coupler of the third layer and the coating amounts of gelatin and the color-mix inhibitor and the coating amount thereof of the second layer were changed as shown in Table 2 were prepared.

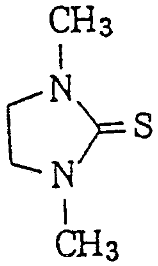
Silver halide emulsions used in the third layer were prepared as follows:

First, a chemically unsensitized silver chlorobromide emulsion (I) was prepared as follows:

First solution:	
H_2O	900 mℓ
NaCℓ	6.9 g
KBr	0.4 g
Gelatin	32.0 g

Second solution:

Compound shown below	3.8 mℓ



Third solution:	
KBr	88.2 g
NaCℓ	4.8 g
K_2IrCl_6 (0.001%)	7.4 mℓ
H_2O to make	400.0 mℓ

Fourth solution:	
$AgNO_3$	140.0 g
NH_4NO_3 (50%)	1.5 mℓ
H_2O to make	60.0 mℓ

Fifth solution:	
KBr	11.8 g
NaCℓ	2.5 g
H_2O to make	240.0 mℓ

Sixth solution:	
$AgNO_3$	20.0 g
NH_4NO_3 (50%)	0.5 mℓ
H_2O to make	200.0 mℓ

The first solution was heated to 65° C and the second solution was added thereto. Thereafter the third solution and fourth solution were added simultaneously over 50 minutes. After 10 minutes, the fifth solution and the sixth solution were added simultaneously over 12 minutes and 10 minutes, respectively. Five minutes after the completion of the addition, the temperature was lowered, and desalting was effected. Then water and dispersed gelatin were added thereto, and the pH was adjusted to 6.5, thereby obtained a monodisperse cubic silver chlorobromide emulsion (I) having an average grain size of 0.46 µm, a deviation coefficient (the value obtained by dividing the standard deviation by the average grain size: s/ $\overline{d}$) of 0.09, and a silver bromide content of 90 mol%.

Chemically unsensitized emulsion (II) was prepared by the same procedure as above for emulsion (I) except that the addition period of the fifth solution was changed to 10 minutes.

Chemically unsensitized emulsion (III) was prepared by the same procedure as above for emulsion (I) except that in the third solution, 87.5 g of KBr and 6.3 g of NaCℓ were used, and in the fifth solution, 12.5 g of KBr and 1.2 g of NaCℓ were used.

Chemically unsensitized emulsion (IV) was prepared by the same procedure as above for emulsion (I) except that in the third solution, 55.5 g of KBr and 0.5 g of NaCℓ were used, in the fourth solution, 80 g of $AgNO_3$ was used, in the fifth solution, 45.0 g of KBr and 6.8 g of NaCℓ were used, and in the sixth solution, 80 g of $AgNO_3$ was used.

Emulsions (II) to (IV) had the same average grain size, the same deviation coefficient, and the same bromide content as those of emulsion (I).

Note:

Emulsion (I) : Core/shell conversion emulsion
Emulsion (IV) : Core/shell conversion emulsion
Emulsion (II) : Core/shell emulsion (conversion was not effected.)
Emulsion (III): Conversion emulsion (not a core/shell emulsion)

A ribonucleic acid (available under the trade name RNA-F, manufactured by Sanyo-kokusaku Pulp Co., Ltd.) in the amount of 300 mg/mol of AgI was added to each of the chemically unsensitized emulsions (I) to (IV), the pH was adjusted to 7.7, and each of them was chemically sensitized with triethyl thiourea. The temperature was 50° C, and the time was selected so that the maximum sensitivity might be obtained under the conditions. For the adjustment of the pH, sodium hydroxide was used.

The obtained silver halide emulsions were designated Emulsions A to D.

A: the chemically unsensitized emulsion (I) was used.
B: the chemically unsensitized emulsion (II) was used
C: the chemically unsensitized emulsion (III) was used.
D: the chemically unsensitized emulsion (IV) was used.

Table 2

Sample No.	Third layer		Second layer		
	Emulsion	Coupler	Coating amount of Gelatin (g/m^2)	Color-mix inhibitor coating amount (g/m^2)	
101	A	ExM	0.89	(H-1)	0.024
102	A	1-7	0.89	(H-1)	0.024
103	A	1-7	1.34	(H-1)	0.040
104	B	1-7	1.34	(H-1)	0.040
105	C	1-7	1.34	(H-1)	0.040
106	D	1-7	1.34	(H-1)	0.040
107	A	1-7	2.00	(H-1)	0.024
108	A	1-7	3.10	(H-1)	0.024
109	A	1-7	0.89	(H-1)	0.040
110	A	1-7	0.89	(H-1)	0.310
111	A	1-7	3.10	(H-1)	0.310
112	A	1-8	1.34	(H-1)	0.040
113	A	1-47	1.34	(H-1)	0.040
114	A	1-7	1.34	(H-2)	0.040
115	A	1-7	1.34	(H-5)	0.040
116	A	1-7	1.50	(H-7)	0.040
117	A	1-7	1.50	(H-12)	0.040

Each of photographic materials above described was subjected to a gradation exposure through three color separated filters for sensitometry using a sensitometer (FWH model made by Fuji Photo Film Co., Ltd., the color temperature of light source was 3200° K).

At that time, the exposure was carried out in such a manner that the exposure was 250 CMS with the exposure time being 0.1 second. After exposure of light, each sample was processed by the processing process shown below.

Processing step	Temperature	Time
Color Development	33 °C	3 min. 30 sec.
Bleach-fixing	33 °C	1 min. 30 sec.
Water Washing ①	30 - 34 °C	60 sec.
Water Washing ②	30 - 34 °C	60 sec.
Water Washing ③	30 - 34 °C	60 sec.
Drying	70 - 80 °C	50 sec.
(Three tanks counter-current flow system from tank of water washing ③ toward tank of water washing ① was employed.)		

The compositions of each processing solution were as follows:

Color developer	
Water	800 mℓ
Diethylenetriaminepentaacetic acid	1.0 g
Nitrilotriacetic acid	1.5 g
Benzyl alcohol	15 mℓ
Diethylene glycol	10 mℓ
Sodium sulfite	2.0 g
Potassium bromide	0.5 g
Potassium carbonate	30.0 g
N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfonate	5.0 g
Hydroxylamine sulfonate	4.0 g
Fluorescent brightening agent (WHITEX-4, made by Sumitomo Chemical Ind. Co.)	1.0 g
Water to make	1000 mℓ
pH (25 °C)	10.20

Bleach-fixing solution	
Water	400 mℓ
Ammonium thiosulfate (700 g/ℓ)	150 mℓ
Sodium sulfite	18 g
Iron (III) ammonium ethylenediaminetetraacetate dihydrate	55 g
Disodium ethylenediaminetetraacetate	5 g
Water to make	1000 mℓ
pH (25 °C)	6.70

The results of the magenta density measured by using a green filter are shown in Table 3. The sensitivity is expressed by the reciprocal of the exposure amount that gave an optical density higher than the fog density by 0.5, and is given by the relative value with the sensitivity of Sample 101 assumed to be 100. The gradation is given by the difference of logarithms of exposure amounts that gave optical densities higher than the fog densities by 1.0 and 0.2 respectively.

Table 3

Sample	Result				Remarks
	Emulsion	Sensitivity	Gradation	Fogging	
101	A	100	0.25	0.07	Comparative Example
102	A	101	0.26	0.07	Comparative Example
103	A	101	0.26	0.07	This Invention
104	B	41	0.32	0.07	Comparative Example
105	C	69	0.42	0.07	Comparative Example
106	D	98	0.30	0.07	This Invention
107	A	101	0.26	0.07	Comparative Example
108	A	101	0.26	0.07	Comparative Example
109	A	100	0.26	0.07	Comparative Example
110	A	95	0.26	0.07	Comparative Example
111	A	95	0.30	0.07	Comparative Example
112	A	100	0.26	0.07	This Invention
113	A	100	0.26	0.07	This Invention
114	A	100	0.26	0.07	This Invention
115	A	100	0.26	0.07	This Invention
116	A	100	0.26	0.07	This Invention
117	A	100	0.26	0.07	This Invention

As is apparent from the results in Table 3, it can be understood that the samples that used the core/shell coversion emulsions A and D of the present invention are high in sensitivity and contrast.

Next, with respect to the magenta color image, the spectral density and the light fastness were evaluated. The spectral density was measured at 430 nm, 540 nm, and 650 nm, and the light fastness was evaluated by the stain density (D_B) of the white background and by the residual ratio of the initial density Dm = 1.0, after test for 14 days by an Xenon fade-o-meter (100,000 luxes).

Table 4

Sample No.	Coupler	Spectral Density			Light Fastness	
		430nm	540nm	650nm	Residual	Stain
101	ExM	0.34	1.00	0.12	50 %	0.20
102 to 111	1-7	0.15	1.00	0.06	76 %	0.10
112	1-8	0.16	1.00	0.07	76 %	0.10
113	1-47	0.15	1.00	0.05	74 %	0.10
114 to 117	1-7	0.15	1.00	0.06	76 %	0.10

As is apparent from the results in Table 4, it can be understood that in the case of the magenta coupler represented by formula (I), the density at the yellow section and on the longer wavelength side is low, favorable performance in view of color reproduction is exhibited, and also favorable performance in view of light fastness is exhibited.

Next, the yellow color-formed section of the samples subjected to the above process was measured by a green filter to evaluate the magenta density component.

Further, after Samples 101 to 117 were stored for 2 weeks under conditions of 35° C and 60 % RH, they were exposed to light and processed in the same manner as described above, and the changes in sensitivity and gradation between before and after the storage were evaluated.

Further, the dependability on the development time in the above processing was evaluated.

The results are shown in Table 5.

Table 5

	Color-mix	Change during Storage		
	Magenta Density	(35° C, 60% 2W.)		
Sample No.	(DY= 1.70)	Sensitivity	Gradation	Remarks
101	0.47	-0.01	+0.05	Comparative Example
102	0.50	-0.01	+0.02	Comparative Example
103	0.35	-0.01	+0.02	This Invention
104	0.35	-0.11	+0.12	Comparative Example
105	0.35	-0.08	+0.10	Comparative Example
106	0.35	-0.02	+0.02	This Invention
107	0.45	-0.01	+0.01	Comparative Example
108	0.41	-0.01	+0.01	Comparative Example
109	0.39	-0.02	+0.02	Comparative Example
110	0.34	-0.05	+0.10	Comparative Example
111	0.34	-0.04	+0.10	Comparative Example
112	0.35	-0.01	+0.02	This Invention
113	0.35	-0.01	+0.02	This Invention
114	0.34	-0.01	+0.02	This Invention
115	0.35	-0.01	+0.02	This Invention
116	0.35	-0.01	+0.02	This Invention
117	0.35	-0.01	+0.02	This Invention

As is apparent from the results in Table 5, it can be understood that, in the samples that used the constitution according to the present invention, the contamination of magenta color at the yellow part was remarkably improved. That is, this is clear when the results of Sample 103 of the present invention are compared with the results of Samples 101, 102, 107, 108, and 109, which are comparative examples.

In Sample 104 and 105, which used silver halide emulsions that fell outside of the scope of the present invention, and Samples 110 and 111, wherein the added amounts of compounds represented by formula (II) in the second layer were beyond the range of the present invention, the sensitivity and the gradation changed greatly under the storage conditions, and therefore stable performance could not be attained.

Further, according to the evaluation results of the dependentability on the development time, in Samples 108, 110, and 111 it is clear that the progress of the development of the blue-sensitive silver halide emulsion layer positioned nearest to the support became considerably slow in the initial stage.

Example 2

Samples 101 to 117 which were prepared in Example 1 were subjected to the processing according to the following processing process.

Processing step	Temperature	Time
Color development	38° C	1 min. 40 sec.
Bleach-fixing	35° C	60 sec.
Rinsing 1	33 - 35° C	20 sec.
Rinsing 2	33 - 35° C	20 sec.
Rinsing 3	33 - 35° C	20 sec.
Drying	70 - 80° C	50 sec.

The composition of the respective processing solution were as follows:

Color developer	
Water	800 m
Diethylenetriaminepentaacetic acid	1.0 g
Nitrilotriacetic acid	2.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Benzyl alcohol	16 m
Diethylene glycol	10 m
Sodium sulfite	2.0 g
Potassium bromide	0.5 g
Potassium carbonate	30.0 g
N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.5 g
Hydroxylamine sulfonate	2.0 g
Fluorescent brightening agent (WHITEX-4, made by Sumitomo Chemical Ind. Co.)	1.5 g
Water to make	1000 m
pH (25° C)	10.20

Bleach-fixing solution	
Water	400 m
Ammonium thiosulfate (700 g/)	80 m
Sodium sulfite	24 g
Iron (III) ammonium ethylenediaminetetraacetate dihydrate	30 g
Disodium ethylenediaminetetraacetate	5 g
Water to make	1000 m
pH (25° C)	6.50

Rinsing solution

Ion-exchanged water (each of calcium and magnesium was 3 ppm or below)

The above shown process was used for evaluation of Samples 101 to 117 in the same manner as in Example 1, and the exactly same results as in Example 1 were obtained.

Having described our invention as related to the embodiment, it is our intention that the invention be not limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

Claims

1. A silver halide color photographic material that has photographic layers that include at least one silver halide emulsion layer containing a yellow coupler, at least one silver halide emulsion layer containing a magenta coupler, and at least one silver halide emulsion layer containing a cyan coupler, on a support in the stated order, with said yellow coupler-containing silver halide emulsion layer nearest the support, wherein

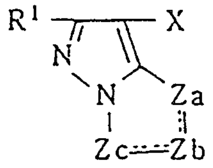
(a) said magenta coupler is a compound represented by the below-given formula (I),

(b) the coating amount of the hydrophilic colloid in the nonphotosensitive layer positioned between said yellow coupler-containing silver halide emulsion layer and said magenta coupler-containing silver halide emulsion layer is 1.1 g/m^2 or over,

(c) said nonphotographic layer contains a compound represented by the below-given formula (II) in an amount between 7.75 x 10^{-5} mol/m^2 and 9.00 x 10^{-4} mol/m^2, and

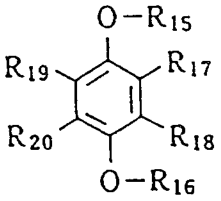
(d) at least one silver halide emulsion layer on the support contains a surface latent image-type monodisperse silver chlorobromide emulsion that comprises silver chlorobromide substantially free from silver iodide, and is obtained by subjecting the surface of silver halide grains having plural partial structures different in halogen composition to halogen conversion:

Formula (I)



wherein R^1 represents a hydrogen atom or a substituent, X represents a group capable of being released upon coupling reaction with the oxidized product of an aromatic primary amine developing agent, Za, Zb, and Zc each represent a 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; if the Zb-Zc is a carbon-carbon double bond, it may be part of the aromatic ring; a dimer or higher polymer may be formed through R^1 or X; or if Za, Zb, or Zc is a substituted methine, a dimer or higher polymer may be formed through the substituted methine;

Formula (II)



wherein R_{15} and R_{16} each represent a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an acyl group, a cycloalkyl group, or a nitrogen-containing heterocyclic group, R_{17}, R_{18}, R_{19}, and R_{20} each represent a hydrogen atom, a halogen atom, an alkyl group, an alkenyl group, an aryl group, a cycloalkyl group, an alkoxy group, an alkylthio group, an arylthio group, a nitrogen-containing heterocyclic thio group, an aryloxy group, an acyl group, an acylamino group, an alkylamino group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, or a sulfonic acid group, provided that when R_{17}, R_{18}, R_{19}, and R_{20} are hydrogen atoms at the same time, R_{15} and R_{16} are not hydrogen atoms at the same time, and R_{18} and R_{20} may bond together to form a 5-membered ring or a 6-membered ring.

2. The silver halide color photographic material as claimed in claim 1, wherein the silver halide emulsion in the silver halide photographic material has a silver iodide content of 1 mol% or below.

3. The silver halide color photographic material as claimed in claim 1, wherein the silver halide emulsion in the silver halide photographic material has a silver bromide content between 0.3 mol% and 97 mol%.

4. The silver halide color photographic material as claimed in claim 3, wherein the silver bromide content is 45 mol% or over.

5. The silver halide color photographic material as claimed in claim 1, wherein the difference of the silver bromide content of at least two partial structures in the silver halide grain is 10 mol% or over.

6. The silver halide color photographic material as claimed in claim 1, wherein the silver halide grain has a layered structure having plural layers as partial structure.

7. The silver halide color photographic material as claimed in claim 1, wherein the silver halide grain has a core-shell structure inside and surface of which are different in halogen composition.

8. The silver halide color photographic material as claimed in claim 7, wherein the constitutional silver halide molar ratio of the core to the shell is in the range of 2 : 98 to 98 : 2.

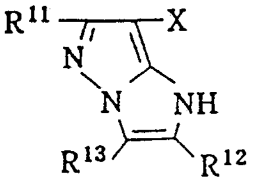
9. The silver halide color photographic material as claimed in claim 7, wherein the difference of the silver bromide content between the core section and the shell section of core-shell structure is in a range between 10 mol% and 50 mol%.

10. The silver halide color photographic material as claimed in claim 1, wherein the halogen conversion of the grain surface is carried out by adding bromide ions in the form of a soluble bromide compounds or a bromide donor.

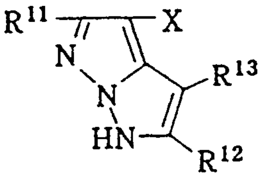
11. The silver halide color photographic material as claimed in claim 1, wherein the amount of halogen conversion is between 0.5 mol% and 15 mol% for the total silver halide.

12. The silver halide color photographic material as claimed in claim 1, wherein the halogen conversion of the grain surface is effected before a chemical ripening step.

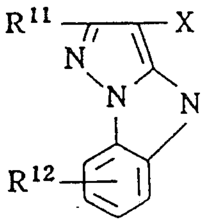
13. The silver halide color photographic material as claimed in claim 1, wherein the compound represented by formula (I) is selected from the group consisting of compounds represented by formulae (Ia), (Ib), (Ic), (Id), (Ie), (If), and (Ig):



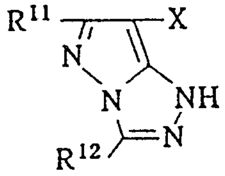
(Ia)



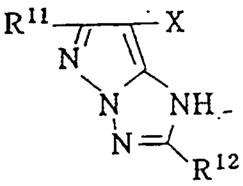
(Ib)



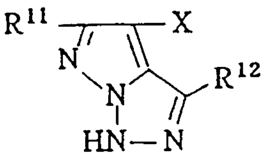
(Ic)



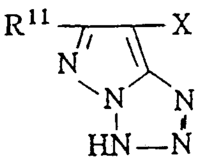
(Id)



(Ie)



(If)



(Ig)

wherein R^{11}, R^{12}, and R^{13}, which may be the same or different, each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonyl group, or an aryloxycarbonyl group, X represents a halogen atom, a carboxyl group, or a group that bonds to the carbon atom in the coupling position through an oxygen atom, a nitrogen atom, or a sulfur atom, and which is capable of being released upon coupling reaction, and R^{11}, R^{12}, R^{13}, or X may become a bivalent group to form a bis-form.

14. The silver halide color photographic material as claimed in claim 1, wherein the magenta coupler represented by formula (I) is contained in an amount of 0.005 to 4 mol in the silver halide emulsion layer.

15. The silver halide color photographic material as claimed in claim 1, wherein the coating amount of the hydrophilic colloid in the nonphotosensitive layer situated between the yellow coupler-containing silver halide layer and the magenta coupler-containing silver halide layer is in the range of 1.1 to 3.0 g/m^2.

16. The silver halide color photographic material as claimed in claim 1, wherein the coating amount of the compound represented by formula (II) is in the range of 1.00×10^{-4} mol/m^2 to 8.00×10^{-4} mol/m^2.

17. The silver halide color photographic material as claimed in claim 1, wherein each of R_{15} and R_{16} in formula (II) is hydrogen atom or an alkyl group having 1 to 8 carbon atoms and each of R_{17}, R_{18}, R_{19}, and R_{20} in formula (II) is a hydrogen atom or an alkyl group having 1 to 18 carbon atoms.