(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 378 236 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
10.04.1996 Bulletin 1996/15

(51) Int Cl.[6]: **G03C 7/305**, G03C 1/035, G03C 1/015

(21) Application number: **90100640.3**

(22) Date of filing: **12.01.1990**

(54) **Silver halide color photographic light-sensitive material**

Farbphotographisches lichtempfindliches Silberhalogenidmaterial

Matériau photographique couleur à l'halogénure d'argent sensible à la lumière

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: **13.01.1989 JP 4704/89**

(43) Date of publication of application:
18.07.1990 Bulletin 1990/29

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- **RESEARCH DISCLOSURE, no. 242, June 1984, HAVANT, GB, pages 286-292; R. Pollet et al.; Agfa-Gev.: "Compounds capable of releasing a development-influencing moiety"**
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Description

The present invention relates to a silver halide color photographic light-sensitive material.

In a known conventional technique, a compound which releases a development inhibitor in correspondence with an image density upon development is added to a photographic light-sensitive material. This compound generally coupling-reacts with the oxidized form of a color developing agent and releases a development inhibitor. Typical examples of a compound of this type are a compound which is coupled with the oxidized form of a color developing agent to form a dye and releases a development inhibitor as described in, e.g., U.S. Patents 3,148,062, 3,227,554, 3,701,783, and 3,733,201; and a compound which is coupled with the oxidized form of a color developing agent to release a development inhibitor without forming a dye as described in U.S. Patents 3,632,345 and 3,928,041, and JP-A-49-77635, JP-A-49-104630, JP-A-50-36125, JP-A-50-15273, and JP-A-51-6724 ("JP-A" means unexamined published Japanese patent application). These compounds can effectively form a fine-grain image, improve the sharpness of an image by an edge effect, improve color reproduction by an interlayer effect, and enable to control the tone of an image.

None of these conventional compounds, however, can satisfy all the above effects. In addition, the above effects largely depend on the type of light-sensitive silver halide emulsion. Therefore, a silver halide photographic emulsion capable of forming an optimal combination with a development inhibitor is required. In particular, a silver halide photographic emulsion having uniform development property is desired.

EP-A-0326853 discloses silver halide photographic emulsions comprising a dispersion medium and silver halide grains, the silver halide grains of which include a silver halide localized region microscopically uniformly containing at least 3 mol% silver iodide. This patent also relates to color photographic materials employing such emulsions. These materials may additionally comprise DIR compounds capable of releasing a development inhibitor along with coupling.

It is an object of the present invention to provide a silver halide color photographic light-sensitive material having an optimal combination of a compound for releasing a development inhibitor with a silver halide photographic emulsion.

It is another object of the present invention to provide a silver halide color photographic light-sensitive material having an improved interlayer effect.

According to the present invention the above objects have been solved by providing a silver halide color photographic light-sensitive material comprising at least one light-sensitive silver halide emulsion layer and at least one non-light-sensitive colloid layer on a support, said light-sensitive silver halide emulsion layer comprising silver halide grains containing a microscopically uniform silver halide localized region containing not less than 3 mol% of silver iodide, wherein said silver halide localized region has at most two lines indicating a microscopic silver iodide non-uniform distribution at an interval of 0.2 μm in a direction perpendicular to the lines in a transmission image of-the grains obtained by using a cryo-transmission electron microscope and the number of the silver halide grains having such a silver halide localized region account for at least 60% of the number of all the grains in the emulsion, said light-sensitive silver halide emulsion layer or said non-light-sensitive colloid layer containing at least one development inhibitor releasing (DIR) compound which reacts with the oxidized form of a color developing agent to a cleavage compound, said cleavage compound reacting with another molecule of the oxidized form of a color developing agent to form a development inhibitor or a precursor thereof.

The silver halide grains used in the silver halide color photographic light-sensitive material according to the present invention may be formed by supplying fine silver halide grains, formed beforehand by supplying and mixing an aqueous water-soluble silver salt solution and an aqueous halide solution into a mixer vessel provided outside a reactor vessel for causing nucleation and/or crystal growth, to the reactor vessel to cause nucleation and/or crystal growth of silver halide grains.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a transmission electron microscopic photograph showing a conventional silver halide grain crystal structure in which an iodide distribution of a silver iodobromide phase is not microscopically uniform (magnification = 20,000);

Fig. 2 is a view schematically showing a method of supplying silver halide grains from a mixer vessel outside a reactor vessel, as one of the methods for manufacturing emulsions used in the present invention;

Fig. 3 is a view showing in detail a mixer vessel which may be used in the present invention;

Figs. 4A, 4B and 4C are transmission electron microscopic photographs showing typical silver halide grain crystal structures in emulsions I-C, I-D, and I-E prepared in Example 1, respectively (magnification = 20,000);

Fig. 5 is a graph showing characteristic curves of a silver halide color photographic light-sensitive material of the present invention, in which the ordinate represents a color forming density, the abscissa represents a logarithmic value of an exposure amount E, a curve A-B is a characteristic curve concerning a yellow image of a blue-sensitive layer, and a curve a-b represents a magenta density of a green-sensitive layer obtained by uniform green exposure; and

Fig. 6 is a graph showing a preferable half-value width of an X-ray diffraction profile of silver iodobromide emulsion

grains having a microscopically uniform halide composition used in the present invention.

Silver halide grains used in the present invention will be described in detail below.

The crystal habit of the silver halide grains used in the present invention may or may not be a regular crystal, and may or may not have an internal structure. In addition, the grain size distribution of the silver halide grains may be wide or narrow. The total composition of the silver halide grains is silver iodobromide, silver iodochloride, or silver iodochlorobromide, and preferably silver iodobromide or silver iodochlorobromide.

The silver halide grains used in the present invention have a silver halide localized region microscopically uniformly containing silver iodide. In this case, 3 to 45 mol%, and preferably, 5 to 35 mol% of silver iodide are contained in the localized region. The localized region can be present as a continuous or non-continuous phase inside a grain or on the surface of a grain. When the entire grain has only one phase without having an internal structure, this phase is considered as a localized region. This localized region may be present at either a core or shell portion of a silver halide grain, may be non-continuously present at a corner of a cubic grain, and may be present at an edge or corner of a tabular grain. The localized region need only be present at least at one position. A plurality of localized regions having different halogen compositions such as different silver iodide contents may be present.

3 mol% or more of silver iodide are microscopically uniformly contained in the localized region of the silver halide grains.

This microscopic distribution of the silver iodide can be observed by a direct method at a low temperature using a transmission electron microscope as described in J.F. Hamilton, "Photographic Science and Engineering", Vol. 11, 1967, P. P57 or Takeaki Shiozawa, "Japan Photographic Society", Vol. 35, No. 4, 1972, P. P213. That is, silver halide grains, which have been extracted under safe light so that emulsion grains are not printed out, are placed on a mesh for electron microscopic observation, and this sample is observed by a transmission method while it is cooled by liquid nitrogen or liquid helium so as to prevent a damage (e.g., print out) caused by an electron beam.

In this case, as an accelerated voltage of an electron microscope is increased, the sharpness of a transmission image is improved. The accelerated voltage is preferably 200 kV for a grain thickness of up to 0.25 μm, and is preferably 1,000 kV for a grain thickness exceeding this value. Since a damage to grains caused by an electron beam is increased as the accelerated voltage is increased, it is more preferable to cool the sample by liquid helium than by liquid nitrogen.

Although the photographing magnification can be arbitrarily changed in accordance with the grain size of a sample, it is 20,000 to 40,000 times.

When silver iodobromide tabular grains are photographed by a transmission electron microscope as described above, a very fine annual ring-like stripe pattern is observed at a portion of a silver iodobromide phase. Fig. 1 shows an example of this stripe pattern. The tabular grain shown in the Fig. 1 is a tabular core/shell grains prepared by forming silver iodobromide shell containing 10 mol% of silver iodide as a shell around a tabular silver bromide grain core. This structure can be clearly observed by the transmission electron microscopic photograph. That is, since the core portion consists of silver bromide and therefore is naturally uniform, only a uniform flat image is obtained. In a silver iodobromide phase, however, a very fine annular ring-like stripe pattern can be clearly confirmed. An interval between the respective stripes in the pattern is as small as in the order of 100 Å or less, i.e., indicates very microscopic non-uniformity. The fact that this very fine stripe patterns indicate non-uniformity of the silver iodide distribution can be proved by various methods. This can be concluded more directly, however, by the fact that the stripe pattern completely disappears when the tabular grains are annealed under the conditions such that iodide ions can move in a silver halide crystal (e.g., at 250°C for three hours).

The annual ring-like stripe pattern indicating the non-uniformity of a silver iodide distribution of a tabular silver iodobromide emulsion grains described above is clearly observed also in a transmission electron microscopic photograph attached to JP-A-58-113927 obtained by measuring a silver iodide distribution by using a 0.2 μm electron beam spot. This pattern is also clearly shown in a transmission electron microscopic photograph in topography studies of a silver iodide content in a silver iodobromide tabular grain described in M.A. King, M.H. Lorretto, T.J. Maternaghan, and F.J. Berry, " The Investigation of Iodide Distribution by Analytical Electron Microscopy", Progress in Basic Principles of Imaging Systems, International Congress of Photographic Science Köln, 1986, by analytical electron microscopy. As described above, silver iodobromide grains prepared to have a determined silver iodide content in order to obtain a uniform silver iodide distribution have a very microscopically non-uniform distribution of silver iodide, contrary to its manufacture purpose.

In the photographic material of the present invention an emulsion having a microscopically uniform silver iodide distribution is used.

As described above, a silver halide grain containing a silver halide localized region having a "microscopically uniform silver iodide distribution" used in the present invention can be clearly distinguished from a conventional silver halide grain by observing a transmission image of the grain by using a cooling type transmission electron microscope. That is, the silver halide localized region containing silver iodide of the grains used in the present invention has two or less, preferably one, and more preferably no microscopic line caused by the microscopic non-uniformity of silver iodide at an

interval of 0.2 μm in the direction perpendicular to the line. Lines constituting the annual ring-like stripe pattern indicating the microscopic non-uniformity of silver iodide are formed in a direction perpendicular to a grain growth direction and distributed concentrically from the center of a grain. For example, in the tabular grain shown in Fig. 1, since lines constituting the annual ring-like stripe pattern indicating the non-uniformity of silver iodide are perpendicular to a growth direction of the tabular grain, they are parallel to the edge of the grain. In addition, since a direction perpendicular to the lines is directed toward the center of the grain, the lines are distributed concentrically around the center.

When the silver iodide content is abruptly changed during growth of the grains, boundaries are observed as lines as described above by the above observation method. Such a silver iodide content change, however, constitutes only a single line which can be clearly distinguished from a plurality of lines caused by the microscopic non-uniformity of silver iodide. In addition, the line caused by the silver iodide content change can be clearly confirmed by measurement of the silver iodide content in both sides separated by the line using the above-mentioned analytical electron microscopy. The line caused by the silver iodide change entirely differs from the lines caused by the microscopic non-uniformity of silver iodide and indicates a "macroscopic silver iodide distribution".

When the silver iodide content is substantially continuously changed during the growth of grains, the silver iodide content does not change abruptly. Therefore, no lines indicating the variation of the microscopic silver iodide content as described above are observed. Therefore, if at least three or more lines are present at an interval of 0.1 μm, the microscopic non-uniformity of a silver iodide content is present.

In the present invention, therefore, a silver halide localized region having a microscopically uniform silver iodide distribution is a grain having at most only two lines indicating a microscopic silver iodide distribution at an interval of 0.2 μm in a direction perpendicular to the lines in a transmission image of the grain obtained by using a cryo-transmission electron microscope. The silver halide grain has preferably one, and more preferably, no such lines. Such silver halide grains account for at least 60%, preferably, at least 80%, and more preferably, at least 90% of all the grains.

The microscopic uniformity of a halide distribution of a silver halide mixed crystal can be measured by utilizing X-ray diffraction.

A method of determining a halide composition by using an X-ray diffractometer is known to those skilled in the art.

This principle will be briefly described below. That is, in X-ray diffraction, a lattice constant a can be determined by the following Bragg equation upon measurement of a Bragg angle:

$$2d_{hkl} \sin\theta_{hkl} = \lambda$$

$$d_{hkl} = a/\sqrt{h^2 + k^2 + l^2}$$

wherein λ : wavelength of X rays
θ_{hkl}: Bragg angle from (hkl) face
d_{hkl}: face interval of (hkl) face
a : lattice constant

The relationship between the lattice constant a and a halide composition for each of silver iodobromide, silver chlorobromide, and silver iodochloride is described in T.H. James, "The Theory of the Photographic Process", 4th ed., Chapter I, Macmillan Co. Ltd., New York. That is, when the lattice constant (halide composition) changes, an angle of a diffraction peak changes. Therefore, a silver halide grain having a good uniformity of a the halide composition distribution with less variation in lattice constant has a narrow half-value width of the diffraction profile. Upon measurement of this diffraction profile, K_α -rays having a high intensity and a good monochromatic property are used more preferably than K_β-rays as a ray source. Note that since the K_α-rays are double rays, a half-value width can be determined by obtaining a single profile by using a Rachinger method. Examples of the sample are powdery grains prepared by removing gelatin from an emulsion, and a coated emulsion film dipped in a 50% glycerine solution for 20 minutes to remove the pressure on a grain surface by gelatin in a dry film in accordance with the method described in, G.C. Farnell, R.J. Jenkins, L.R. Solman, "Journal of Photographic Science", Vol. 24. P. 1, 1976. In order to accurately obtain the angle of the diffraction profile, an Si powder or Nacℓ powder having a known diffraction angle is mixed in the sample. In order to precisely measure the diffraction angle and the line width of the diffraction profile, a diffraction profile having a large diffraction angle from a high-index face is preferably used. Therefore, in the present invention, a diffraction profile of a (420) face was measured within a diffraction angle (twice the Bragg angle) range of 71° to 77° by using K_α-rays of a copper target.

In the X-ray diffraction measurement, since measurement precision obtained by using a coated emulsion film is higher than that obtained by using a powder, the measurement was performed by using a coated emulsion film.

The half-value width of a diffraction profile of a system in which no strain is caused by an external stress as in the form of a sample described in the present invention is determined not only by a halide distribution. That is, this half-value width includes, in addition to the above half-value width, the half-value width caused by an optical system of a diffractometer and the half-value width caused by the size of a crystallite of a sample. Therefore, in order to obtain the half-value

width caused by a halide composition distribution, the contribution of the two half-value widths must be subtracted. The half-value width by an optical system of a diffractometer can be obtained as the half-value width of a diffraction profile of a single crystal having no strain (not having a lattice constant variation) and having a grain size of 25 μm or more. As an example of this sample, a material prepared by annealing α-quartz of 25 to 44 μm size (500 mesh on, 350 mesh under) at 800°C can be used. This is described in "X-ray Diffraction Handbook", revised, reprint, Chapter II, Paragraph 8, Rigaku Denki K.K. E.g., Si grains and a Si single-crystal wafer can also be used. Since the half-value width by an optical system has a dependency on diffraction angle, it must be obtained at a plurality of points of diffraction profile. If necessary, extrapolation or interpolation is performed to obtain the half-value width by an optical system at a diffraction angle of a measuring system. The half-value width by the size of a crystallite is determined by the following equation:

$$\beta = (K_{\lambda}/D_{\cos\theta}) \times (180/\pi)$$

where β: half-value width by size of crystallite (°)
K: constant value (generally, 0.9)
D: size of crystallite (Å)
λ: wavelength of X rays (Å)
θ: Bragg angle

The half-value width by a halide composition distribution is obtained by subtracting the half-value widths by the optical system and the size of a crystallite, which are obtained by the above method, from the half-value width of the measured diffraction profile. The half-value width by an optical system and the half-value width by the size of a crystallite for a mixed crystal grain to be measured are equal to the half-value width of a diffraction profile of a silver halide grain having the same crystallite size as the grain of interest and having a uniform halide composition distribution (that is, having constant lattice constant). Generally, when no strain caused by an external stress is present, the size (e.g., an edge length and an equi-volume sphere-equivalent diameter) of a grain not having a lattice defect coincides with the size of a crystallite. F.W. Willets reports that, although not in a diffractometer method but in a photographic method, the size of a crystallite of AgBr obtained by a diffraction ray width coincides with the size of the grain, in "British Journal of Applied Physics", 1965, Vol. 16, P. 323. In this report, not the half-value width but the standard deviation of a profile is used and 1.44 is selected as a sheller constant in the photographic method. In the measurement system used in the present invention, a diffractometer is used and it is found that the size of a crystallite obtained by the half-value width obtained by subtracting the half-value width by an optical system obtained by using a Si single crystal coincides well with the size of the grain in the case of AgBr grains prepared by a balanced double jet method.

That is, the half-value width by an optical system and the half-value width by the size of a crystallite for a mixed crystal emulsion grain can be obtained as the half-value width of the diffraction profile of an AgBr grain, an AgCℓ grain, and an AgI grain having the same grain size as the mixed crystal emulsion grain. The half-value width by only the halide composition distribution of the mixed crystal emulsion grain can be obtained by subtracting the half-value width of the diffraction profile of the AgBr grain, the AgCℓ grain, and the AgI grain having the same grain size as the interest grain from the half-value width of the measured diffraction profile.

The preferable half-value width of an X-ray diffraction profile of the silver iodobromide emulsion grain having the uniform microscopic halide composition used in the present invention obtained by the method described above is shown in Fig. 6. Referring to Fig. 6, the uniformity of a grain of the halide composition is represented by the value obtained by subtracting the half-value width of pure silver bromide having the same grain size from the half-value width of X-ray diffraction of the grain. The grain used in the present invention has a half-value width indicated by the curve A or less, and preferably, a half-value width indicated by the curve B or less.

The silver halide grain conventionally called a silver halide grain uniformly containing silver iodide is simply prepared by adding silver nitrate and a mixture of halide salts having a determined composition (determined iodide content) to a reactor vessel upon growth of the grains in a double jet method. In such a grain, although the macroscopic silver iodide distribution is constant, the microscopic silver iodide distribution is not uniform. In the present invention, such a grain is called a grain having a "determined halide composition" and is clearly distinguished from the "microscopically uniform" grain used in the present invention.

The silver iodide content in the localized region can be obtained by analysis using an electron microscope.

This analytical electron microscopic method is described in detail in various patent and academic literatures. For example, this method is described in JP-A-58-113927 (36), upper right column, line 7 to lower left column, line 6; and Japan Photographic Society Annual Meeting 1984 Spring Meeting Manuscripts A-10, from page 49, and Autumn Meeting Manuscripts A-16, from page 49, by Masamitsu Inoue and Kiyomitsu Mine.

A very thin sample piece is cut from a portion to be measured as needed before measurement and measured by using a transmission electron microscope equipped with an energy dispersion type X-ray diffraction apparatus under cooling by liquid nitrogen at an acceleration voltage of 75 kV with a radiation current of 2.5 μA.

If the silver iodide content of the localized region is 3 mol% or less, the influence of the microscopically non-uniform distribution is small. For example, assume that an outermost layer of a silver halide grain is a localized region containing silver iodide. Upon chemical sensitization of this grain, if the silver iodide content of the outermost layer is less than 3 mol%, the obtained sensitivity, fog, and rate of development are not much influenced regardless whether the silver iodide distribution of the silver halide phase is "microscopically uniform". If, however, the silver iodide content of the silver halide phase of the outermost layer containing the silver iodide is 3 mol% or more, and particularly, 5 mol% or more, only a very low reached sensitive and a low rate of development can be obtained upon chemical sensitization by using conventional grains having a non-uniform silver iodide distribution. That is, the chemical sensitization of a grain having a silver halide phase of a conventional "determined halide composition of silver iodide" in its outermost layer is interfered. Therefore, improvements in photographic properties as merits of addition of silver iodide, such as an increase in latent image formation efficiency, an increase in light absorption, an improvement in additive adsorption, and an improvement in graininess could not be achieved by these grains. If, however, a silver halide phase having the "microscopically uniform" silver iodide distribution used in the present invention is present in an outermost layer, the chemical sensitization is not interfered at all, and all the merits of addition of silver iodide can be achieved. As a result, a high sensitivity, a low log, a good graininess, a high sharpness, and a uniform development property which are not obtained conventionally can be obtained.

If the silver halide phase containing silver iodide is present inside the grain and the silver iodide content in the outermost layer is low or no silver iodide is present therein, it is assumed that a band structure is expected to be bent in the interface between the two phases, holes produced by light absorption caused by bending are directed toward the interior of the grain to accelerate the charge separation between electrons and holes, and silver iodide in the grain traps the holes to prevent recombination with the electrons, thereby increasing the sensitivity. It is found that the photographic sensitivity is high when the silver iodide distribution inside the grain is microscopically uniform and is low when the silver iodide distribution is non-uniform. This is a surprising effect although a reason for this has not been clarified yet. It is assumed, however, that an internal hole trapping ability is uniform when the silver iodide distribution is microscopically uniform and the ability is non-uniform when the silver iodide distribution is microscopically non-uniform, i.e., an electron-hole recombination preventing effect largely differs in the two cases.

In this case, as described above, when the internal silver iodide content is less than 3 mol%, the obtained sensitivity is substantially not changed even if the uniformity of the silver iodide distribution is different. When the silver iodide content is 3 mol% or more, and particularly, 5 mol% or more, a grain having a microscopically uniform silver iodide distribution apparently has a higher sensitivity than that of a grain having a microscopically non-uniform silver iodide distribution.

The total silver iodide content of the emulsion grains used in the present invention is 2 mol% or more. The total silver iodide content is preferably 4 mol% or more, and more preferably, 5 mol% or more. Although the size of the silver halide emulsion grain containing a silver halide localized region having a microscopically uniform silver iodide distribution is not particularly limited, it is preferably 0.3 μm or more, more preferably, 0.8 μm or more, and most preferably, 1.4 μm or more. The shape of the silver halide grain used in the present invention may be a regular crystal shape (regular crystal grain) such as a cube, an octahedron, a dodecahedron, a tetradecahedron, an icositetrahedron (a tri octa hedron, a tetra hexa hedron, and a rhombic icositetrahedron), and a tetrahexahedron, or an irregular crystal shape such as a sphere and a potato-like shape. In addition, the silver halide grain may take various shapes having one or more twinned crystal faces, and more particularly, may be a hexagonal tabular grain or a triangular tabular grain having two or three parallel twinned crystal faces.

A method of manufacturing the silver halide grains used in the present invention will be described in detail below.

For a method of manufacturing the light-sensitive silver halide grains used in the present invention, and a method of preparing "fine silver halide grains" for use in the above method, Japanese Patent Application Nos. 63-7851, 63-195778, 63-7852, 63-7853, 63-194861, and 63-194862 are helpful.

That is, the method for preparing the grains is characterized in that except for adjustment of a pAg of an emulsion in the reactor vessel, no aqueous silver salt solution nor aqueous halide solution is added to a reactor vessel to perform nucleation and/or grain growth, and circulation of an aqueous protective colloid solution (containing silver halide grains) from the reactor vessel to a mixer vessel is not performed at all.

A system for grain formation as shown Fig. 2 can be preferably used in the present invention (a method of supplying fine silver halide grains immediately from a mixer vessel is called a "method A" hereinafter).

In Fig. 2, reference numeral 1 denotes a reactor vessel, 2 denotes an aqueous protective colloid solution, 3 denotes a propeller, 4 denotes an aqueous halide salt solution adding system, 5 denotes an aqueous silver salt solution adding system, 6 denotes a protective colloid adding system, and 7 denotes a mixer vessel.

Referring to Fig. 2, the reactor vessel 1 contains an aqueous protective colloid solution 2. The aqueous protective colloid solution is stirred and mixed by a propeller 3 mounted on a rotating shaft. After the silver halide grains as a core are added to the reactor vessel or after nucleation is performed in the reactor vessel, an aqueous silver salt solution, an aqueous halide solution, and an aqueous protective colloid solution are introduced in the mixer vessel 7 located

outside the reactor vessel by adding systems 4, 5, and 6, respectively (in this case, the aqueous protective colloid solution may be mixed in the aqueous halide solution and/or the aqueous silver salt solution and then added). These solutions are rapidly and strongly mixed in the mixer vessel and immediately introduced to the reactor vessel 1 by the system 8.

Fig. 3 shows the mixer vessel 7 in detail.

In Fig. 3, reference numerals 4, 5, and 7 have the same meanings as in Fig. 1 and 8 denotes an introducing system for the reactor vessel, 9 denotes a stirring blade, 10 denotes a reactor chamber, and 11 denotes a rotating shaft.

The mixer vessel 7 has an internal reactor chamber 10. Stirring blades 9 mounted on a rotating shaft 11 are provided inside the reactor chamber 10. The aqueous silver salt solution, aqueous halide salt solution, and aqueous protective colloid solution are added from three introducing ports (4 and 5, the remaining one is omitted from the drawing) to the reactor chamber 10. The solution which is rapidly and strongly mixed and contains very fine grains by rotation of the rotating shaft at high speed (1,000 rpm or more, preferably, 2,000 rpm or more, and more preferably, 3,000 rpm or more), is exhausted from the external exhaust port 8.

Since very fine grains formed upon reaction in the mixer vessel in this manner and introduced to the reactor vessel are very small in grain size, the grains are dissolved very easily to be silver ions and halide ions, thereby causing uniform grain growth. In this case, a halide composition of the very fine grains is set to the same as that of an interest silver halide localized region in the silver halide grains. The very fine grains introduced in the reactor vessel are scattered therein upon stirring, and halide ions and silver ions of the intented halide composition are released from each very fine grain. In this case, the grains formed by the mixer vessel are very fine, and the number of the grains is very large. In addition, silver and halide ions (having an intented halide ion composition in the case of growth of a mixed crystal) are released from each grain, and this reaction occurs throughout the protective colloid in the reactor vessel. Therefore, a microscopically uniform growth of grains can be achieved. The fine grains formed as described above normally have substantially the same size as that of a so-called Lippmann emulsion. The average grain size of the grains is 0.1 μm or less. In this method, it is important not to add aqueous solutions of silver and halide ions to the reactor vessel except for pAg adjustment and not to circulate the protective colloid solution in the reactor vessel to the mixer vessel. As a result, unlike a conventional method, this method can achieve surprising effects in uniform growth of silver halide grains.

The fine grains formed in the mixer vessel have a high solubility since their grain size is very small. Therefore, when the grains are added to the reactor vessel, they are converted into silver and halide ions and precipitate on grains already existing in the reactor vessel to cause grain growth. During grain growth, the fine grains cause Ostwald ripening therebetween since they have a high solubility, thereby increasing the grain size. When the grain size of the fine grains is increased, the solubility is decreased to decelerate dissolution in the reactor vessel. When the speed of the grain growth is significantly low, the some grains are not dissolved but become a core to cause growth.

In the present invention, the following three techniques are preferably used in as in the techniques disclosed in Japanese Patent Application Nos. 63-7851 and 63-195778 described above.

(1) After fine grains are formed in a mixer vessel, they are immediately added to the reactor vessel.

In the method used in the present invention the mixer vessel is located very close to the reactor vessel, and the residence time of the addition solutions in the mixer vessel is shortened. Therefore, since the fine grains are added to the reactor vessel immediately after formation, Ostwald ripening is prevented. More specifically, the residence time $\underline{t}$ of the solutions added to the mixer vessel is represented by the following equation:

$$t = v/(a + b + c)$$

where v : volume of reactor chamber in mixer vessel (mℓ)
a : addition amount of silver nitrate solution (mℓ/min)
b : addition amount of halide solution (mℓ/min)
c : addition amount of protective colloid solution (mℓ/min)

In the manufacturing method used in the present invention, $\underline{t}$ is ten minutes or less, preferably, five minutes or less, more preferably one minute or less, and most preferably, twenty seconds or less. In this manner, the fine grains obtained in the mixer vessel are immediately added to the reactor vessel without being increased in grain size.

(2) Strong and efficient stirring is performed in a mixer vessel.

T.H. James, "The Theory of The Photographic Process", p.p. 93 describes "Another form in addition to Ostwald ripening, is coalescence. In coalescence ripening, crystals which have been far remote from one another before this are directly contacted and fused together to give grater crystals so that the grain size of thus fused grains rapidly varies thereby. Both Ostwald ripening and coalescence ripening occur not only after deposition but also during deposition". Coalescence ripening described in above tends to occur especially when the grain size is very small and when stirring is insufficient. In an extreme case, coarse mass grains may be formed. In the method used in the present invention, since a closed type mixer vessel as shown in Fig. 3 is used, the stirring blades in a reactor

chamber can be rotated at high speed. Therefore, strong and efficient stirring/mixing which cannot be performed by a conventional open type reactor vessel can be performed (the open type reactor vessel is not practical because solutions are scattered by a centrifugal force and the problem of foaming is posed if the stirring blades are rotated at high speed in the open type reactor vessel), thereby preventing the above coalescence ripening. As a result, fine grains having a very small grain size can be obtained. In the method used in the present invention, a rotational speed is 1,000 rpm, preferably, 2,000 rpm, and more preferably, 3,000 rpm.

(3) Injection of an aqueous protective colloid solution to a mixer vessel.

Coalescence ripening described above can be prevented well by a protective colloid of silver halide fine grains. In the method used in the present invention, the aqueous protective colloid solution is added to a mixer vessel by the following methods.

(a) An aqueous protective colloid solution is singly injected in a mixer vessel.

The concentration of the protective colloid is 0.2 wt% or more, and preferably, 0.5 wt% or more, and its flow rate is at least 20%, preferably, at least 50%, and more preferably, 100% or more of a total flow rate of a silver nitrate solution and an aqueous halide solution.

(b) A protective colloid is added to an aqueous halide solution.

The concentration of the protective colloid is 0.2 wt% or more, and preferably, 0.5 wt% or more.

(c) The protective colloid is added to an aqueous silver nitrate solution.

The concentration of the protective colloid is 0.2 wt% or more, and preferably, 0.5 wt% or more. When gelatin is used, silver gelatin is formed by silver ions and gelatin and this gives a silver colloid by photolysis and pyrolysis. Therefore, the silver nitrate solution and the protective colloid solution are preferably mixed immediately before they are used.

The methods described in items (a) to (c) described above can be used singly or in a combination of two thereof. Alternatively, the three methods can be simultaneously used.

In the present invention, a method in which a fine silver halide emulsion prepared beforehand is added to a reactor vessel to perform nucleation and/or grain growth as disclosed in Japanese Patent Application Nos. 63-6852, 63-7853, 63-194861, and 63-194862 described above can be also used (a method in which a time interval from formation of fine silver halide grains to supply of the grains to a reactor vessel exceeds ten minutes is called a "method B" hereinafter). As described above, as the grain size of the emulsion prepared beforehand is reduced, a better result is obtained. In this method, as in the above method, neither of an aqueous solution of a water-soluble silver salt and an aqueous solution of a water-soluble halide is added to the reactor vessel except for pAg adjustment of the emulsion in the reactor vessel. For pAg adjustment, not both of but only one of the aqueous solutions of the water-soluble silver salt and water-soluble halide is added to the reactor vessel. An addition amount of silver ions or a halide added for adjustment is several mol% or less of a prepared number of moles of the entire silver halide emulsion. This emulsion prepared beforehand may be washed and/or solidified before it is added to the reactor vessel.

Examples of a polymer having a protective colloidal action with respect to the silver halide grains used in the present invention are as follows.

(a) Polyacrylamide polymer

Examples are an acrylamide homopolymer; a copolymer of a polyacrylamide and imidated polyacrylamide disclosed in U.S. Patent 2,541,474; a copolymer of acrylamide and methacrylamide disclosed in West German Patent 1,202,132; a partially aminated acrylamide polymer disclosed in U.S. Patent 3,284,207; and substituted acrylamide polymers disclosed in JP-B-45-14031 ("JP-B" means examined Japanese patent application), U.S. Patents 3,713,834 and 3,746,548, and British Patent 78,343.

(b) Aminopolymer

Examples are aminopolymers disclosed in U.S. Patents 3,345,346, 3,706,504, and 4,350,759, and West German Patent 2,138,872; a polymer having quarternary amine disclosed in British Patent 1,413,125 and U.S. Patent 3,425,836; a polymer having an amino group and a carboxyl group disclosed in U.S. Patent 3,511,818; and a polymer disclosed in U.S. Patent 3,832,185.

(c) Polymer having a thioether group

Examples are polymers having a thioether group disclosed in U.S. Patents, 3,615,624, 3,860,428, and 3,706,564.

(d) Polyvinyl alcohol

Examples are a homopolymer of vinyl alcohol; an organic monoester of polyvinyl alcohol disclosed in U.S. Patent 3,000,741; a maleic ester of polyvinyl alcohol disclosed in U.S. Patent 3,236,653; and a copolymer of polyvinyl alcohol and polyvinyl pyrrolidone disclosed in U.S. Patent 3,479,189.

(e) Acrylic acid polymer

Examples are an acrylic acid polymer; an acrylic ester polymer having an amino group disclosed in U.S. Patents 3,832,185 and 3,852,073; a halogenated acrylic ester polymer disclosed in U.S. Patent 4,131,471; and a cyanoalkylacrylic ester disclosed in U.S. Patent 4,120,727.

(f) Polymer having hydroxyquinoline

Examples are polymers having hydroxyquinoline disclosed in U.S. Patents 4,030,929 and 4,152,161.

(g) Cellulose, Starch Derivaties

Examples are derivatives of cellulose or starch disclosed in British Patents 542,704 and 551,659, and U.S. Patents 2,127,573, 2,311,086, and 2,322,085.

(h) Acetal

Examples are polyvinylacetal disclosed in U.S. Patents 2,358,836, 3,003,879, and 2,828,204, and British Patent 771,155.

(i) Polyvinylpyrrolidone

Examples are a homopolymer of vinylpyrrolidone; and a copolymer of acrolein and pyrrolidone disclosed in French Patent 2,031,396.

(j) Polystyrene

Examples are a polystyrylamine polymer disclosed in U.S. Patent 4,315,071; and a halogenated styrene polymer disclosed in U.S. Patent 3,861,918.

(k) Terpolymer

Examples are terpolymers of acrylamide, acrylic acid, and vinylimidazole disclosed in JP-B-43-7561 and West German Patents 2,012,095 and 2,012,970.

(1) Others

Other examples are a vinyl polymer having an azaindene group disclosed in JP-A-59-8604; a poly-alkyleneoxide derivative disclosed in U.S. Patent 2,976,150; a polyvinylamineimide polymer disclosed in U.S. Patent 4,022,623; polymers disclosed in U.S. Patents 4,294,920 and 4,089,688; polyvinylpyridine disclosed in U.S. Patent 2,484,456; a vinyl polymer having an imidazole group disclosed in U.S. Patent 3,520, 857; a vinyl polymer having a triazole group disclosed in JP-B-60-658; polyvinyl-2-methylimidazole and an acrylamide-imidazole copolymer disclosed in "Japanese Photographic Society", Vol. 29, No. 1, P. 18; dextran;, and water-soluble polyalkyleneaminotriazoles disclosed in "Zeitschrift Wissenschaftlich Photographie", Vol. 45, P. 43 (1950).

In the method used in the present invention, a low molecular weight gelatin is used as the protective colloid. An average molecular weight of gelatin is preferably 30,000 or less, and more preferably, 10,000 or less.

The low molecular weight gelatin for use in the method used in the present invention can be normally prepared as follows. That is, gelatin which is normally used and has an average molecular weight of 100,000 is dissolved in water, and a gelatin-decomposing enzyme is added to the resultant aqueous gelatin solution, thereby decomposing gelatin molecules by the enzyme. For the method, R.J. Cox., "Photographic Gelatin II", Academic Press, London, 1976, PP. 233 to 251 and PP. 335 to 346 is helpful. Since the bonding position to be decomposed by the enzyme is predetermined, low molecular weight gelatin having a comparatively narrow molecular weight distribution is preferably obtained. As the enzyme decomposition time is prolonged, the molecular weight is reduced. In addition, gelatin may be heated and hydrolyzed in a low-pH (pH = 1 to 3) or high-pH (pH = 10 to 12) atmosphere.

When the synthetic protective colloid, the natural protective colloid, and the low molecular weight gelatin described above are used, grain formation of a fine grain silver halide can be performed at 40°C or less, and preferably, 35°C or less. As a result, problems posed when normal gelatin is used as the protective colloid can be perfectly solved.

In the method A, when the protective colloid is to be added to the mixer vessel, its concentration is 0.2 wt% or more, preferably 1 wt% or more, and more preferably, 2 wt% or more. When the protective colloid is to be added to the aqueous silver nitrate solution and/or aqueous halide solution, its concentration is 0.2 wt% or more, preferably, 1 wt% or more, and more preferably, 2 wt% or more.

In the method B, the concentration of the aqueous protective colloid solution in the vessel (another reactor vessel or the mixer vessel of the present invention) upon preparation of the fine grain emulsion is 0.2 wt% or more, preferably, 1 wt% or more, and more preferably, 2 wt% or more.

In the method A, the temperature of the mixer vessel is 40°C or less, and preferably, 35°C or less. The temperature of the reactor vessel is 50°C or more, preferably, 60°C or more, and more preferably, 70°C or more.

In the method B, the grain formation temperature of the fine grain emulsion prepared beforehand is 40°C or less, and preferably, 35°C or less. The temperature of the reactor vessel to which the fine grain emulsion is added is 50°C or more, preferably 60°C or more, and more preferably, 70°C or more.

The grain size of the fine grain silver halide for use in the present invention can be confirmed by observing a grain placed on a mesh by a transmission electron microscope. In this case, a magnification is preferably 20,000 to 40,000 times. The grain size of the fine grains used in the present invention is 0.06 μm or less, preferably, 0.03 μm or less, and more preferably, 0.01 μm or less.

In the method used in the present invention, if a silver halide solvent is added to the reactor vessel, a higher fine grain dissolution speed and a higher growth speed of grains in the reactor vessel can be obtained.

Examples of the silver halide solvent are a water-soluble bromide, a water-soluble chloride, a thiocyanate, ammonia, thioether, and thioureas.

More specifically, examples of the silver halide solvent are thiocyanates (e.g., U.S. Patents 2,222,264, 2,448,534, and 3,320,069); ammonia; thioether compounds (e.g., U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439, and 4,276,347); thion compounds (e.g., JP-A-53-144319, JP-A-53-82408, and JP-A-55-77737); an amine compound (e.g., JP-A-54-100717); a thiourea derivative (e.g., JP-A-55-2982); an imidazole (e.g., JP-A-54-100717); and a substituted mercaptotetrazole (e.g. JP-A-57-202531).

The halide composition of the emulsion prepared by the method used in the present invention may be any of silver iodobromide, silver chlorobromide, silver chloroiodobromide, and silver chloroiodide. Silver halide mixed crystal grains having a uniform microscopic distribution of a halide, i.e., "perfectly uniform" silver halide mixed crystal grains can be obtained as described in Japanese Patent Application Nos. 63-195778, 63-7851, 63-7852, 63-7853, 63-7451, and 63-7449. The grains can be obtained for any halide composition.

The method used in the present invention is very effective in the manufacture of pure silver bromide or pure silver chloride. According to the conventional manufacturing method, local distributions of silver ions and halide ions are inevitable in a reactor vessel. Therefore, the silver halide grains in the reactor vessel are placed in an environment different from another uniform portion through such a local non-uniform portion. As a result, not only the non-uniformity of growth is caused, but also reduced silver or fogged silver is produced at the portion having a high silver ion concentration. Therefore, in silver bromide and silver chloride, although the non-uniform distribution of the halide is not caused, non-uniformity of another sense as described above is caused. This problem, however, can be perfectly solved by the method used in the present invention.

After nucleation, the grain growth is performed in accordance with the following arrangement.

	1st Coating Layer	2nd Coating Layer	3rd Coating Layer
1	*Uniform AgBrI	-	-
2	AgBr	Uniform AgBrI	-
3	Uniform AgBrI	AgBr	-
4	do	Uniform AgBrI	-
5	AgBr	do	AgBr
6	AgBr	Non-uniform AgBrI	Uniform AgBrI
7	Uniform AgBrI	AgBr	Uniform AgBrI
8	Non-uniform AgBrI	do	do
9	do	Uniform AgBrI	AgBr
10	Uniform AgBrI	Non-uniform AgBrI	do

* Uniform means "microscopically uniform" as used in the present invention.

In the case of silver iodochlorobromide, silver chloride need only be added to the above arrangement. The silver chloride containing layer may be any of the 1st, 2nd, and 3rd coating layers.

In the present invention, the ratio of the microscopically uniform AgBrI phase in the grains is preferably 5 to 95 mol%.

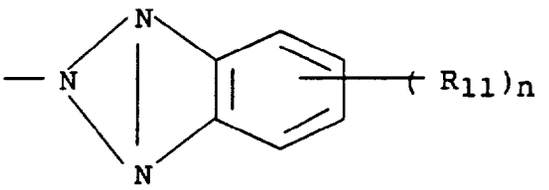
The compound which reacts with the oxidized form of a color developing agent to form a cleavage compound, said cleavage compound reacting with another molecule of the oxidized form of a color developping agent to form a development inhibitor or a precursor thereof, will be described below. This compound (to be referred to as development inhibitor releasing compound hereinafter) is e.g. represented by the following formula:

A (or B)-P-Z wherein A represents a coupling component which reacts with the oxidized form of a color developing agent to release -P-Z, B represents a redox component which undergoes oxidation-reduction reaction with the oxidized form of a color developing agent and alkali hydrolysis to release -P-Z, Z represents a development inhibitor or a precursor of a development inhibitor, -P-Z represents a group which is cleaved from A or B and reacts with the oxidized form of a colour developing agent to release Z, and P represents a moiety which undergoes a bimolecular reaction with the oxidized form of a colour developing agent to release Z.

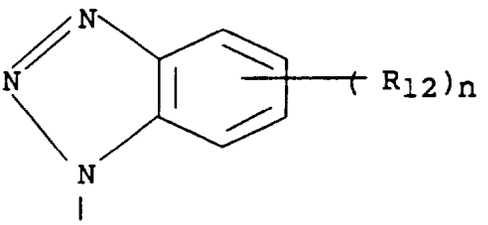
Z may be a diffusible development inhibitor or a development inhibitor having a slightly diffusible property. By way of the diffusible property of -P-Z, the distance which diffusion-resistant compound A (or B)-P-Z can exert its inter-layer effect can be changed.

The development inhibitor represented by Z includes a development inhibitor as described in Research Disclosure, Vol. 176, No. 17643, (December, 1978). Preferable examples of the development inhibitor are mercaptotetrazole, selenotetrazole, mercaptobenzothiazole, selenobenzothiazole, mercaptobenzooxazole, selenobenzooxazole, mercaptobenzimidazole, selenobenzimidazole, benzotrrazole, mercaptotriazole, mercaptooxadiazole, mercaptothiadiazole, and their derivatives. Preferable development inhibitors are represented by the following formulas:

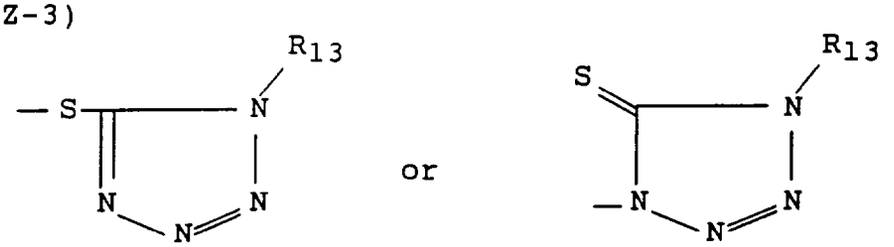
(Z-1)



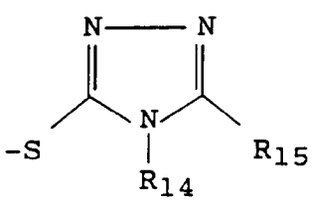
(Z-2)



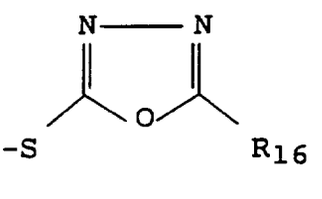
(Z-3)



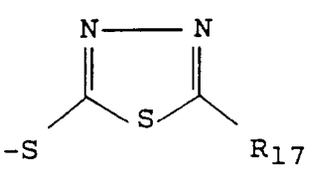
(Z-4)



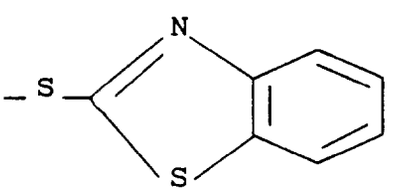
(Z-5)



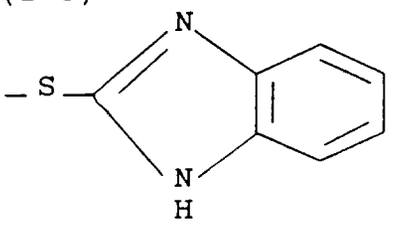
(Z-6)



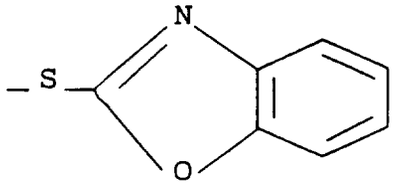
(Z-7)



(Z-8)



(Z-9)



In formulas (Z-1) and (Z-2), R_{11} and R_{12} each represent alkyl, alkoxy, acylamino, a halogen atom, alkoxycarbonyl, thiazolilideneamino, aryloxycarbonyl, acyloxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, sulfonamido, N-alkylcarbamoyloxy, ureido, hydroxy, alkoxycarbonylamino, aryloxy, alkylthio, arylthio, anilino, aryl, imido, a heterocyclic ring, cyano, alkylsulfonyl, or aryloxycarbonylamino.

n represents 1 or 2. When n is 2, R_{11} and R_{12} may be the same or different. The total number of the carbon atoms contained in n R_{11} and R_{12} is 0 to 20.

In formulas (Z-3), (Z-4), (Z-5), and (Z-6), R_{13}, R_{14}, R_{15}, R_{16}, and R_{17} each represent alkyl, aryl, or a heterocyclic group.

When each of R_{11} to R_{17} represents an alkyl group, the alkyl may be substituted or nonsubstituted, or chained or cyclic. Examples of the substituting group are a halogen atom, nitro, cyano, aryl, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, sulfamoyl, carbamoyl, hydroxy, alkanesulfonyl, arylsulfonyl, alkylthio, and arylthio.

When R_{11} to R_{17} each represent an aryl group, the aryl may be substituted. Examples of the substituting group are alkyl, alkenyl, alkoxy, alkoxycarbonyl, a halogen atom, nitro, amino, sulfamoyl, hydroxy, carbamoyl, aryloxycarbonylamino, alkoxycarbonylamino, acylamino, cyano, and ureido.

When R_{11} to R_{17} each represent a heterocyclic group, it represents a 5- or 6-membered single- or condensed-ring containing a nitrogen atom, an oxygen atom, or a sulfur atom as a hetero atom. Examples of the heterocyclic group are pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl imidazolyl, thiazolyl, triazolyl, benzotriazolyl, imido, and oxadine. These compounds may be substituted by the substituting groups enumerated above for the aryl group.

In formulas (Z-1) and (Z-2), the number of carbon atoms contained in R_{11} and R_{12} is 1 to 20, and more preferably, 7 to 20.

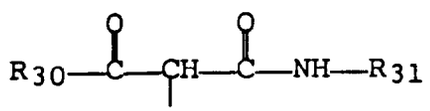
In formulas (Z-3), (Z-4), (Z-5), and (Z-6), the total number of carbon atoms contained in R_{13} to R_{17} is 1 to 20, and more preferably, 4 to 20.

In the present invention, a preferable development inhibitor is a compound which is released upon reaction with the oxidized form of a color developing agent and diffuses from a layer in which it is contained upon development to another layer, thereby exhibiting a development inhibiting effect. A compound having a small diffusing property is also used.

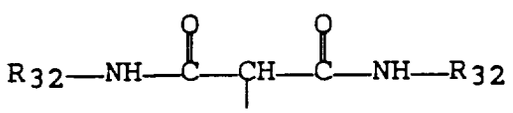
Examples of the coupler component represented by A are dye forming couplers such as acylacetoanilides, malondiesters, malondiamides, benzoylmethanes, pyrazolones, pyrazolotriazoles, pyrazolobenzimidazoles, indazolones, phenols, and naphthols; and coupler components essentially not forming a dye such as acetophenones, indanones, and oxazolones.

Examples of the preferable coupler components are formulas (V) to (IX).

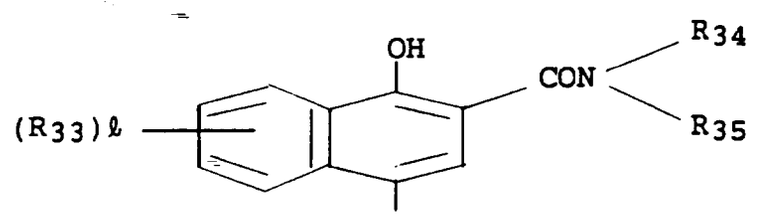
Formula (V)



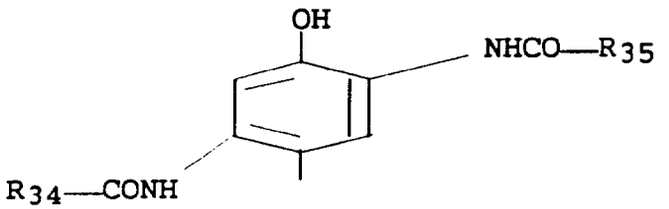
Formula (VI)



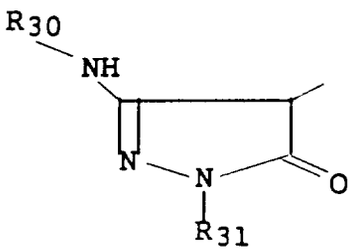
Formula (VII]



Formula (VIII)



Formula (IX)



wherein R_{30} represents an aliphatic group, an aromatic group, an alkoxy group, or a heterocyclic group, and each of R_{31} and R_{32} independently represents an aromatic group or a heterocyclic group.

The aliphatic group represented by R_{30} preferably has 1 to 20 carbon atoms, and is substituted or nonsubstituted and chained or cyclic. Examples of the preferable substituting groups on the alkyl group are groups of alkoxy, aryloxy, and acylamino.

If R_{30}, R_{31}, or R_{32} is an aromatic group, it represents, e.g., phenyl or naphthyl. In particular, phenyl is effective. In this case, a phenyl group may have a substituting group. Examples of the substituting groups are alkyl, alkenyl, alkoxy, alkoxycarbonyl, and alkylamido having 30 or less carbon atoms. Phenyl represented by R_{30}, R_{31}, and R_{32} may be substituted by alkyl, alkoxy, cyano, or a halogen atom.

R_{33} represents, e.g., a hydrogen atom, alkyl, a halogen atom, carbonamido, or a sulfonamido, and ℓ represents an integer of 1 to 5. Each of R_{34} and R_{35} independently represents hydrogen, alkyl or aryl. Phenyl is preferred as aryl. Alkyl and aryl may have substituting groups. Examples of the substituting groups are a halogen atom, alkoxy, aryloxy, and carboxyl. R_{34} and R_{35} may be the same or different.

As the development inhibitor in the present invention, P is preferably a group serving as a redox group or coupler after itM $_s$ cleaved from A or B.

These compounds used in the present invention can be easily synthesized by methods described in U.S. Patents 3,227,554, 3,617,291, 3,933,500, 3,958,993, 4,149,886, and 4,234,678, JP-A-51-13239, JP-A-57-56837, British Patents 2,070,266 and 2,072,363, Research Disclosure No. 21228, December 1981, JP-B-58-9942, JP-B-51-16141, JP-A-52-90932, U.S. Patent 4,248,962, JP-A-56-114946, JP-A-57-154234, JP-A-58-98728, JP-A-58-209736, JP-A-58-209737, JP-A-58-209738, JP-A-58-209740, Japanese Patent Application No. 59-278,853, JP-A-61-255342, and JP-A-62-24252.

Typical examples of the development inhibitor releasing compound for use in the present invention are listed in Table A to be presented later.

These development inhibitor releasing compounds are added in amounts of 0.0001 to 0.5 mol, and preferably, 0.01 to 0.3 mol per mol of silver in the light-sensitive silver halide emulsion layer, or if the compounds are to be added to a non-light-sensitive colloid layer, per mol of silver in adjacent light-sensitive silver halide emulsion layers. The develop-

ment inhibitor releasing compounds of the present invention may be used in combination of two or more thereof.

In the present invention, the most significant effect can be obtained when the development inhibitor releasing compounds are added to a layer using emulsion grains containing microscopically uniform silver iodide. In particular, a compound which releases a development inhibitor as a split-off group having a large diffusion property is preferable. More specifically, the diffusion property of a development inhibitor, described in JP-A-59-129849, is preferably 0.4 to 0.95. If the layers of the multilayered light-sensitive material contain the emulsion used in the invention, it suffices to use the development inhibitor releasing compound in at least one of the layers, thereby to attain the object of the invention.

The above development inhibitor releasing compounds can be introduced to a light-sensitive silver halide emulsion layer and/or a non-light-sensitive colloid layer by known methods to be described in detail later, e.g., a method described in U.S Patent 2,322,027.

The silver halide multilayered color photographic light-sensitive material of the present invention preferably has a multilayered structure in which the emulsion layers containing binders and silver halide grains for independently recording blue light, green light, and red light are stacked. Each emulsion layer preferably consists of at least two layers, i.e., high- and low-sensitivity layers. Examples of a most practical layer arrangement are:

(1) BH/BL/GH/GL/RH/RL/S
(2) BH/BM/BL/GH/GM/GL RH/RM/RL/S;
(3) BH/BL/GH/RH/GL/RL/S as described in U.S. Patent 4,184,876; and
(4) BH/GH/RH/BL/GL/RL/S

as described in RD-22534, JP-A-59-177551, and JP-A-59-177552.

In each of the above layer arrangements, B represents a blue-sensitive layer; G, a green-sensitive layer; R, a red-sensitive layer; H, a high-sensitivity layer; M, a medium-sensitivity layer; L, a low-sensitivity layer; and S, a support. Non-light-sensitive layers such as a protective layer, a filter layer, an interlayer, an antihalation layer, and a subbing layer are omitted from the above layer arrangements.

A preferable layer arrangement is (1), (2), or (4).

In addition, layer arrangements

(5) BH/BL/CL/GH/GL/RH/RL/S, and
(6) BH/BL/GH/GL/CL/RH/RL/S

as described in JP-A-61-34541 are also preferable.

In these layer arrangements, CL represents an interlayer effect imparting layer, and the other reference symbols are as described above.

If the layer arrangement is (1), preferably, an emulsion used in the present invention is used in at least one layer of BH, BL, GH, GL, RH, and RL. In this case, preferably, an emulsion used in the present invention having an aspect ratio of 5 to 8 is used in BH and BL, and an emulsion used in the present invention having an aspect ratio of 5 or less is used in GH, GL, RH, and RL.

An emulsion used in the present invention having an aspect ratio of 5 or less is preferably used in all of GH, GL, RH, and RL. Monodisperse silver halide grains may be used in BH as disclosed in Japanese Patent Application No. 61-157656.

In addition, a monodisperse emulsion may be used in a low-sensitivity layer. In this case, the monodisperse emulsion may contain twinned or regular crystals, and preferably, regular crystals. Two or more different types of emulsions may be mixed in a single layer. For example, any mixing such as mixing of monodisperse emulsions or tabular emulsions having different grain sizes can be performed.

If the layer arrangement is (5), an emulsion used in the present invention is preferable used in also CL.

If the layer arrangement is (6), an emulsion used in the present invention, especially, an emulsion having an aspect ratio of 5 or less is preferably used in CL.

In the layer arrangements of (5) and (6), emulsions for use in layers except for CL are similar to those used in (1).

Furthermore, high- and low-sensitivity layers having the same color sensitivity may be arranged in a reverse order. If high-, medium-, and low-sensitivity layers are present, all possible arrangements may be allowed.

Known photographic additives which can be used in the present invention are described in Research Disclosures, Item 17643 and Item 18716, and they are summarized in the following table.

Additives	RD No.17643	RD No.18716
1. Chemical sensitizers	page 23	page 648, right column
2. Sensitivity increasing agents		do
3. Spectral sensitizers, super sensitizers	pages 23-24	page 648, right column to page 649, right column
4. Brighteners	page 24	
5. Antifoggants and stabilizers	pages 24-25	page 649, right column
	pages 24-25	
6. Light absorbent, filter dye, ultraviolet absorbents	pages 25-26	page 649, right column to page 650, left column
7. Stain preventing agents	page 25, right column	page 650, left to right columns
8. Dye image stabilizer	page 25	
9. Hardening agents column	page 26	page 651, left
10. Binder	page 26	do
11. Plasticizers, lubricants	page 27	page 650, right column
12. Coating aids, surface active agents	pages 26-27	do
13. Antistatic agents	page 27	do

In order to prevent degradation in photographic properties caused by formaldehyde gas, a compound which can react with and fix formaldehyde as described in U.S. Patent 4,411,987 or 4,435,503 is preferably added to the light-sensitive material.

In this invention, various color couplers can be used in the light-sensitive material. Specific examples of these couplers are described in the above-described Research Disclosure, No. 17643, VII-C to VII-G as patent references.

Preferred examples of the yellow couplers are described in, e.g., U.S. Patents 3,933,501, 4,022,620, 4,326,024, and 4,401,752, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023, and 4,511,649, and EP 249,473A.

Examples of the magenta couplers are preferably 5-pyrazolone and pyrazoloazole compounds, and more preferably, compounds described in, e.g., U.S. Patents 4,310,619 and 4,351,897, EP 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 2422 (June 1984), JP-A-60-33552, RD No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, and U.S. Patents 4,500,630, 4,540,654, and 4,556,630.

Examples of the cyan couplers are phenol and naphthol couplers, and preferably, those described in, e.g., U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, and 4,327,173, West German Patent Application (OLS) No. 3,329,729, EP 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A-61-42658.

Preferable examples of the colored couplers for correcting additional, undesirable absorption of a colored dye are those described in Research Disclosure No. 17643, VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368.

Preferable examples of the couplers capable of forming colored dyes having proper diffusibility are those described in U.S. Patent 4,366,237, British Patent 2,125,570, EP 96,570, and West German Patent Application (OLS) No. 3,234,533.

Typical examples of the polymerized dye-forming couplers are described in U.S. patents 3,451,820, 4,080,211, 4,367,282, 4,409,320, and 4,576,910, and British Patent 2,102,173.

Couplers releasing a photographically useful moiety upon coupling are preferably used in the present invention.

Preferable examples of the couplers imagewise releasing a nucleating agent or a development accelerator upon development are those described in British Patent 2,097,140, 2,131,188, and JP-A-59-157638 and JP-A-59-170840.

Examples of the couplers which can be used in the light-sensitive material of the present invention are the competing couplers described in, e.g., U.S. Patent 4,130,427; the poly-equivalent couplers described in, e.g., U.S. Patents 4,283,472, 4,338,393, and 4,310,618; the couplers releasing a dye which turns to a colored form after being released described in EP 173,302A; the bleaching accelerator releasing couplers described in, e.g., RD. Nos. 11449 and 24241 and JP-A-61-201247; and the legand releasing couplers described in, e.g., U.S. Patent 4,553,477.

The couplers for use in this invention can be introduced in the light-sensitive materials by various known dispersion methods.

Examples of the high-boiling solvent used in the oil-in-water dispersion method are described in, e.g., U.S. Patent

2,322,027.

Examples of the high-boiling organic solvent to be used in the oil-in-water dispersion method and having a boiling point of 175°C or more at normal pressure are phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, decylphthalate, bis(2,4-di-t-amylphenyl)phthalate, bis(2,4-di-t-amylphenyl)isophthalate, and bis(1,1-diethylpropyl)phthalate), phosphates or phosphonates (e.g., triphelphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trichloropropylphosphate, and di-2-ethylhexylphenylphosphate), benzoates (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, and N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearylalcohol and 2,4-di-tert-amylphenol), aliphatic carboxylates (e.g., bis(2-ethylhexyl)sebacate, dioctylazelate, glyceroltributylate, isostearyllactate, and trioctylcitrate), an aniline derivative (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), and hydrocabons (e.g., paraffin, dodecylbenzene, and diisopropylnaphthalene). An organic solvent having a boiling point of about 30°C or more, and preferably, 50°C to about 160°C can be used as a co-solvent. Typical examples of the co-solvent are ethyl acetate, butyl acetate, ethyl propionate, methylethylketone, cyclohexanone, 2-ethoxyethylacetate, and dimethylformamide.

Steps and effects of the latex dispersion method and examples of the loadable latex are described in, e.g., U.S. Patent 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The present invention can be applied to various color light-sensitive materials. Examples of the material are a color negative film for a general purpose or a movie, a color reversal film for a slide or a television, color paper, a color positive film, and color reversal paper.

Examples of the support suitable for use in this invention are described in the above-mentioned RD. No. 17643, page 28 and ibid., No. 18716, page 647, right column to page 648, left column.

The color photographic light-sensitive materials of this invention can be processed by the ordinary processes as described, for example, in the above-described Research Disclosure, No. 17643, pages 28 to 29 and ibid., No. 18716, page 651, left to right columns.

In order to develop the light-sensitive material of the present invention, a conventional color negative light-sensitive material processing method can be adopted (e.g., CN-16 and CN-16Q available from Fuji Photo Film Co., Ltd.; C-41 and C-41RA available from Eastman Kodak Co.; and CNK-4 available from KONICA CORP.)

As the developing agent, the developing solution additive, the bleaching agent, the bleach accelerator, the fixing agent, and the washing/stabilizing step, materials and the step described in JP-A-63-298344 (Japanese Patent Application No. 62-134402) page 14, lower left column to page 18, upper right column can be used.

EXAMPLES

Examples of the present invention will be described below.

Layers having the following compositions were formed on an undercoated cellulose triacetate film support to form a multilayered color photographic light-sensitive material. The composition of the layer 11 was changed to form various types of samples. The coating amounts of the silver halide and colloid silver are represented in units of g/m^2 of silver, those of the coupler, the additive, and gelatin are represented in units of g/m^2 and that of the sensitizing dye is represented by the number of mols per mol of silver halide in the same layer.

Layer 1: Antihalation Layer

Black Colloid Silver	0.2
Gelatin	1.3
ExM-9	0.06
UV-1	0.03
UV-2	0.06
UV-3	0.06
Solv-1	0.15
Solv-2	0.15
Solv-3	0.05

Layer 2: Interlayer

Gelatin	1.0
UV-1	0.03
ExC-4	0.02
ExF-1	0.004
Solv-1	0.1
Solv-2	0.1

Layer 3: Low-Sensitivity Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4 mol%, determined AgI type, sphere-equivalent diameter = 0.5 μm, variation coefficient of sphere-equivalent diameter = 20%, tabular grain, diameter/thickness ratio = 3.0) coating silver amount	1.2
Silver Iodobromide Emulsion (AgI = 3 mol%, determined AgI type, sphere-equivalent diameter = 0.3μm, variation coefficient of sphere-equivalent diameter = 15%, spherical grain, diameter/thickness ratio = 1.0) coating silver amount	0.6
Gelatin	1.0
EXS-1	4×10^{-4}
EXS-2	5×10^{-5}
ExC-1	0.05
ExC-2	0.50
ExC-3	0.03
ExC-4	0.12
ExC-5	0.01

Layer 4: High-Sensitivity Red-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 6 mol%, internally high AgI type having core/shell ratio of 1 : 1, sphere-equivalent diameter 0.7 μm, variation coefficient of sphere-equivalent diameter = 15%, tabular grain, diameter/thickness ratio = 5.0) coating silver amount	0.7
Gelatin	1.0
EXS-1	3×10^{-4}
EXS-2	2.3×10^{-5}
ExC-6	0.11
ExC-7	0.05
ExC-4	0.05
Solv-1	0.05
Solv-3	0.05

Layer 5: Interlayer

Gelatin	0.5
Cpd-1	0.1
Solv-1	0.05

Layer 6: Low-Sensitivity Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4 mol%, internally high AgI type having core/shell ratio of 1 : 1, sphere-equivalent diameter = 0.5 μm, variation coefficient of sphere-equivalent diameter = 15%, tabular grain, diameter/thickness ratio = 4.0) coating silver amount	0.35
Silver Iodobromide Emulsion (AgI = 3 mol%, determined AgI type, sphere-equivalent diameter = 0.3 μm, variation coefficient of sphere-equivalent diameter = 25%, spherical grain, diameter/thickness ratio = 1.0) coating silver amount	0.20
Gelatin	1.0
ExS-3	5×10^{-4}
Exs-4	3×10^{-4}
ExS-5	1×10^{-4}
ExM-8	0.4
ExM-9	0.07
ExM-10	0.02
ExY-11	0.03
Solv-1	0.3
Solv-4	0.05

Layer 7: High-Sensitivity Green-Sensitive Emulsion Layer

Silver Iodobromide Emulsion (AgI = 4 mol%, internally high AgI type having core/shell ratio of 1 : 3, sphere-equivalent diameter = 0.7 μm, variation coefficient of sphere-equivalent diameter = 20%, tabular grain, diameter/thickness ratio = 5.0) coating silver amount	0.8
Gelatin	0.5
EXS-3	5×10^{-4}
EXS-4	3×10^{-4}
EXS-5	1×10^{-4}
ExM-8	0.1
ExM-9	0.02
ExY-11	0.03
ExC-2	0.03
ExM-14	0.03
Solv-1	0.2
Solv-4	0.01

Layer 8: Interlayer

Gelatin	0.5
Cpd-1	0.05
Solv-1	0.02

Layer 9: Doner Layer Having Interlayer Effect On Red-Sensitive Layer

Silver Iodobromide Emulsion (AgI = 2 mol%, internally high AgI type having core/shell ratio of 2 : 1, sphere-equivalent diamter = 1.0 μm, variation coefficient of sphere-equivalent diameter = 15%, tabular grain, diameter/thickness = 6.0) coating silver amount	0.35
Silver Iodobromide Emulsion (AgI = 2 mol%, internally high AgI type having core/shell ratio of 1 : 1, sphere-equivalent diameter = 0.4 μm, variation coefficient of sphere-equivalent diameter = 20%, tabular grain, diameter/thickness = 6.0) coating silver amount	0.20
Gelatin	0.5
ExS-3	8×10^{-4}
ExY-13	0.11
ExM-12	0.03
ExM-14	0.10
Solv-1	0.20

Layer 10: Yellow Filter Layer

Yellow Colloid Silver	0.05
Gelatin	0.5
Cpd-2	0.13
Solv-1	0.13
Cpd-1	0.10

Layer 11: Blue-Sensitive Emulsion Layer

Emulsion listed in Table 1	0.72
Gelatin	2.56
Emulsfied dispersion listed in Table 2	
ExY-15	2.4
Development Inhibitor Releasing Compound	0.45

Layer 12: 1st Protective Layer

Gelatin	0.8
UV-4	0.1
UV-5	0.15
Solv-1	0.01
Solv-2	0.01

Layer 13: 2nd Protective Layer

Fine Grain Silver Iodobromide Emulsion (AgI = 2 mol%, determined AgI type, sphere-equivalent diameter = 0.07 μm)	0.5
Gelatin	0.45
Polymethylmethacrylate Grain (diameter = 1.5 μm)	0.2
H-1	0.4
Cpd-5	0.5
Cpd-6	0.5

In addition to the above components, the stabilizing agent Cpd-3 (0.04 g/m^2) for the emulsion and the surface active agent Cpd-4 (0.02 g/m^2) were added to the layers as coating aids.

The formulas of the compounds used in the present invention will be listed in Table B to be presented later.

The method of preparing the emulsion used in the layer 11 will be described below.

Silver Iodobromide Fine Grain Emulsion I-A 1,200 mℓ of a 1.2 M silver nitrate solution and 1,200 mℓ of an aqueous halide solution containing 1.08 M potassium bromide and 0.12 M potassium iodide were added to 2.6 ℓ of a 2.0 wt% gelatin solution containing 0.026 M potassium bromide by a double jet method over 15 minutes under stirring. During this addition, the gelatin solution was kept at 35°C. The resultant emulsion was washed by a conventional flocculation method, and 30 g of gelatin were added and dissolved in the emulsion. Thereafter, the pH and the pAg were adjusted to be 6.5 and 8.6, respectively. The obtained silver iodobromide fine grains (silver iodide content = 10%) had an average grain size of 0.07 μm.

Tabular Silver Bromide Core Emulsion I-B

30 ml of a 2.0 M silver nitrate solution and 30 ml of a 2.0 M potassium bromide solution were added to 2 ℓ of a 0.8 wt% gelatin solution containing 0.09 M potassium bromide by a double jet method under stirring. During this addition, the gelatin solution in the reactor vessel was kept at 30°C. After the addition, the temperature was increased up to 75°C, and 40 g of gelatin were added. A 1.0 M silver nitrate solution was added to adjust the pBr to be 2.55, and 150 g of silver nitrate were added at an accelerated flow rate (the final flow rate was ten times an initial flow rate) over 60 minutes, and potassium bromide was simultaneously added by a double jet method so that the pBr was adjusted to be 2.55.

Thereafter, the emulsion was cooled to 35°C and washed by a conventional flocculation method, and 60 g of gelatin were added and dissolved at 40°C. The pH and the pAg were adjusted to be 6.5 and 8.6, respectively. The obtained tabular silver bromide grains were monodisperse tabular grains having an average circle-equivalent diameter of 1.4 μm, a grain thickness of 0.2 μm, and a variation coefficient of the circle-equivalent diameter of 15%.

Tabular Silver Iodobromide Emulsion I-C (Comparative Emulsion)

The emulsion I-B containing silver bromide corresponding to 50g of silver nitrate was added and dissolved in 1.1 ℓ of water, and the temperature and the pBr were kept at 75°C and 1.4, respectively. 1 g of 3.6-dithioctane-1,8-diol was added, and immediately an aqueous silver nitrate solution containing 100 g of silver nitrate and a potassium bromide solution containing 10 M% of potassium iodide were added in an equimolar amount with respect to silver nitrate at constant flow rates over 50 minutes. The emulsion was washed by a conventional flocculation method, and the pH and the pAg were adjusted to be 6.5 and 8.6, respectively. The obtained silver bromide tabular grains were silver iodobromide in which its central portion comprises silver bromide and its outer annular portion comprises silver iodobromide containing 10 M% of silver iodide. The average circle-equivalent grain size of the grains was 2.3 μm, and-their grain thickness was 0.26 μm.

Tabular Silver Iodobromide Emulsion I-D (Present Invention)

An emulsion I-D was prepared following the same procedures as for the emulsion I-C except for the following process. Instead of adding an aqueous silver nitrate solution and an aqueous halide solution to a reactor vessel, the fine grain emulsion I-A was added in an amount corresponding to 100 g of silver nitrate to the reactor vessel at a constant flow rate over 50 minutes. The obtained tabular grains had an average circle-equivalent diameter of 2.5 μm and a grain thickness of 0.23 μm.

Tabular Silver Iodobromide Emulsion I-E (Present Invention)

An emulsion I-E was prepared following the same procedures as for the emulsions I-C and I-D except for the following process. Equimolar amounts of a solution containing 100 g of silver nitrate and a potassium bromide solution containing 10 M% of potassium iodide were added at constant flow rates to a powerful mixer vessel provided near the reactor vessel and having a high stirring efficiency, thereby forming silver iodobromide fine grains. At this time, 300 ml of a 2 wt% gelatin solution were mixed in the aqueous halide solution prior to the above addition. Very fine grains formed by the mixer vessel were immediately, continuously introduced from the mixer to the reactor vessel containing the core emulsion I-B. During this process, the mixer vessel was kept at 40°C. The obtained tabular grains had an average circle-equivalent diameter of 2.6 μm and a grain thickness of 0.21 μm.

Tabular Silver Iodobromide Emulsion I-F (Present Invention)

An emulsion I-F was prepared following the same procedures as for the emulsion I-E except that the pBr was adjusted to be 2.6 during grain growth and no 3,6-dithioctane-1,8-diol was added. 86% of the obtained tabular grains were occupied by hexagonal tabular grains. The obtained tabular grains were a monodisperse tabular silver iodobromide emulsion having an average circle-equivalent diameter of 2.1 μm, a variation coefficient of the circle-equivalent diameter of 17%, and an average grain thickness of 0.23 μm.

The grains of the emulsions I-C, I-D, I-E, and I-F were sampled and their transmission images were observed by a 200 kvolt transmission electron microscope while they were cooled by liquid nitrogen. A clear annular ring-like stripe pattern was observed in the emulsion I-C, while no such pattern was observed in the emulsions I-D, I-E, and I-F used in the present invention. That is, it was confirmed that a tabular silver iodobromide emulsion containing a silver halide localized region having a microscopically uniform silver iodide distribution was obtained by the method used in the present invention. The transmission electron microscopic photographs of the emulsions I-C, I-D, and I-E are shown in Fig. 4. In the grains shown in Fig. 4 the core is a pure silver bromide not containing silver iodide, therefore, no stripe pattern indicating non-uniformity was found, and an outer annular portion (shell) was a silver iodobromide phase containing 10% of silver iodide. The core/shell ratio was 1 : 2.

330 mg/Ag mol of the sensitizing dye ExS-6 were added to each of the emulsions I-C to I-F (pH = 6.5 and pAg = 8.6) at 60°C. Ten minutes after the addition, soda thiosulfate, potassium chloroaurate, and potassium thiocyanate were added and optimally, chemically sensitized.

The characteristics of the emulsions Em-C, Em-D, Em-E, and Em-F are summarized in Table 1.

Table 1

Emulsion No.	Relationship with the Present Invention	Characteristics of Grains
Em-C	Comparative Example	Non-uniform
Em-D	According to the Present Invention	Microscopically Uniform
Em-E	According to the Present Invention	Microscopically Uniform
Em-F	According to the Present Invention	Microscopically Uniform

The method of preparing the emulsified dispersion used in the layer 11 will be described below.

(Method of Preparing the Emulsified Dispersion)

10.6 g of ExY-15 as the yellow coupler and 2 g of the development inhibitor releasing compound were dissolved in 11 mℓ of Solv-1 and 30 mℓ of ethyl acetate, and the resultant mixture was mixed with 200 mℓ of a 5% aqueous gelatin solution, then performing emulsification/ dispersion by using a colloid mill. The emulsified dispersions Vu-D, Vu-E, and Vu-F were prepared by using the development inhibitor releasing compounds T-144, T-104, and T-158, respectively.

The contents of Vu-D, Vu-E, and Vu-F are summarized in Table 2 below.

Table 2

Emulsified Dispersion No.	Yellow Coupler	Development Inhibitor Releasing Compound
Vu-D	ExY-15	T-144

Continuation of the Table on the next page

Table 2 (continued)

Emulsified Dispersion No.	Yellow Coupler	Development Inhibitor Releasing Compound
Vu-E	ExY-15	T-104
Vu-F	ExY-15	T-158

The emulsions listed in Table 1 and the emulsified dispersions listed in Table 2 were used in the layer 11 to prepare samples 101 to 112 listed in Table 3.

Table 3

Sample No.	Used Emulsion No.	Used Emulsified Dispersion No.
101	Em-C	Vu-D
102	Em-D	Vu-D
103	Em-E	Vu-D
104	Em-F	Vu-D
105	Em-C	Vu-E
106	Em-D	Vu-E
107	Em-E	Vu-E
108	Em-F	Vu-E
109	Em-C	Vu-F
110	Em-D	Vu-F
111	Em-E	Vu-F
112	Em-F	Vu-F

The sample Nos. 101 to 112 prepared as described above were imagewise-exposed by using white light and developed as described below, thereby obtaining cyan, magenta, and yellow image characteristic curves.

The color development processing was performed in accordance with the following processing steps at 38°C.

Color Development	3 min. 15 s
Bleaching	6 min. 30 s
Washing	2 min. 10 s
Fixing	4 min. 20 s
Washing	3 min. 15 s
Stabilizing	1 min. 05 s

The processing solution compositions used in the respective steps are as follows.

Color Developing Solution

Diethylenetriaminepentaacetic Acid	1.0 g
1-hydroxyethylidene-1,1-diphosphonic Acid	2.0 g
Sodium Sulfite	4.0 g
Potassium Carbonate	30.0 g

Potassium Bromide	1.4 g
Potassium Iodide	1.3 mg
Hydroxylamine Sulfate	2.4 g
4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline Sulfate	4.5 g
Water to make	1.0 ℓ
	pH 10.0

Bleaching Solution

Ferric Ammonium Ethylenediaminetetraacetate	100.0 g
Disodium Ethylenediaminetetraacetate	10.0 g
Ammonium Bromide	150.0 g
Ammonium Nitrate	10.0 g
Water to make	1.0 ℓ
	pH 6.0

Fixing Solution

Disodium Ethylenediaminetetraacetate	1.0 g
Sodium Sulfite	4.0 g
Ammonium Thiosulfate Aqueous Solution (70%)	175.0 mℓ
Sodium Bisulfite	4.6 g
Water to made	1.0 ℓ
	pH 6.6

Stabilizing Solution

Formalin (40%)	2.0 mℓ
Polyoxyehtylene-p-monononylphenylether (average polymerization degree = 10)	0.3 g
Water to make	1.0 ℓ

Gamma values in main gradation portions of characteristic curves of the obtained yellow and magenta images are summarized in Table 4.

Table 4

Sample No.	Remarks	γ Value of Yellow Image	γ Value of Magenta Image
101	Comparative Example	0.62	0.80
102	Present Invention	0.71	0.73
103	Present Invention	0.73	0.70
104	Present Invention	0.69	0.74

Continuation of the Table on the next page

Table 4 (continued)

Sample No.	Remarks	γ Value of Yellow Image	γ Value of Magenta Image
105	Comparative Example	0.53	0.83
106	Comparative Example	0.66	0.78
107	Comparative Example	0.69	0.74
108	Comparative Example	0.63	0.77
109	Comparative Example	0.48	0.88
110	Comparative Example	0.53	0.82
111	Comparative Example	0.56	0.80
112	Comparative Example	0.53	0.82

As is apparent from Table 4, each sample of the present invention had a small inhibiting effect of the blue-sensitive layer and a large inhibiting effect of the green-sensitive layer. In addition, as the diffusion property of the development inhibitor released upon reaction between the development inhibitor releasing compound and the oxidized form of the developing agent was increased, the inhibiting effect was increased.

The coating silver amounts of the emulsions Em-C to Em-F of the layer 11 were increased so that the γ values of the yellow images of the sample Nos. 101 to 104 are adjusted to be substantially 0.70. In addition, gray gradation of the blue-, green-, and red-sensitive layers were adjusted to be substantially the same.

The sample Nos. 101 to 104 were exposed to uniform green light and further wedge-exposed by using blue light to perform similar processing, thereby obtaining magenta images as shown in Fig. 5. Referring to Fig. 5, Δx represents the degree of the interlayer effect for inhibiting a uniformly fogged magenta emulsion layer when the blue-sensitive layer, from the non-exposed portion (point A) to the exposed portion (point B), is exposed. That is, in Fig.5, the curve A-B is the characteristic curve concerning the yellow image of the blue-sensitive layer, and the curve a-b represents the magenta image density of the green-sensitive layer obtained by uniform green exposure. The point A represents the fogged portion of the yellow image, and the point B represents the portion of the exposure amount for providing a yellow image density of 2.5. The difference (a - b) between the magenta density (a) at the exposure portion A and the magenta density (b) at the portion B was used as a scale representing the degree of the interlayer effect from the blue-sensitive layer to the green-sensitive layer.

The measurement of the MTF value was performed in accordance with the method described in "The Theory of photographic Process", 3rd edd., (by Meese, Macmillan). The results are summarized in Table 5.

Table 5

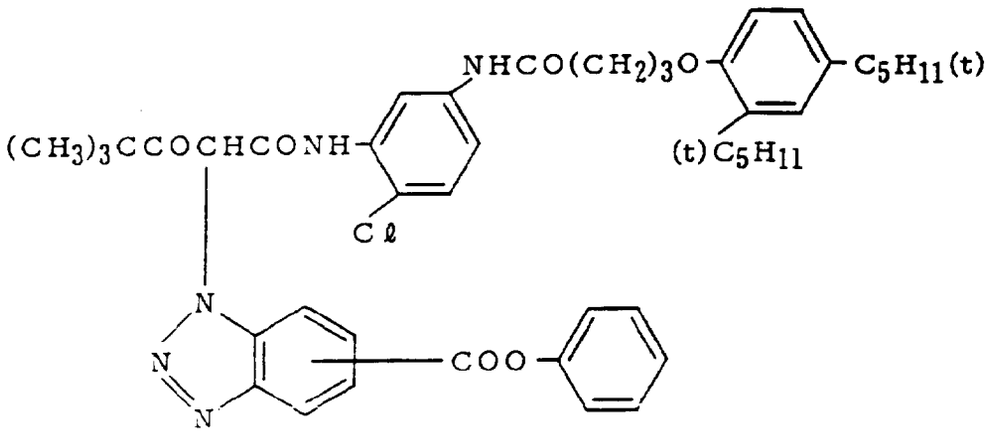
Sample No.	Remarks	Interlayer Effect Δx	MTF Value (GL 5/mm)
101	Comparative Example	0.31	1.12
102	Present Invention	0.33	1.24
103	Present Invention	0.34	1.26
104	Present Invention	0.33	1.25

As is apparent from Table 5, the samples 102, 103 and 104 had a larger interlayer effect and higher sharpness represented by MTF values than those of the comparative sample 101.

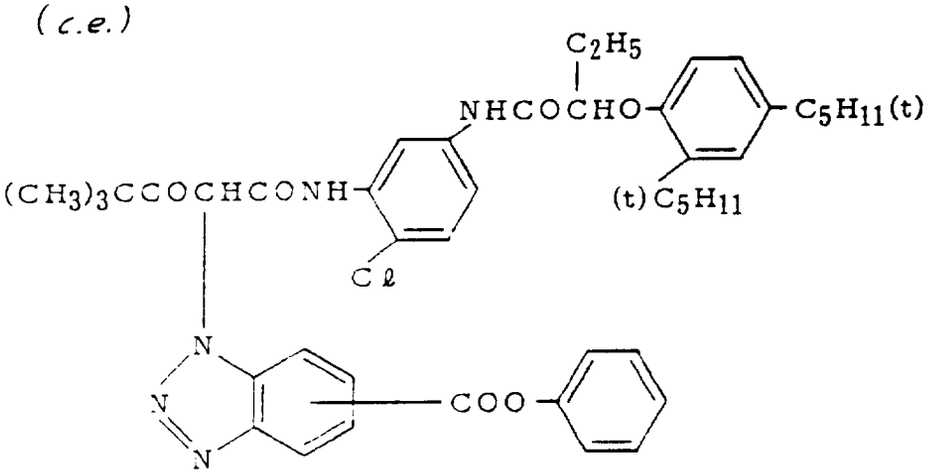
According to the present invention, a silver halide color photographic light-sensitive material having an improved interlayer effect can be obtained.

Table A

T-101
(c.e.)



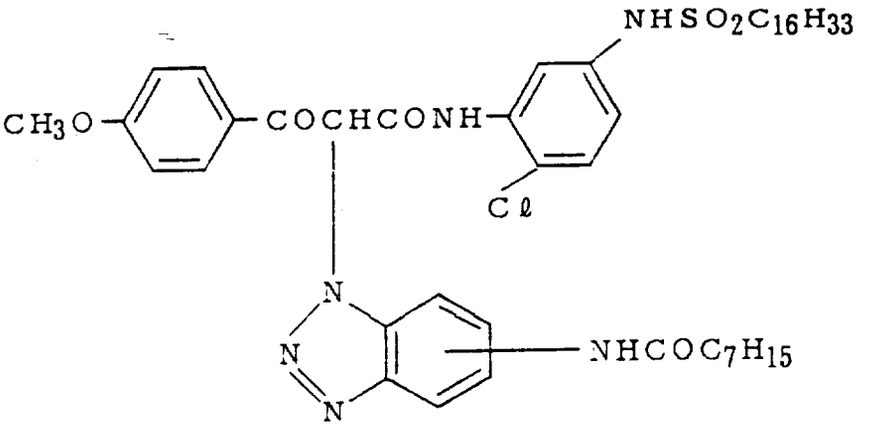
T-102
(c.e.)



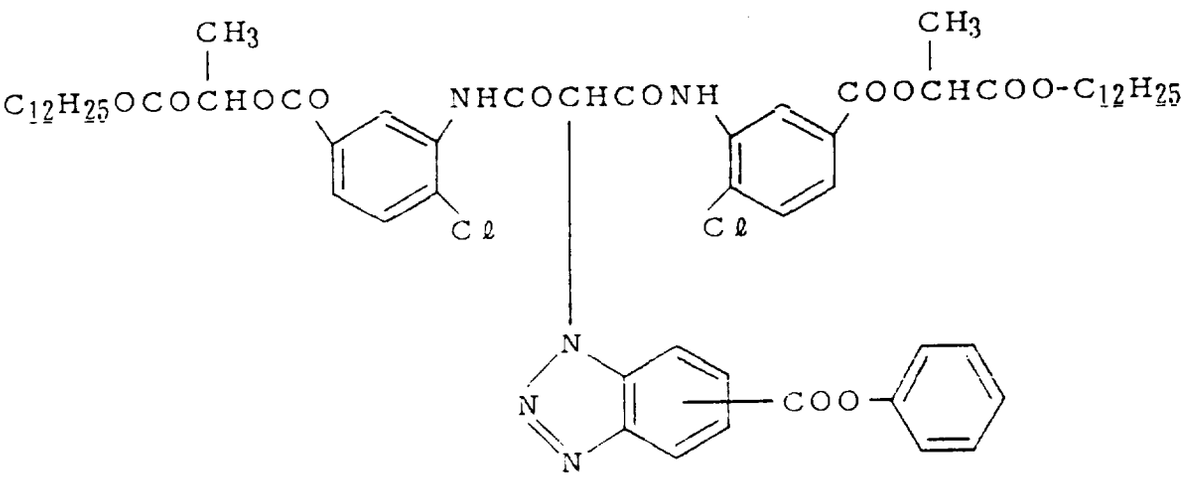
p.i.: DIR compounds used in the present invention

c.e.: Conventially used DIR compounds capable of releasing a development inhibitor along with coupling (comparative examples); e.g. disclosed in EP-A-0326853

T-103
(c.e.)

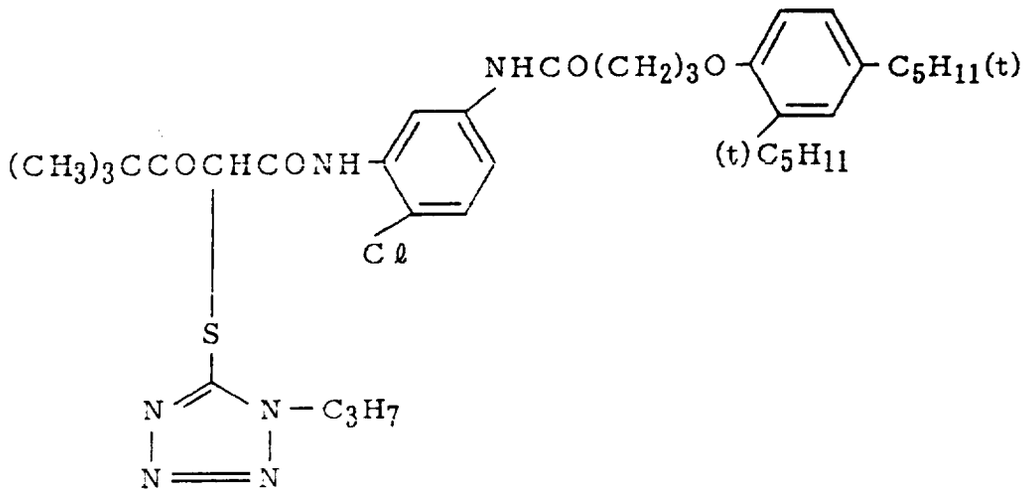


T-104
(c.e.)



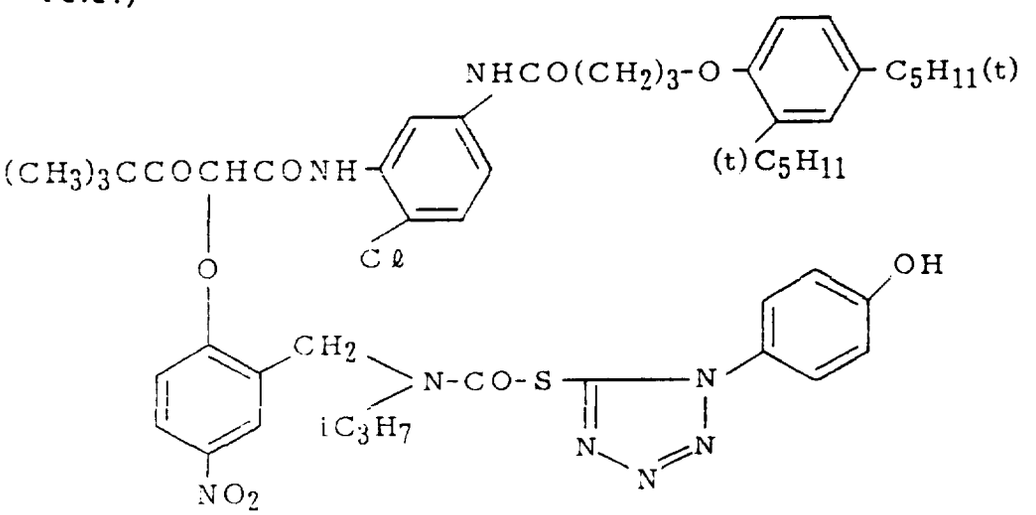
T-105

(c.e.)



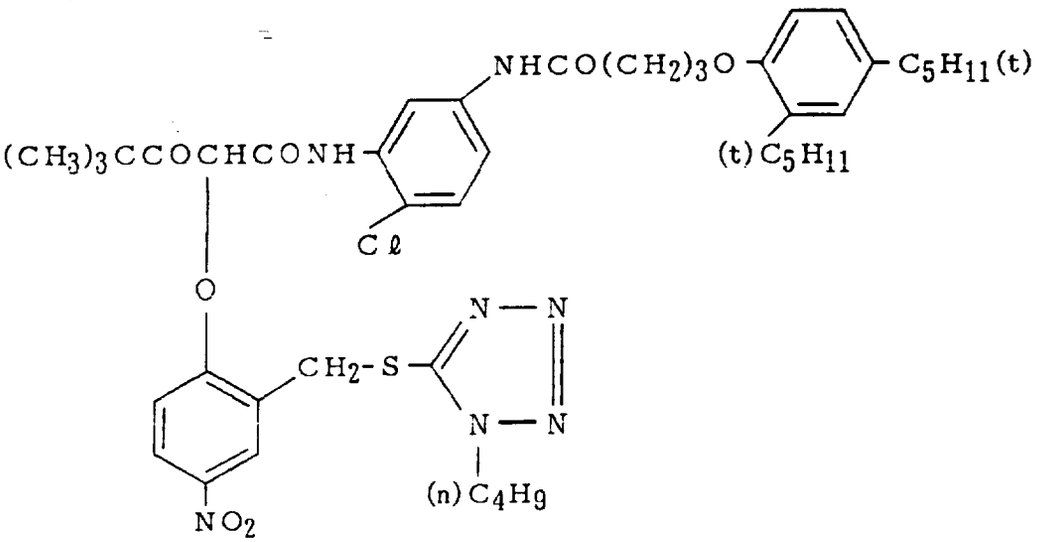
T-106

(c.e.)



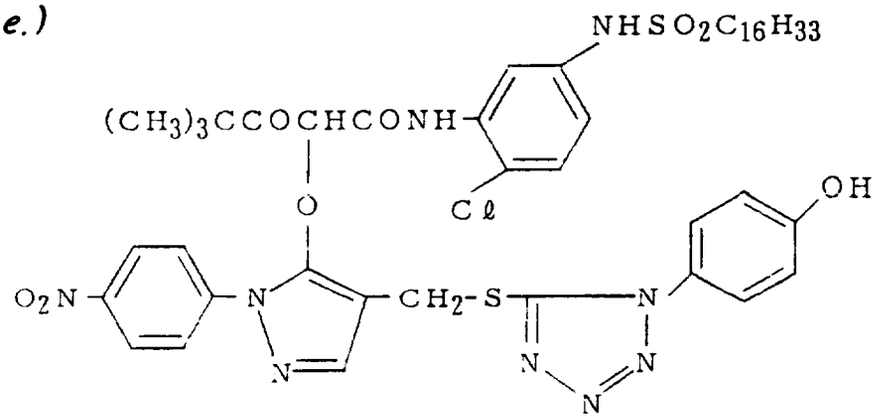
T-107

(c.e.)



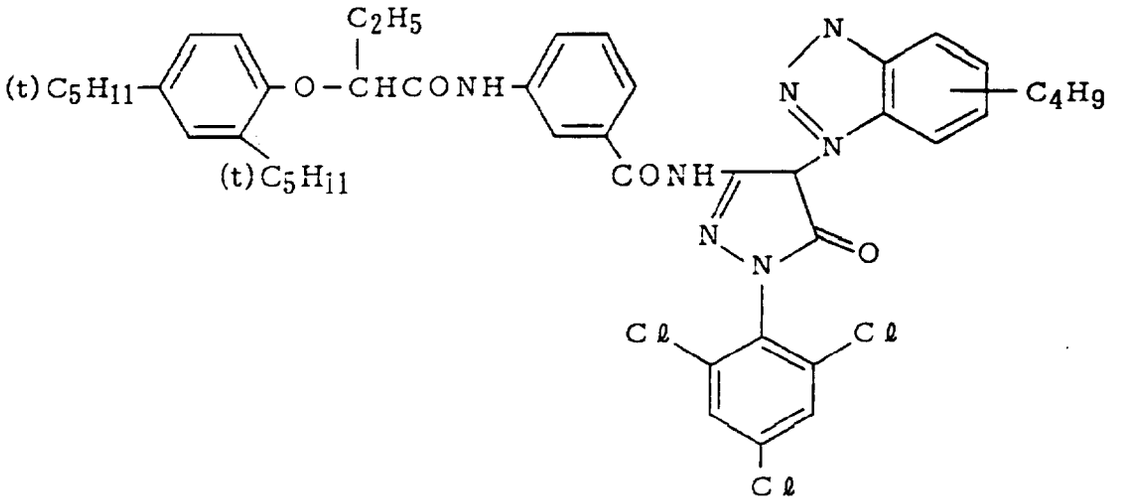
T-108

(c.e.)



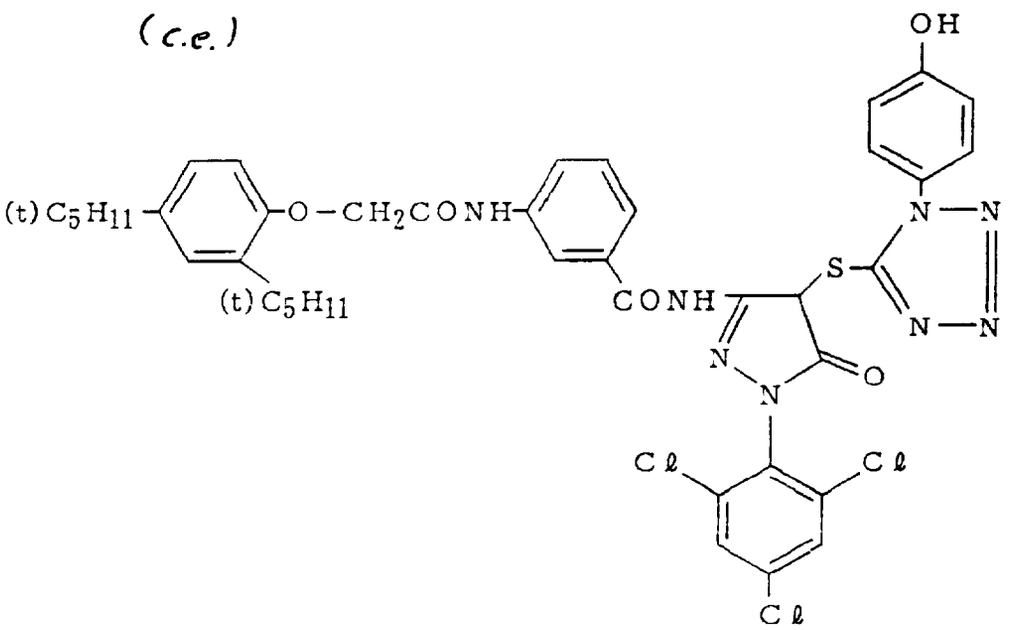
T-109

(c.e.)



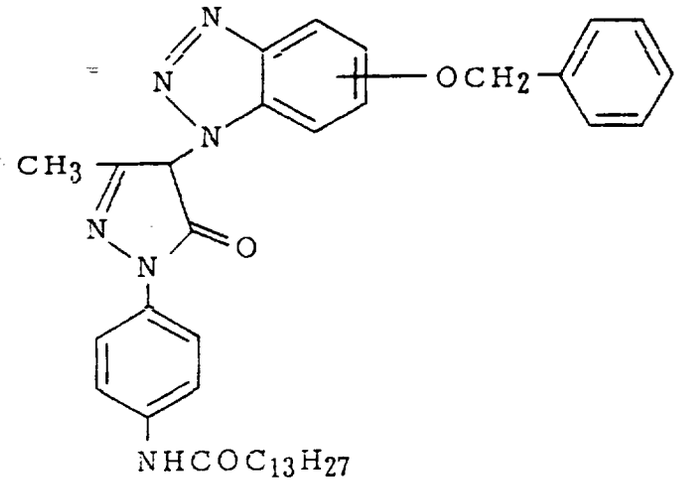
T-110

(c.e.)



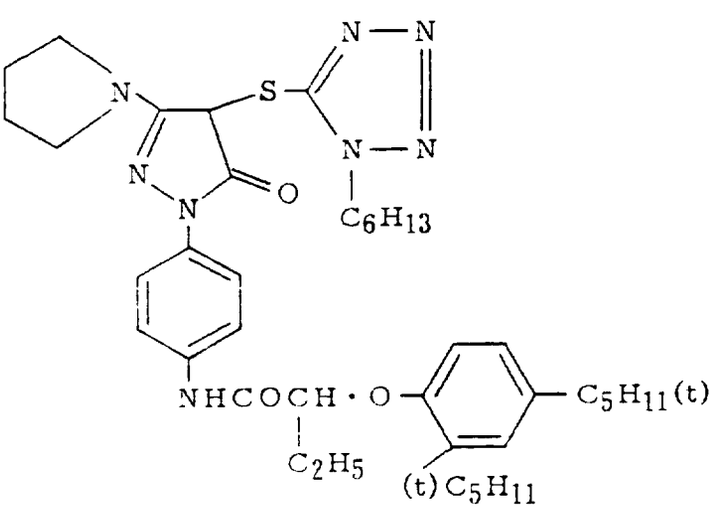
T-111

(c.e.)



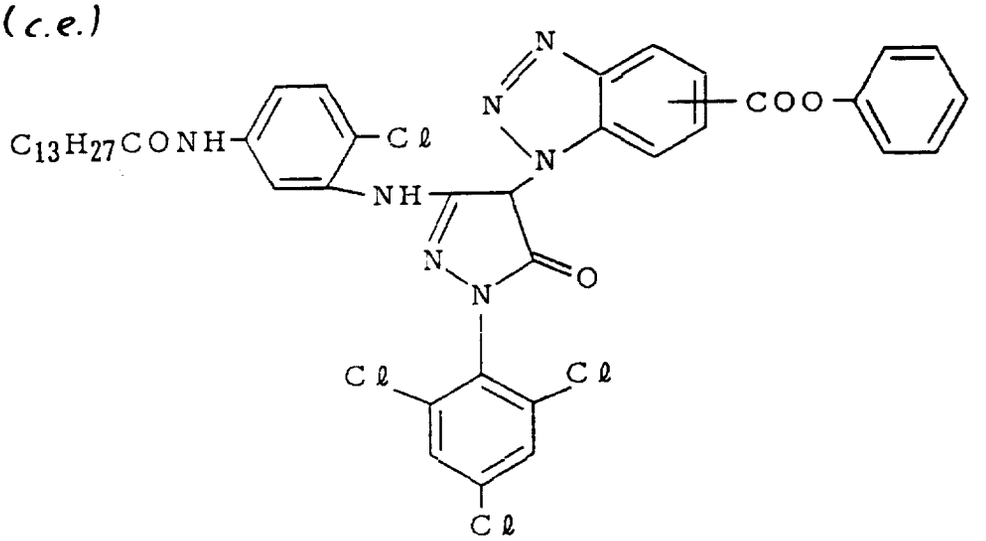
T-112

(c.e.)



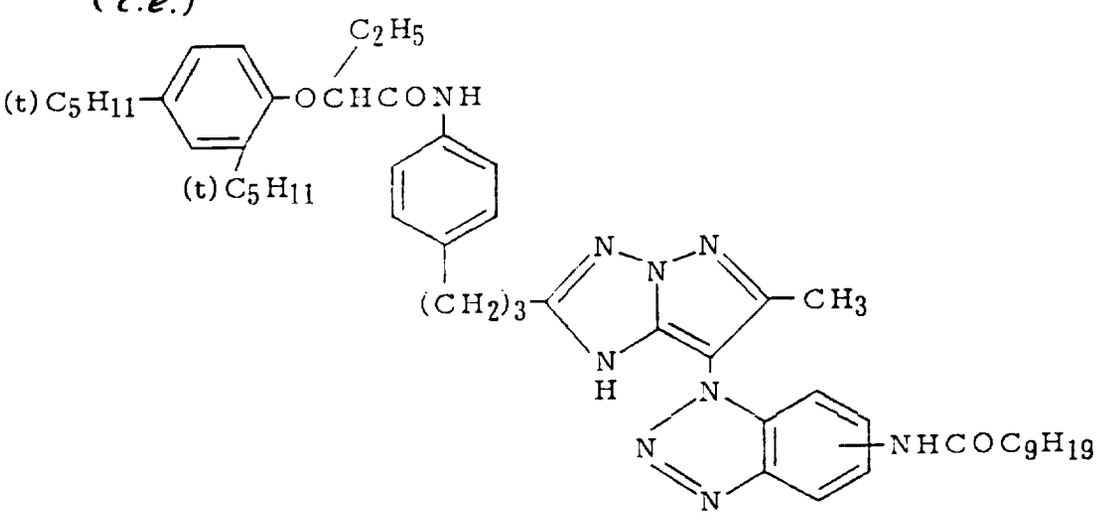
T-113

(c.e.)



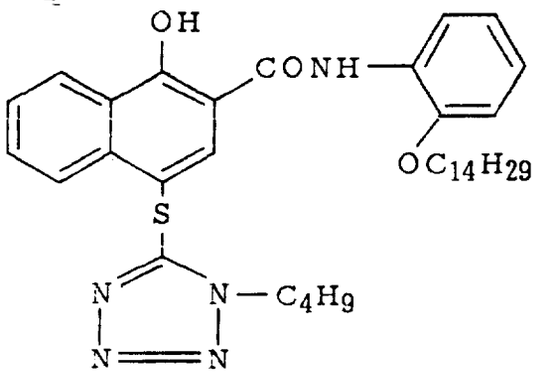
T-114

(c.e.)



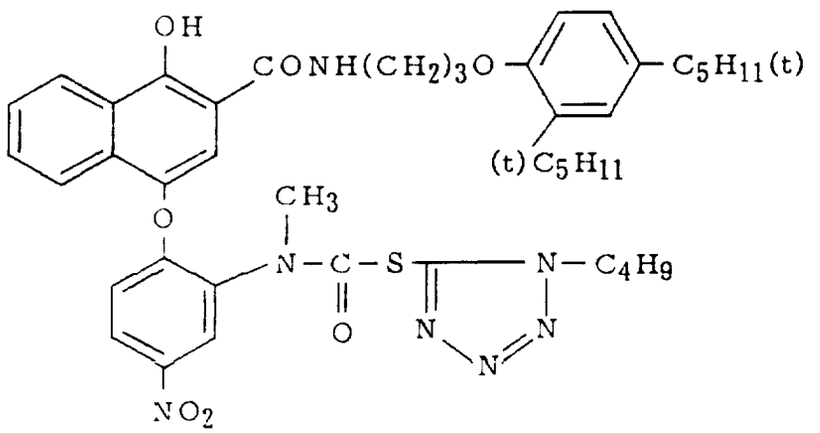
T-115

(c.e.)



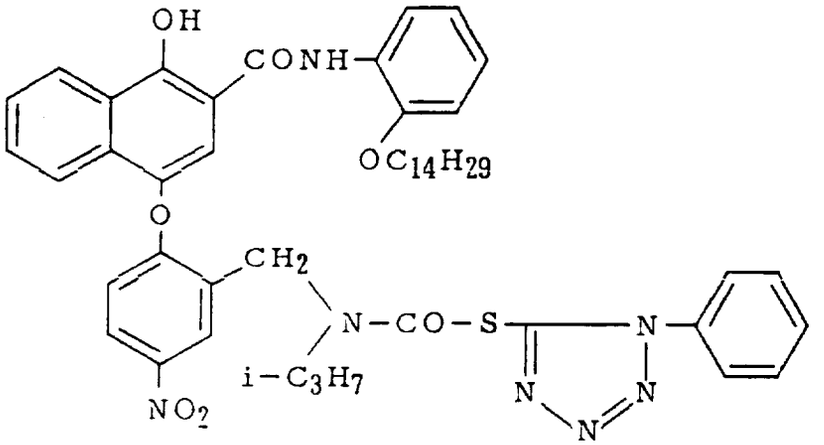
T-116

(c.e.)



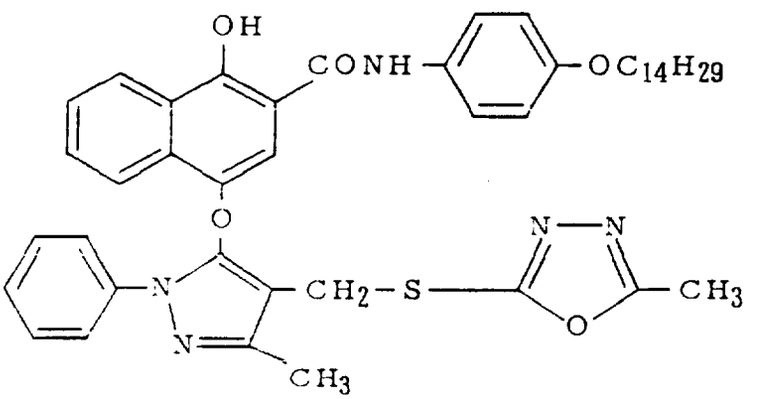
T-117

(c.e.)

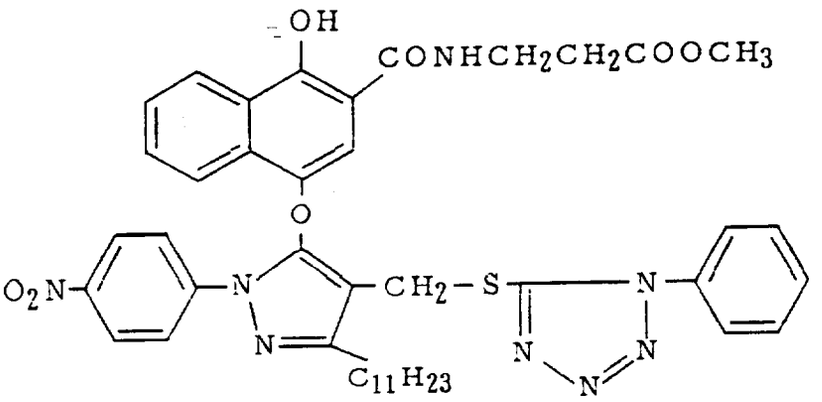


T-118

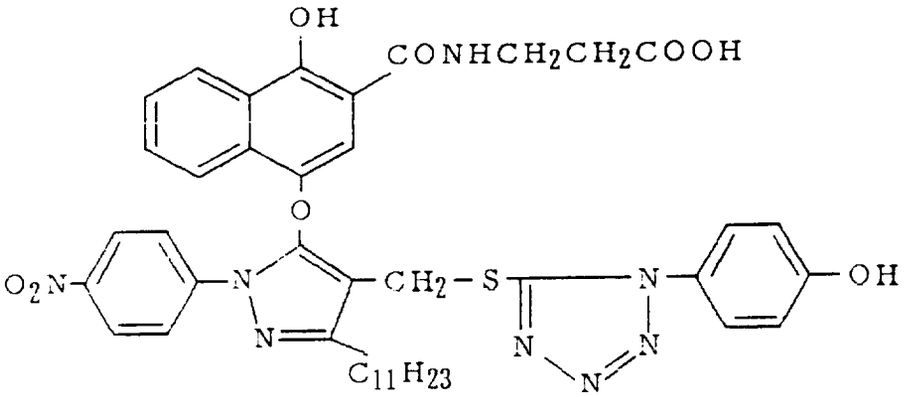
(c.e.)



T-119
(c.e.)

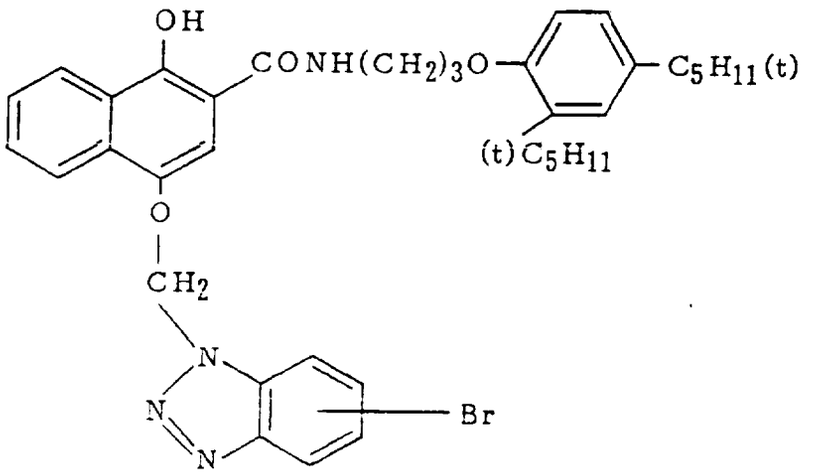


T-120
(c.e.)



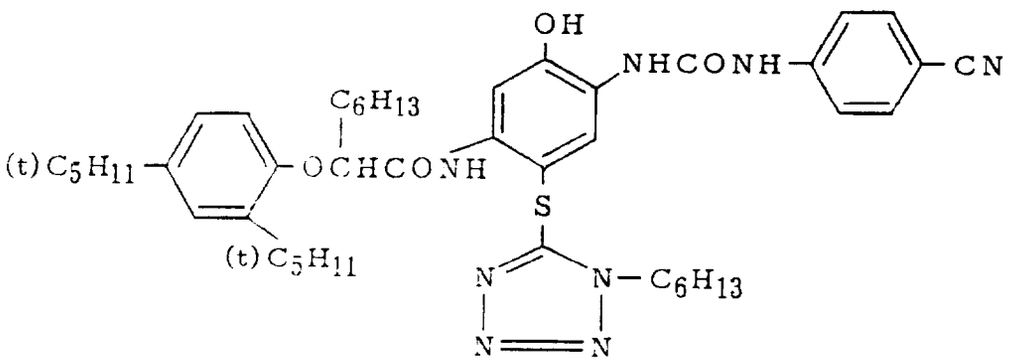
T-121

(c.e.)



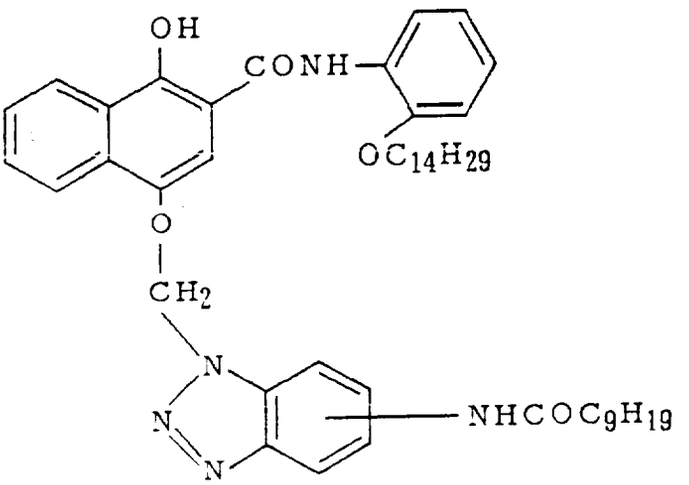
T-122

(c.e.)



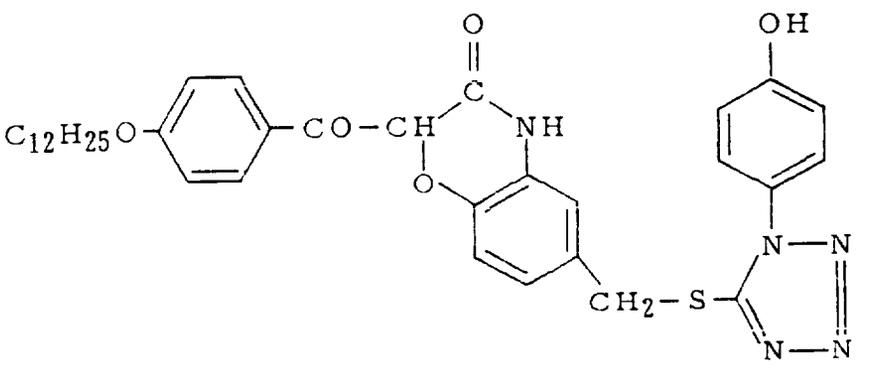
T-123

(c.e.)



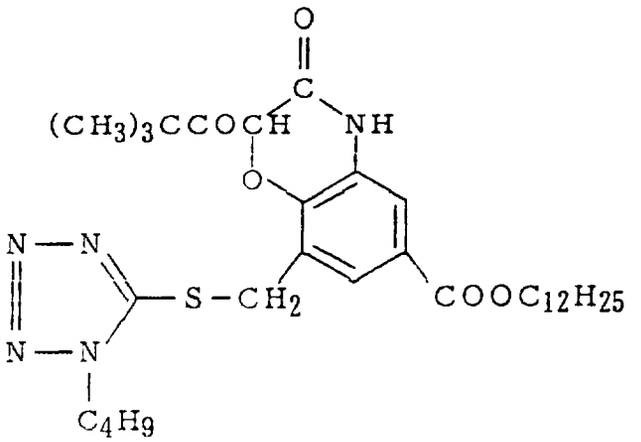
T-124

(c.e.)



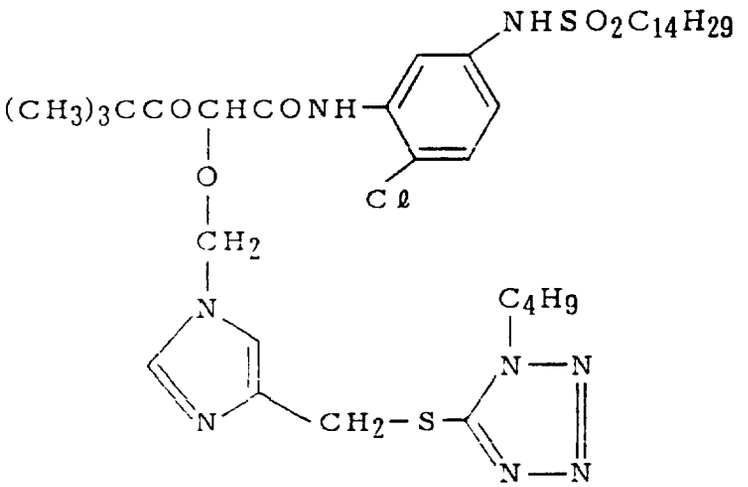
T-125

(c.e.)



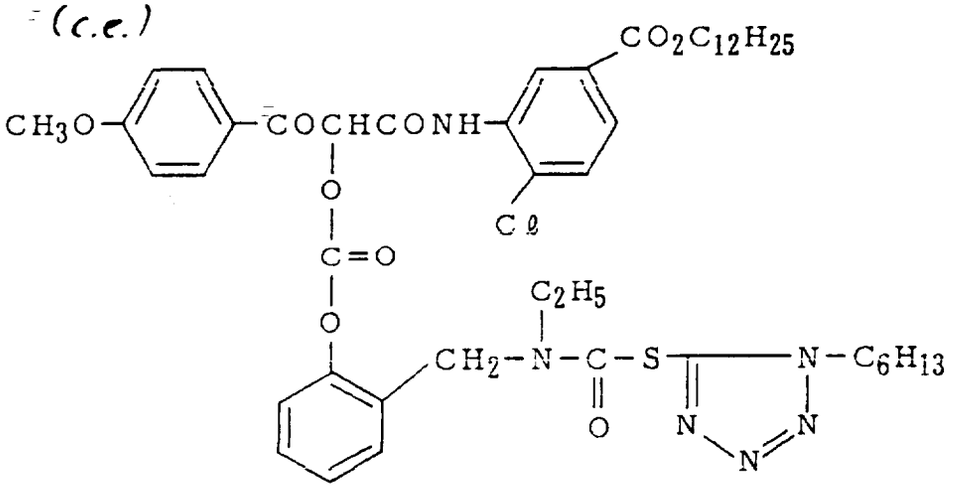
T-126

(c.e.)



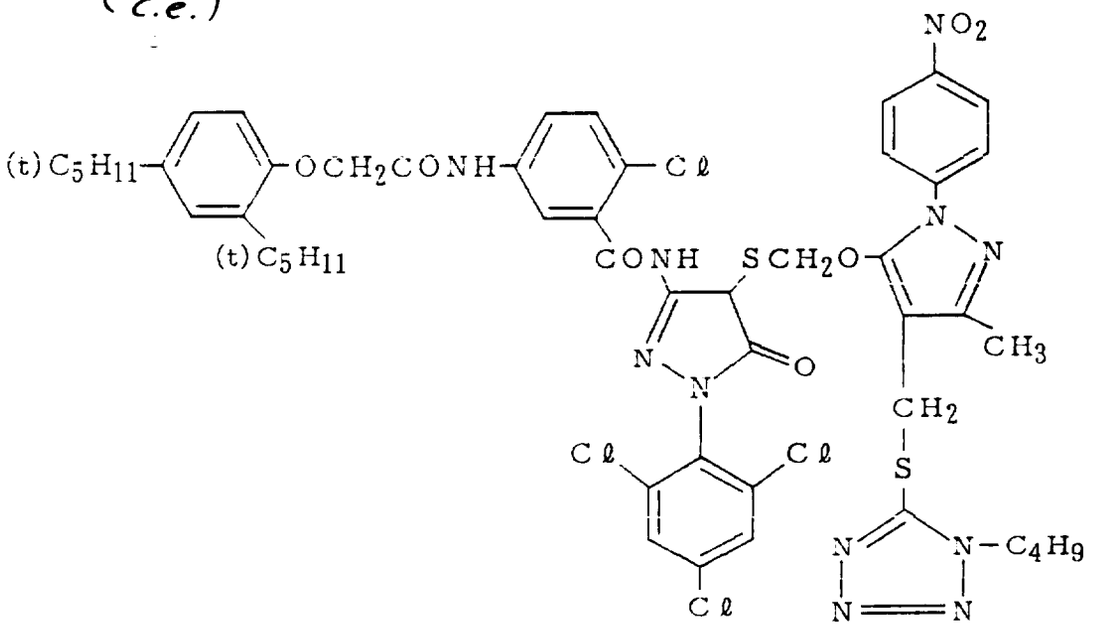
T-127

(c.e.)



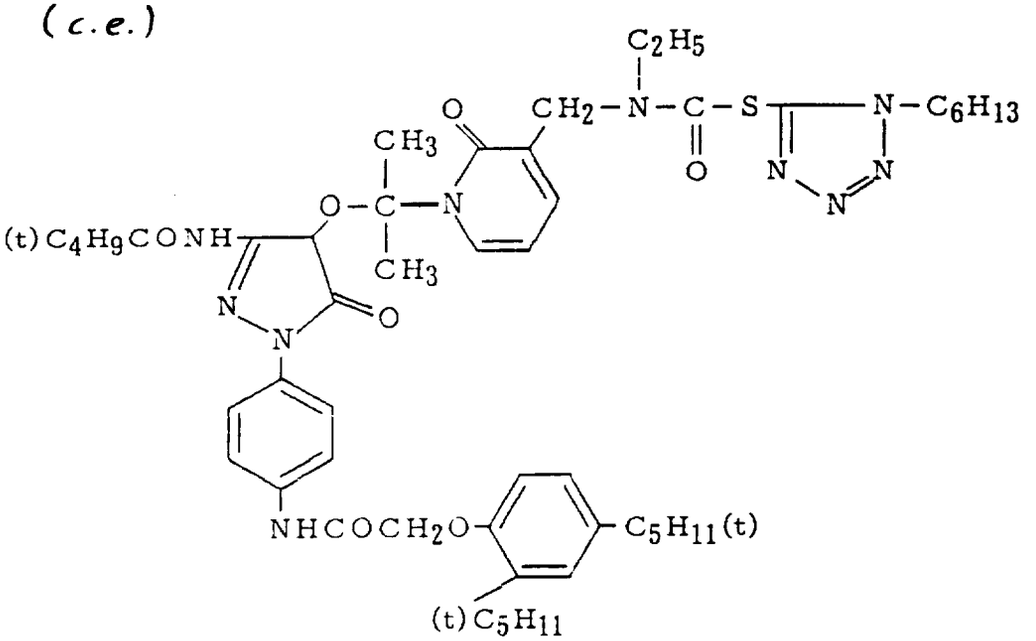
T-128

(c.e.)



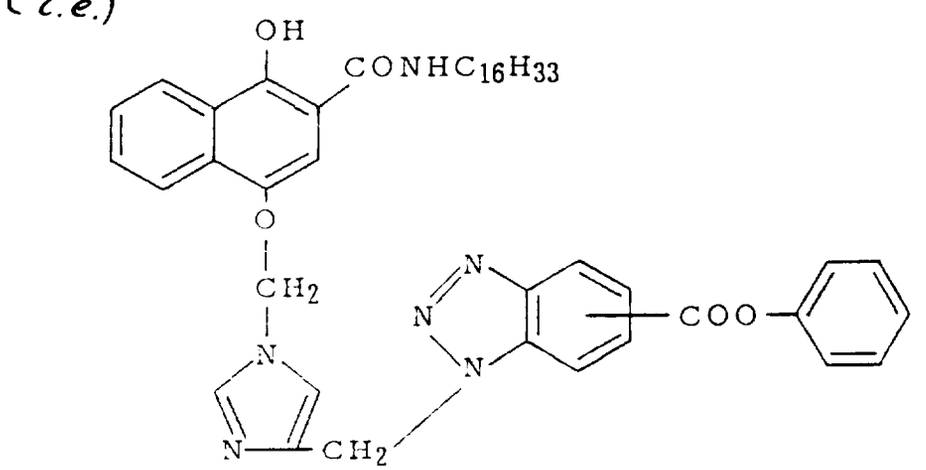
T-129

(c.e.)



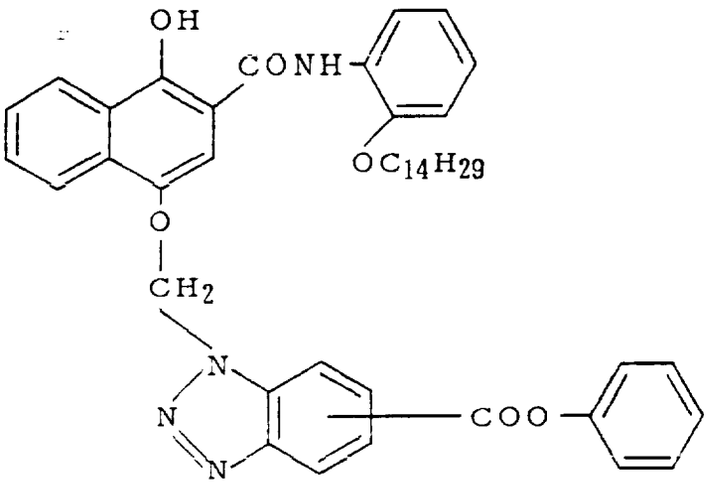
T-130

(c.e.)



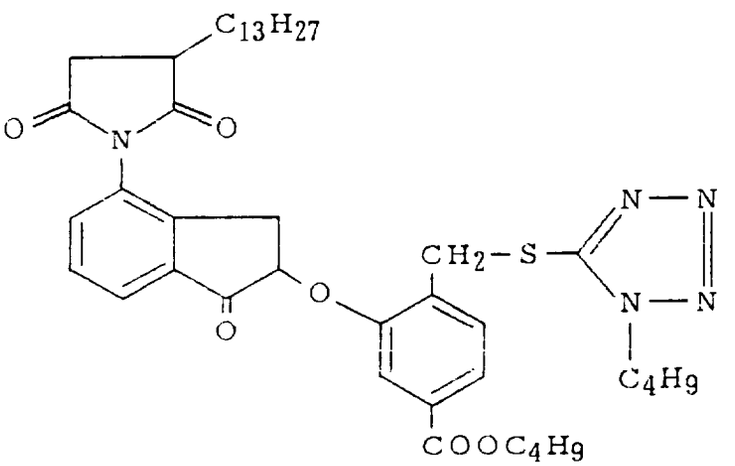
T-131

(c.e.)



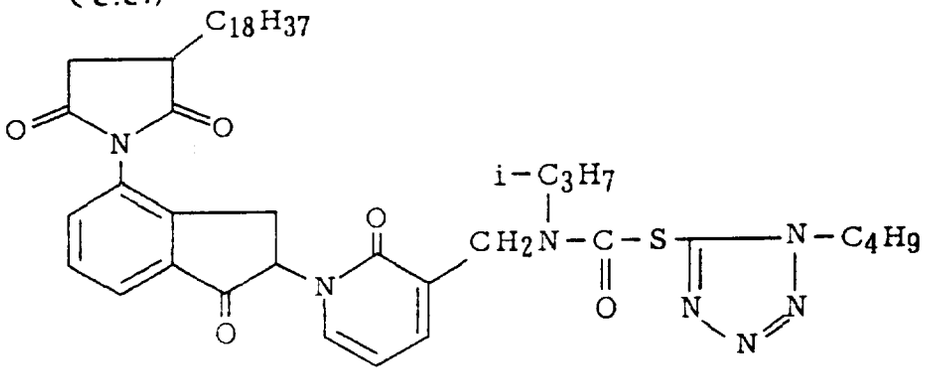
T-i32

(c.e.)



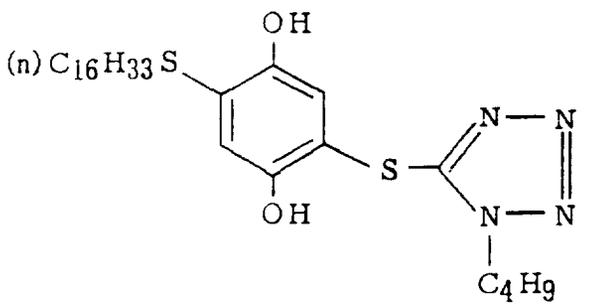
T-133

(c.e.)



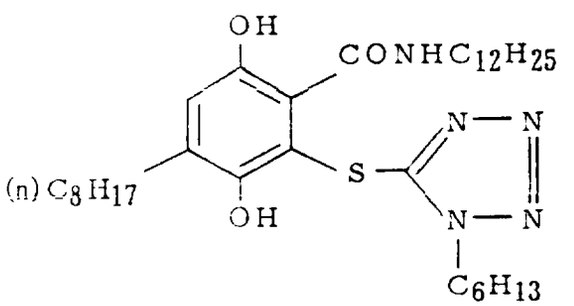
T-134

(c.e.)



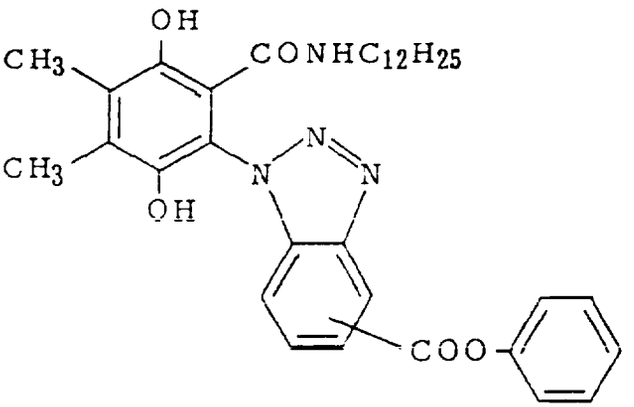
T-135

(c.e.)



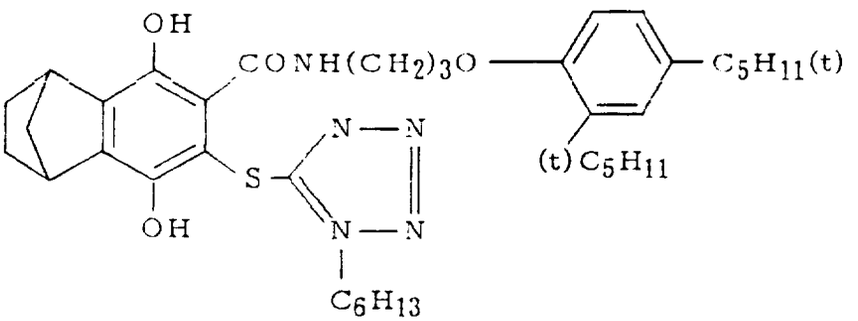
T-136

(c.e.)



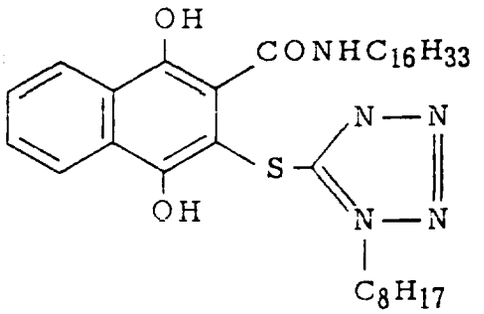
T-137

(c.e.)



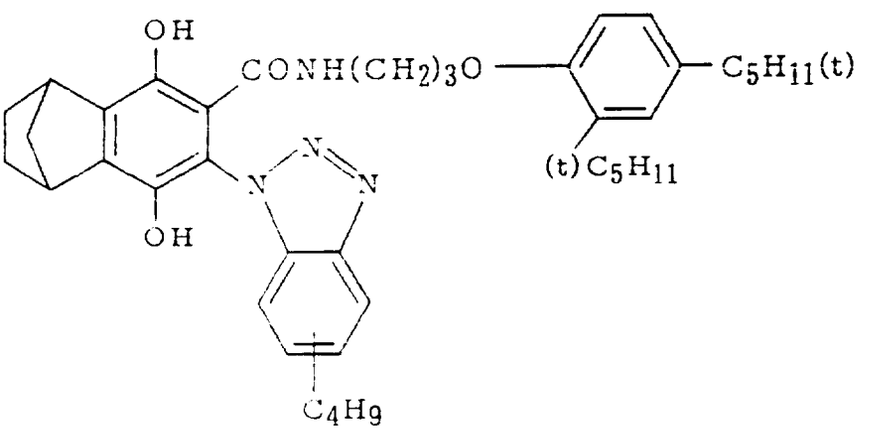
T-138

(c.e.)



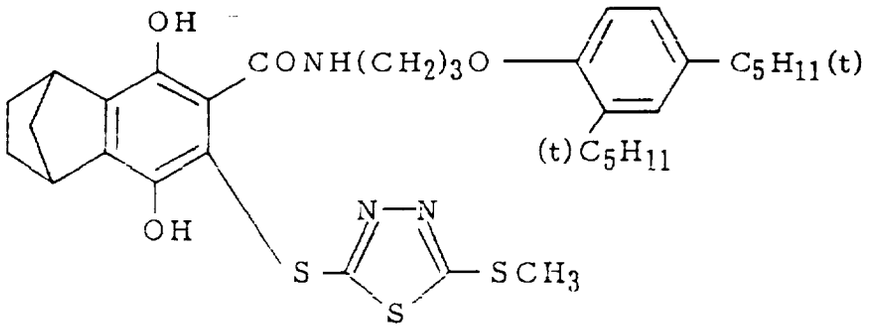
T-139

(c.e.)



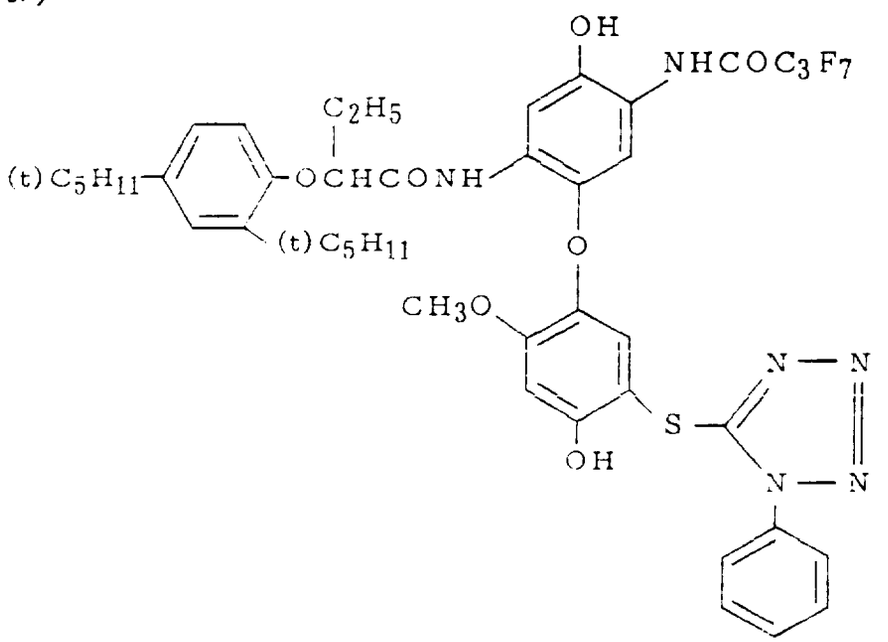
T-140

(c.e.)



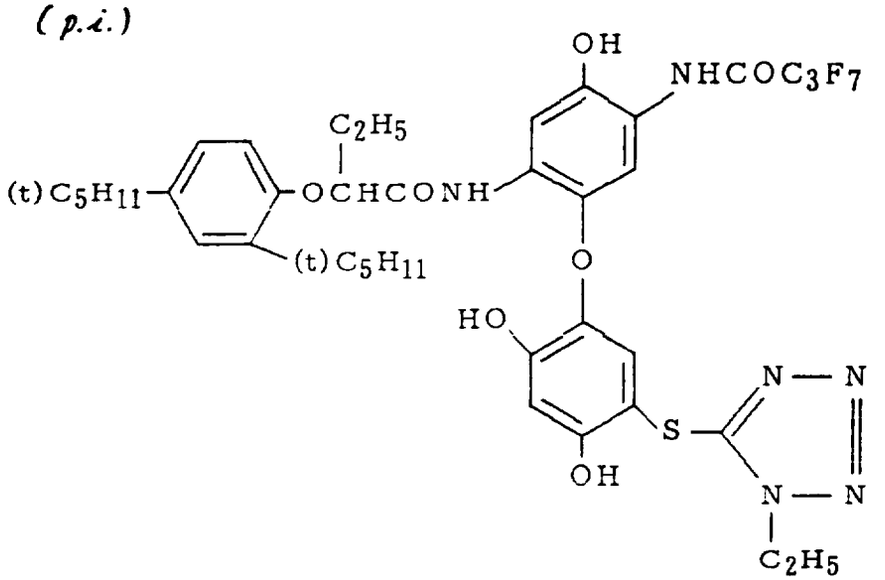
T-141

(p.i.)



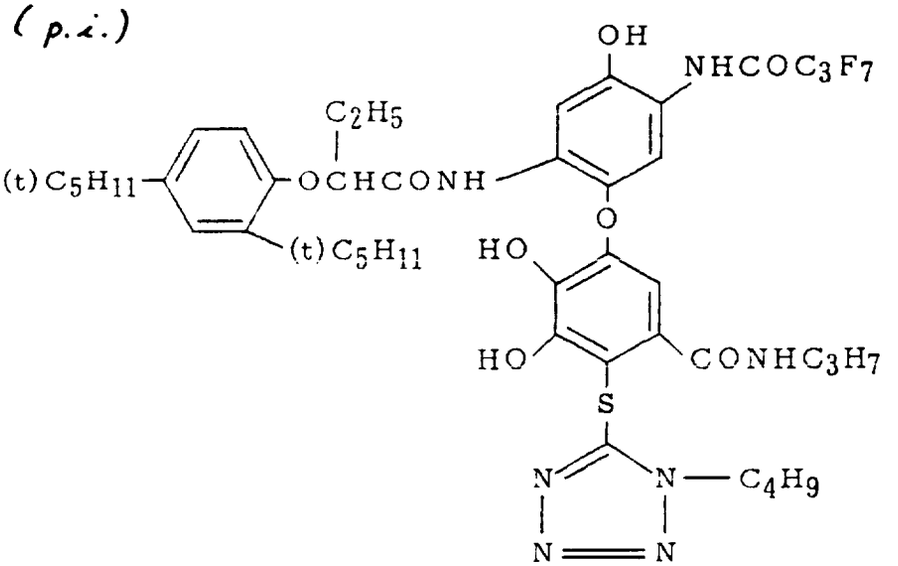
T-142

(p.i.)



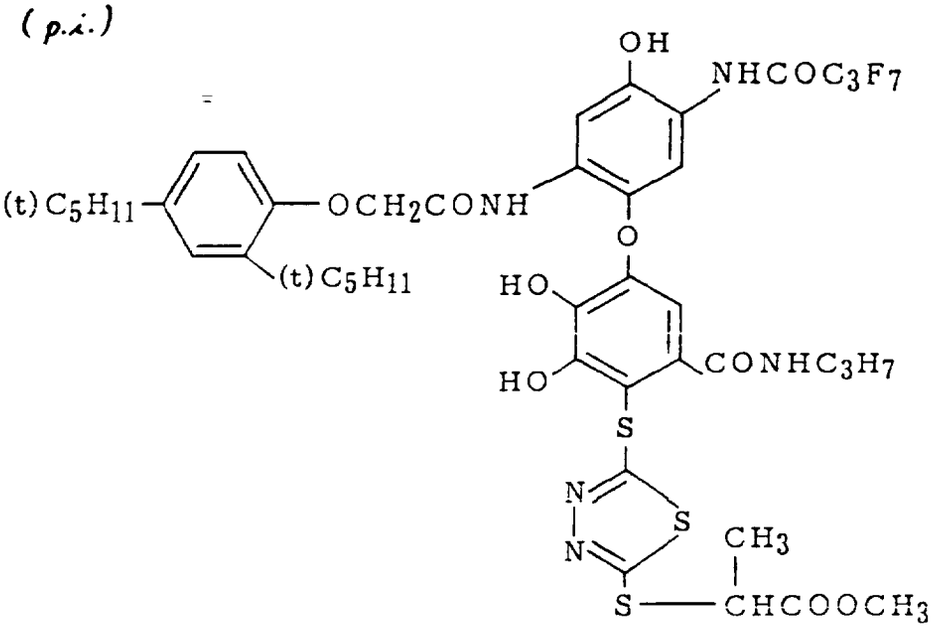
T-143

(p.i.)



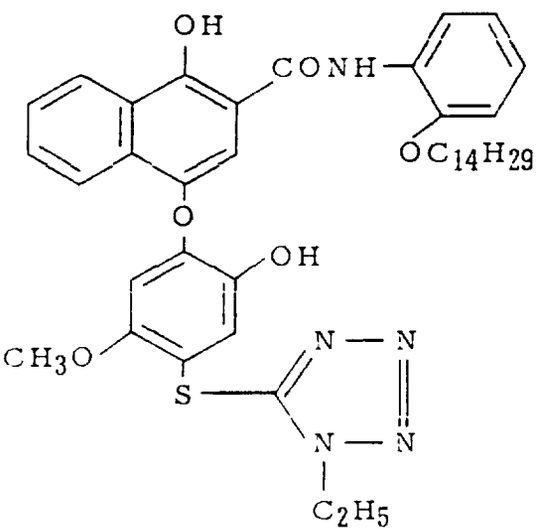
T-144

(p.i.)



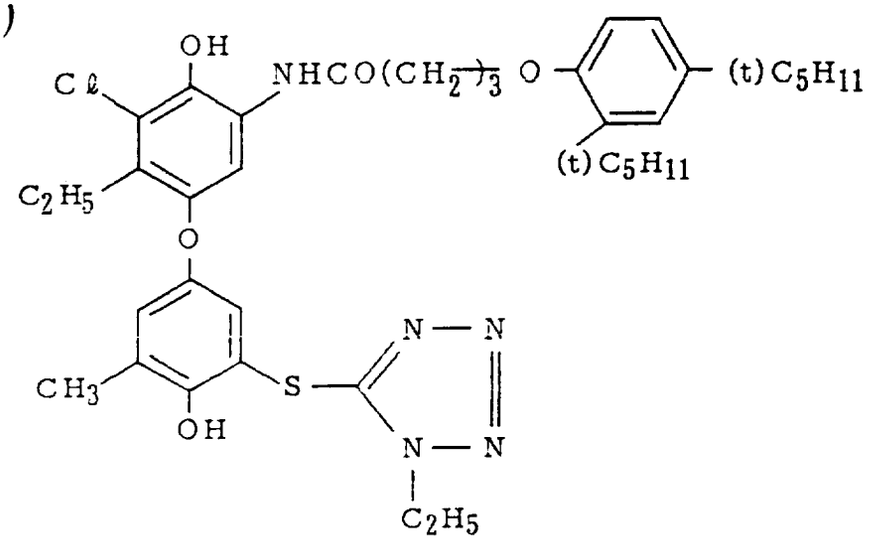
T-145

(p.i.)



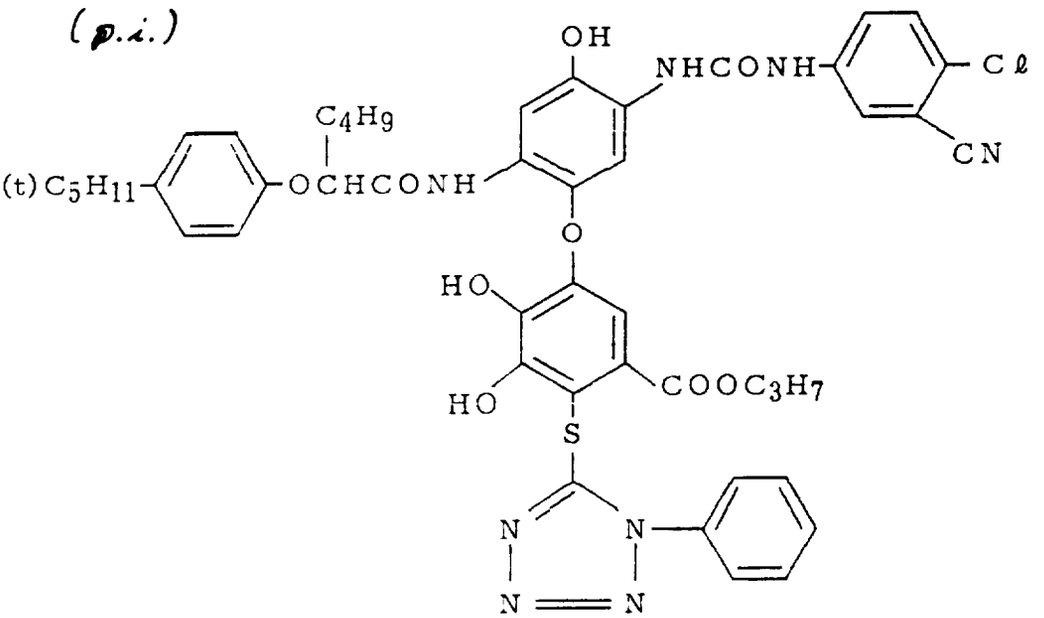
T-146

(p.i.)



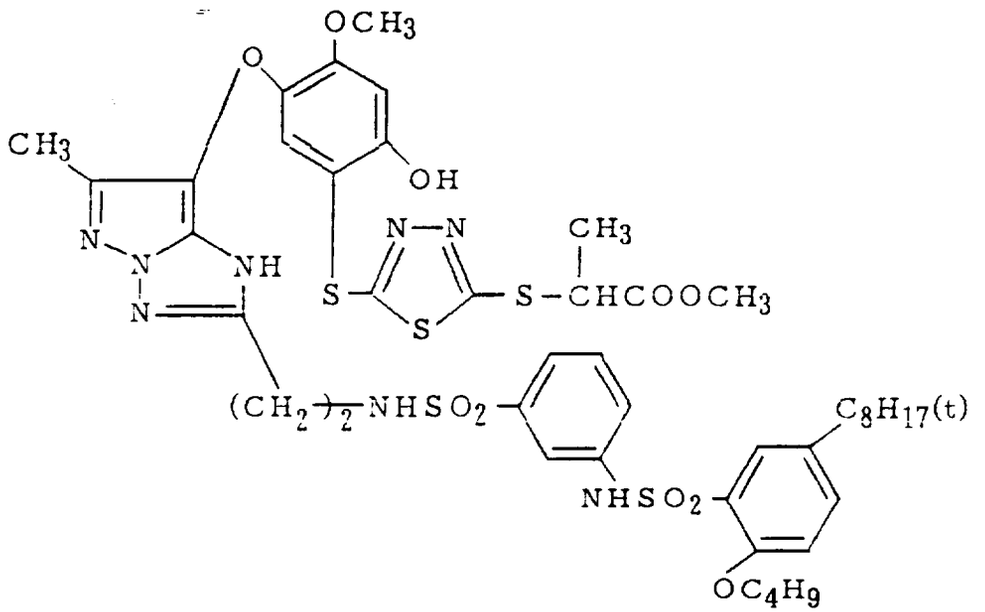
T-147

(p.i.)



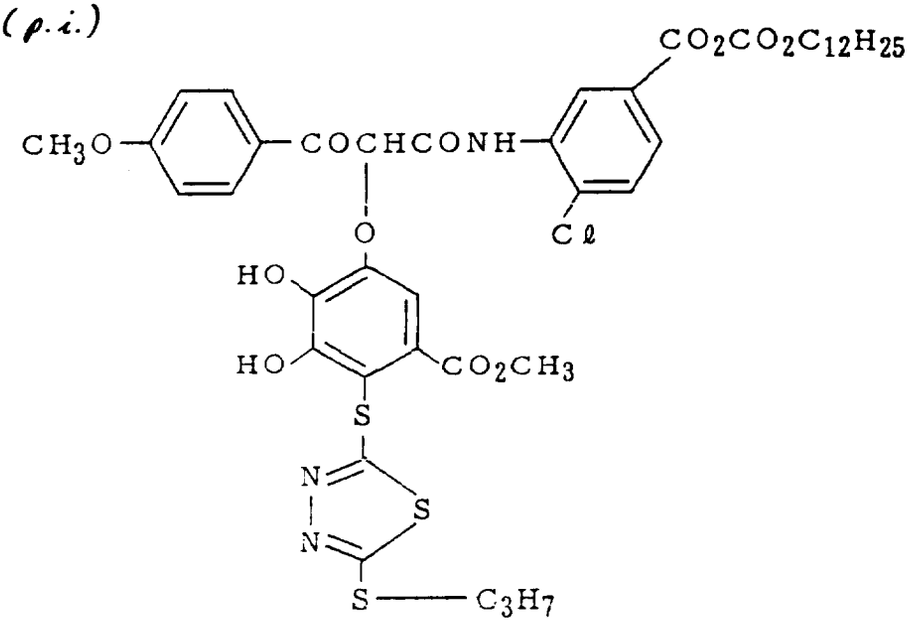
T-148

(p.i.)



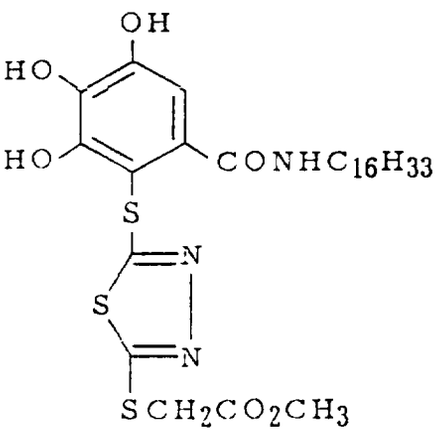
T-149

(p.i.)



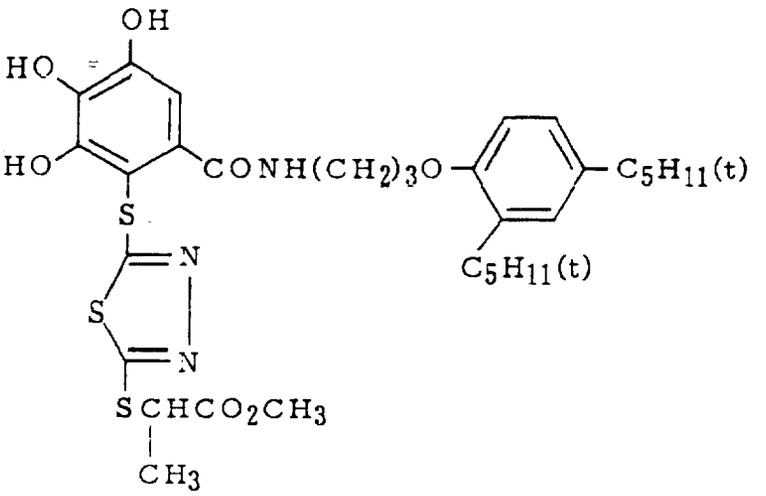
T-150

(c.e.)



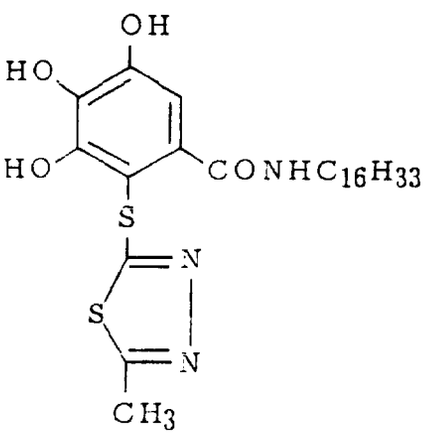
T-151

(c.e.)



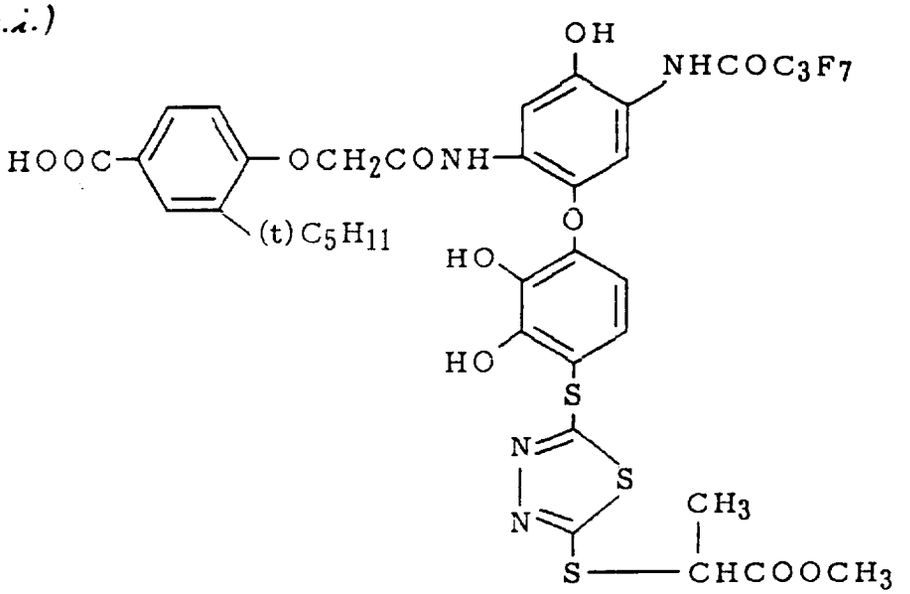
T-152

(c.e.)



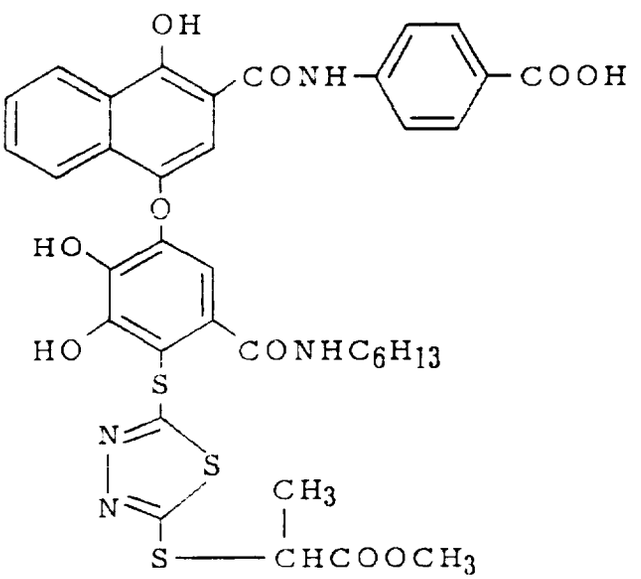
T-153

(p.i.)



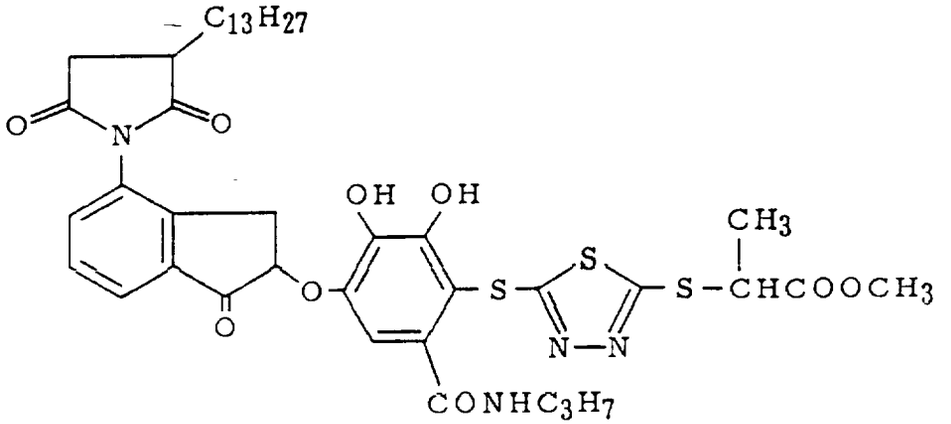
T-154

(p.i.)



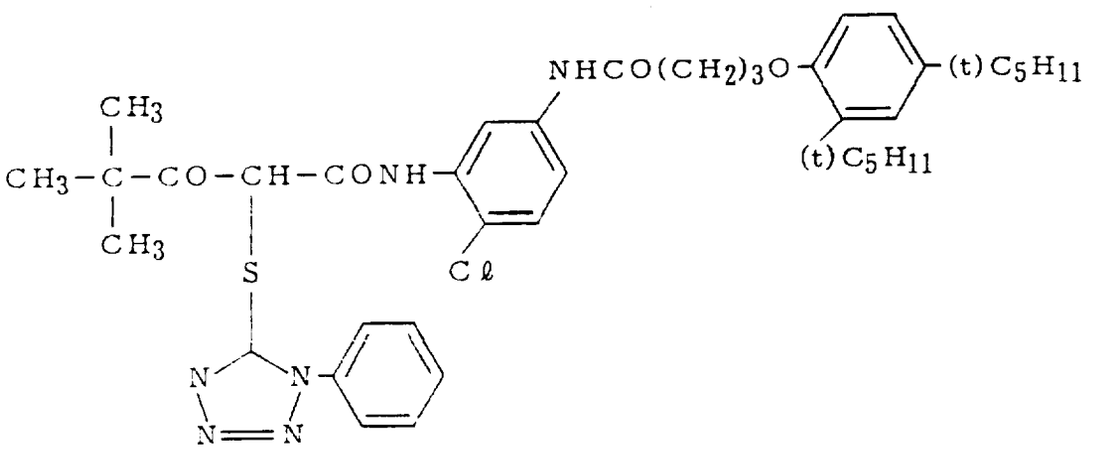
T-155

(p.i.)



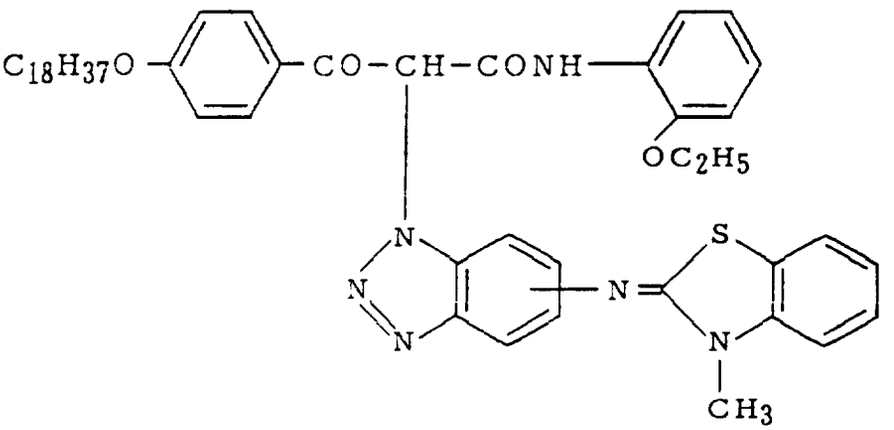
T-156

(c.e.)



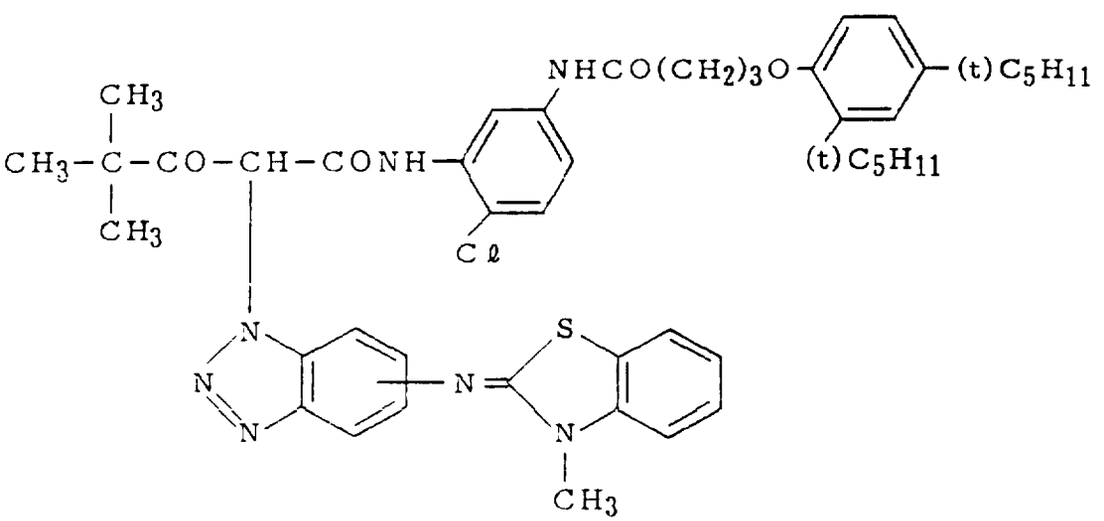
T-157

(c.e.)

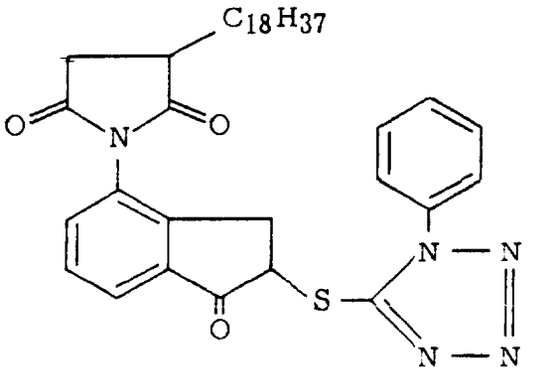


T-158

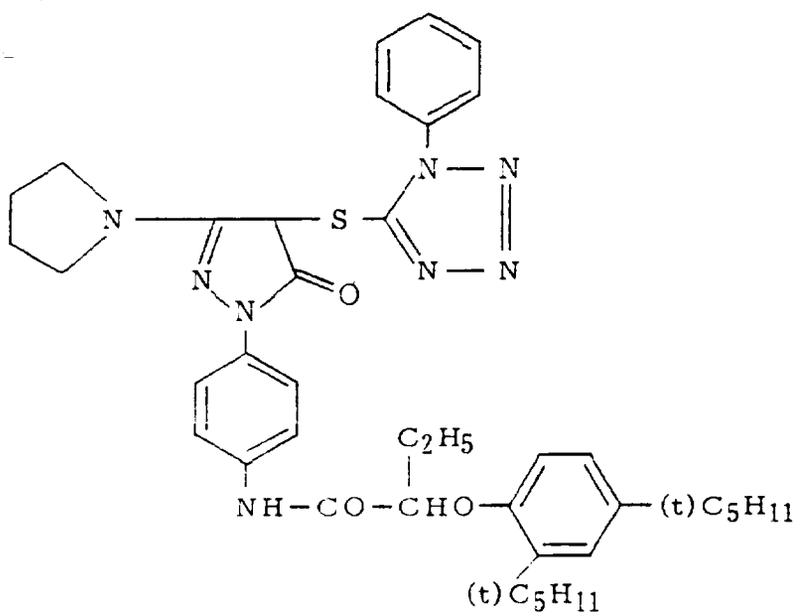
(c.e.)



T-159
(c.e.)

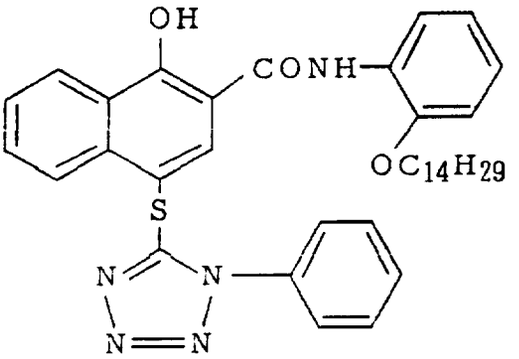


T-160
(c.e.)



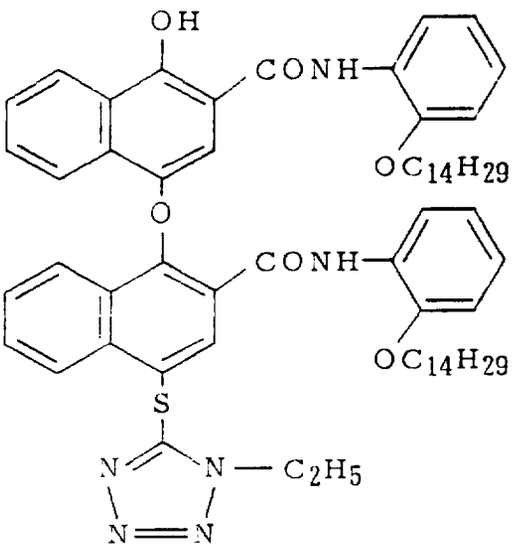
T-161

(c.e.)



T-162

(p.i.)



T-163
(c.e.)

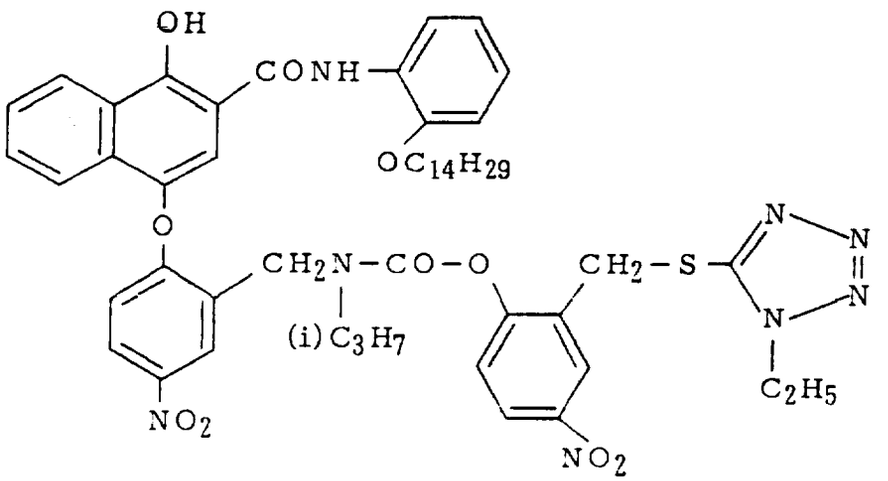
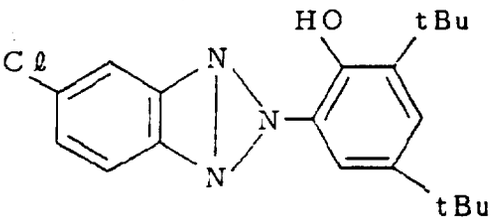
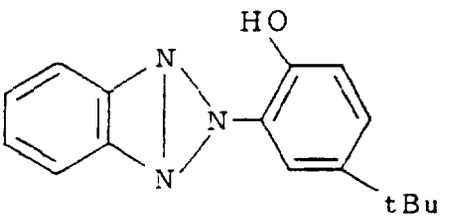


Table B

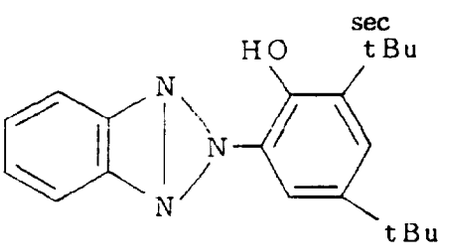
UV-1



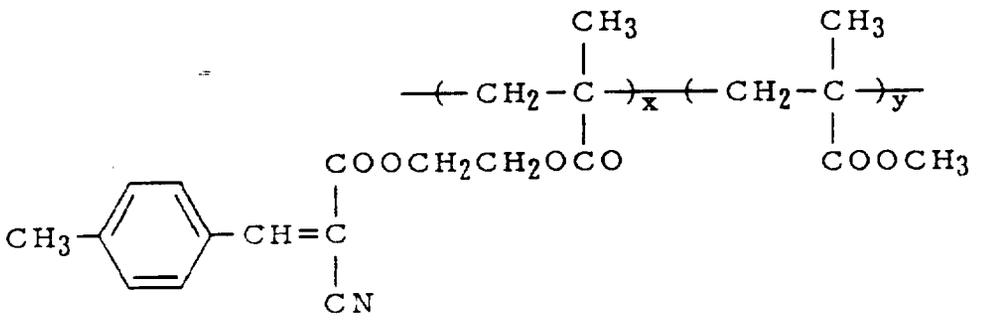
UV-2



UV-3

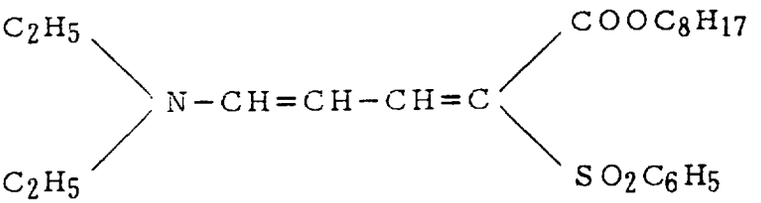


UV-4



x/y = 7/3 weight ratio

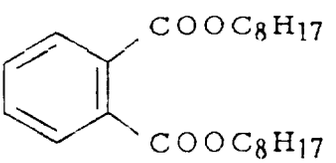
UV-5



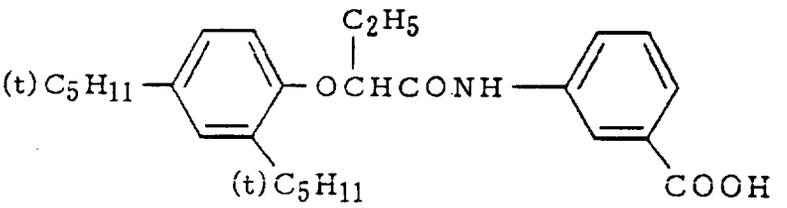
Solv-1 tricresyl phosphate

Solv-2 dibutyl phtalate

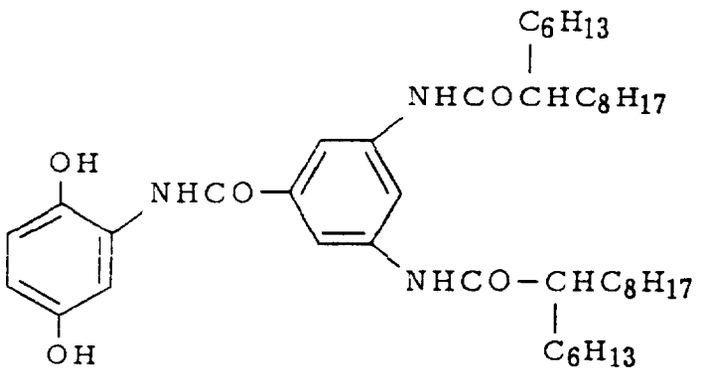
Solv-3



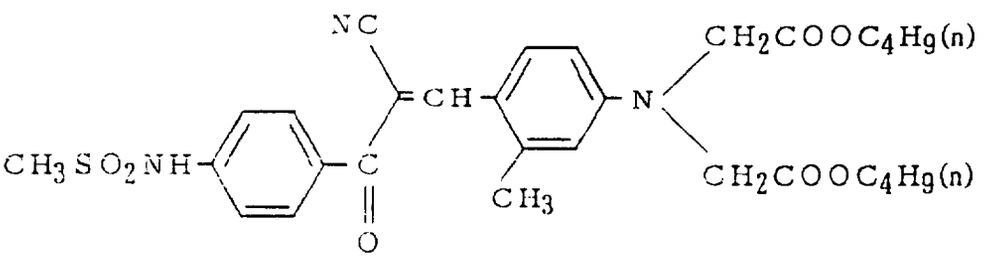
Solv-4



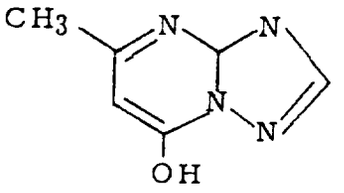
Cpd-1



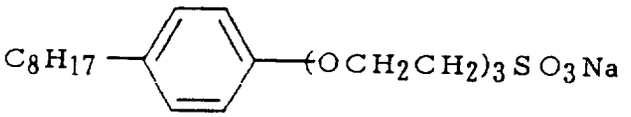
Cpd-2



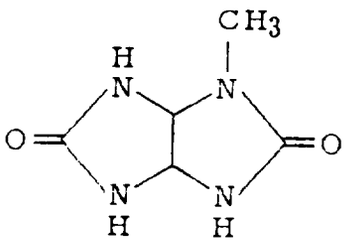
Cpd-3



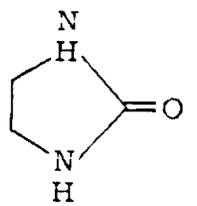
Cpd-4



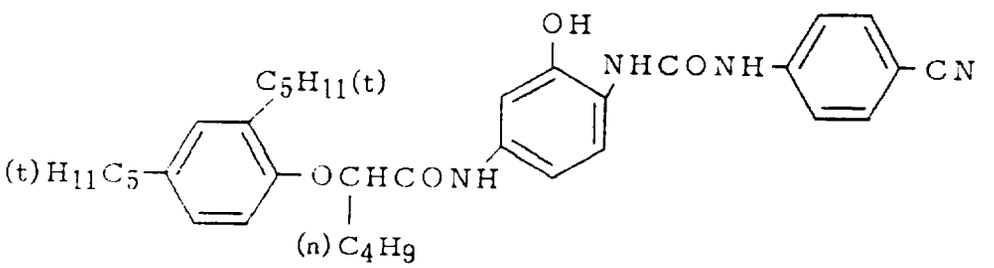
Cpd-5



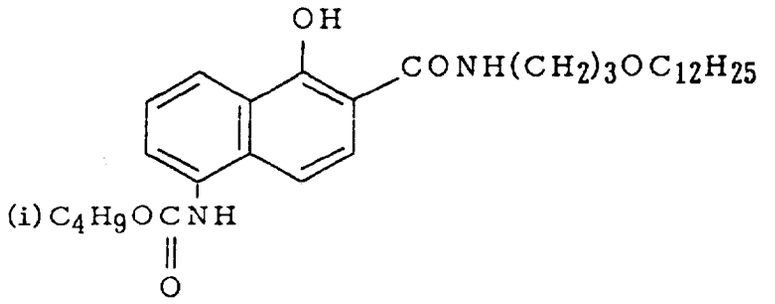
Cpd-6



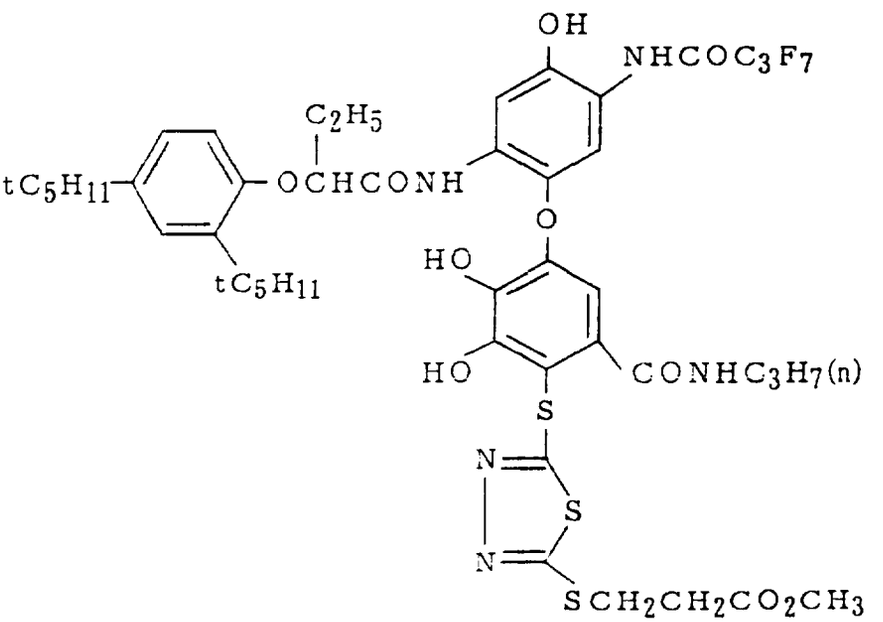
ExC-1



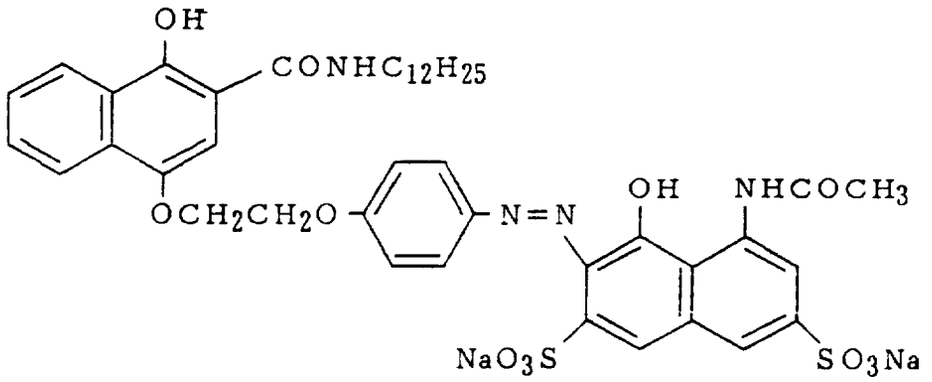
Ex C-2



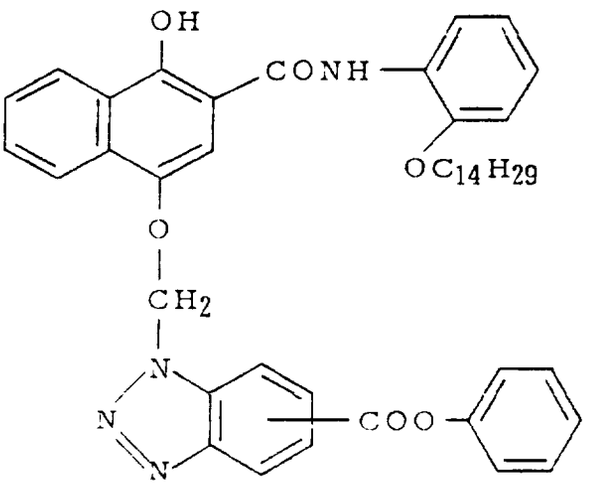
Ex C-3



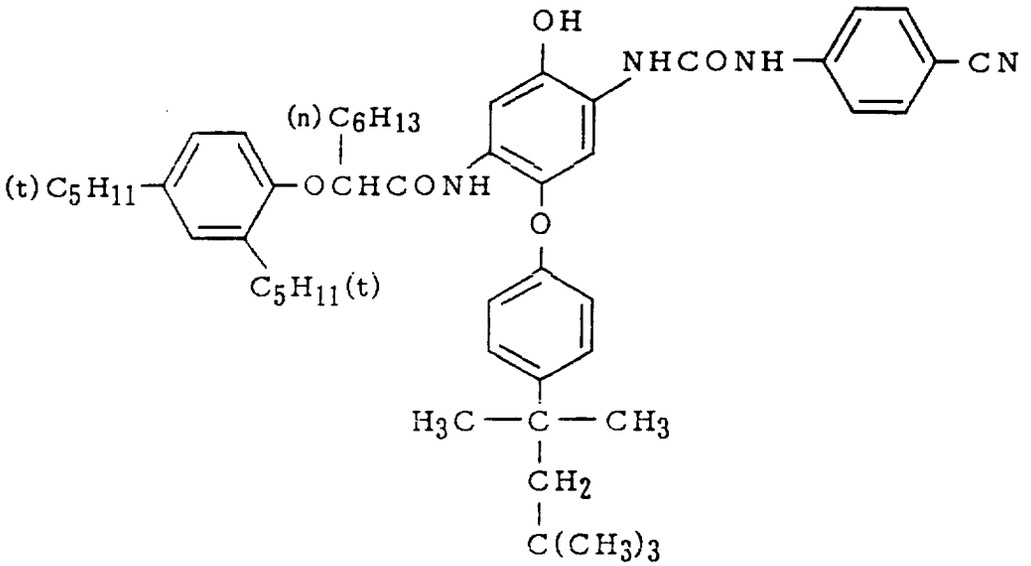
ExC-4



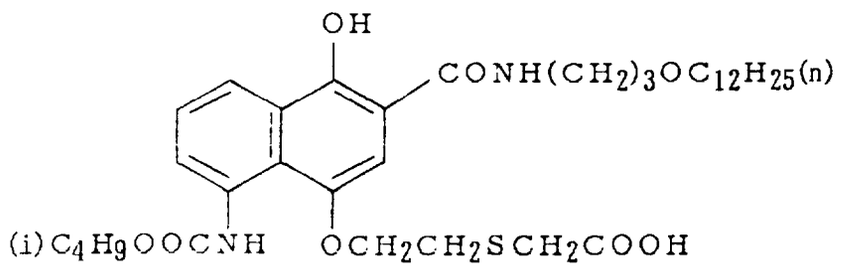
ExC-5



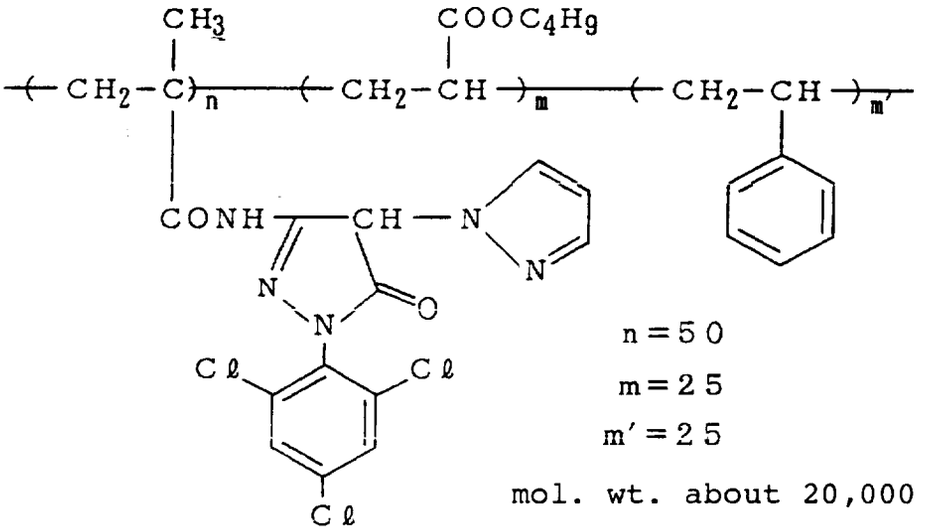
Ex C-6



Ex C-7

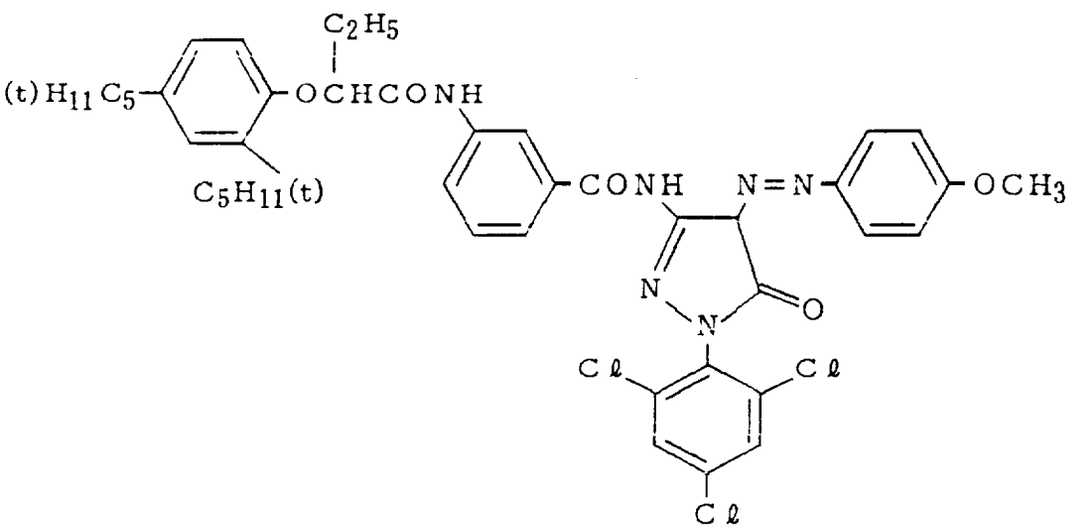


ExM-8

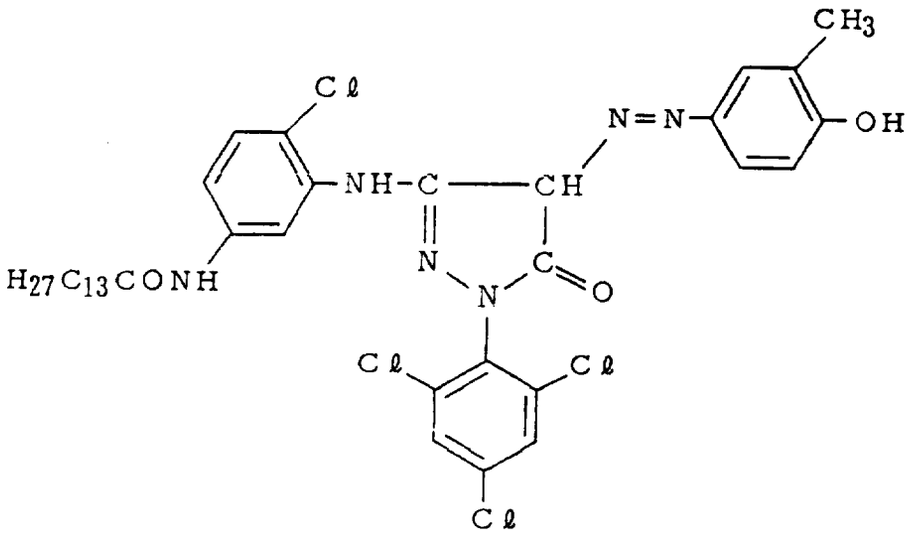


n = 50
m = 25
m′ = 25
mol. wt. about 20,000

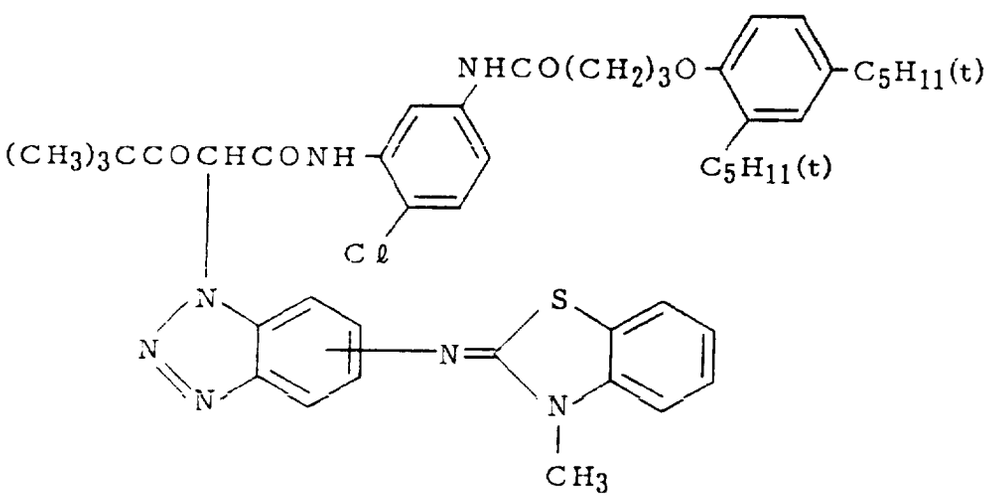
ExM-9



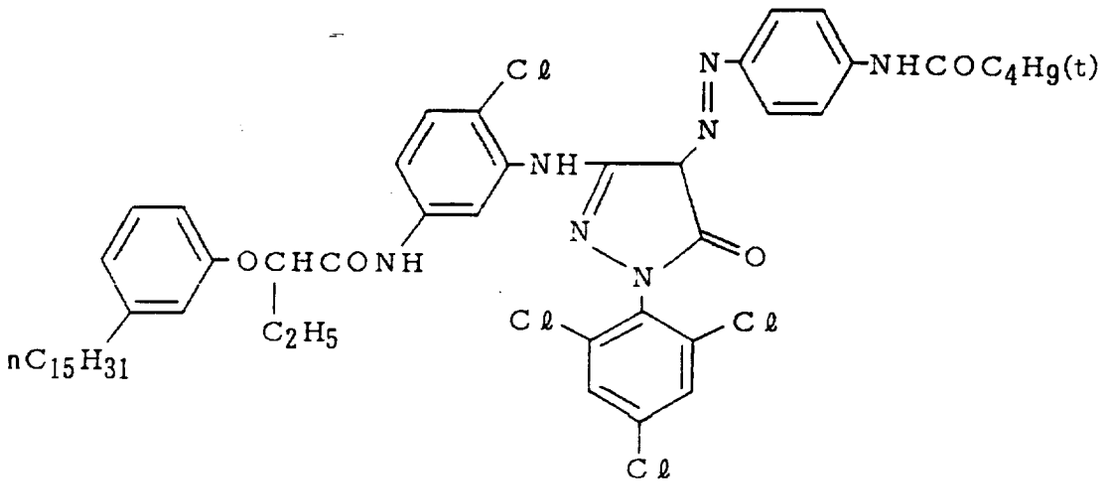
ExM-10



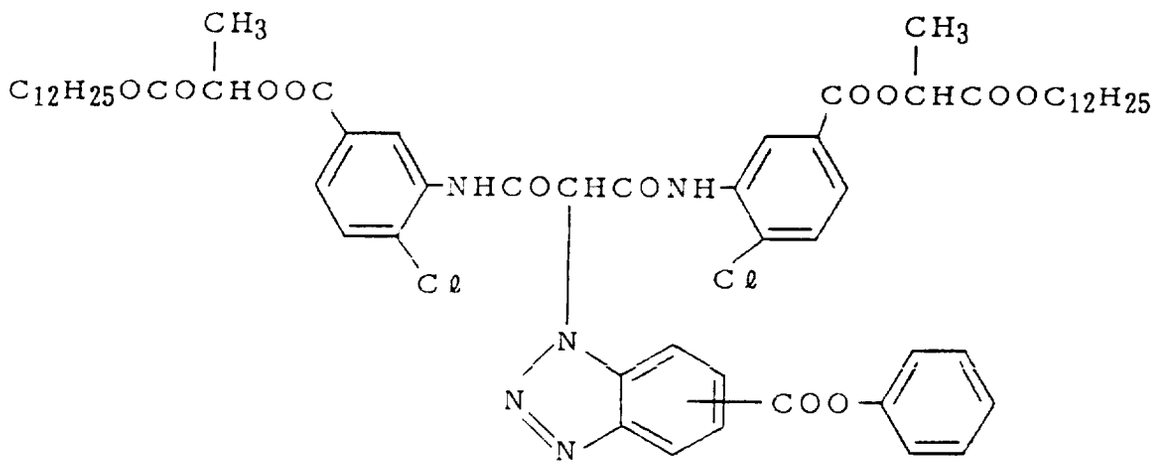
ExY-11



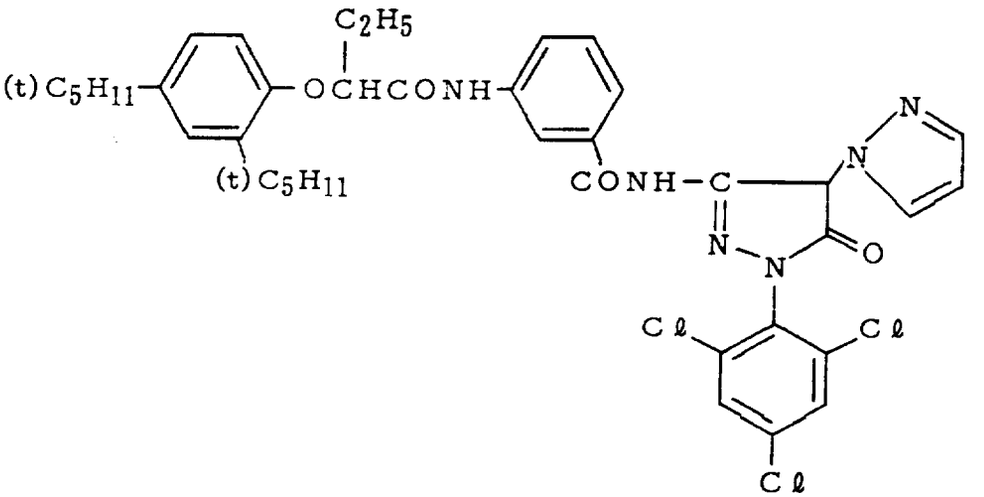
Ex M－12



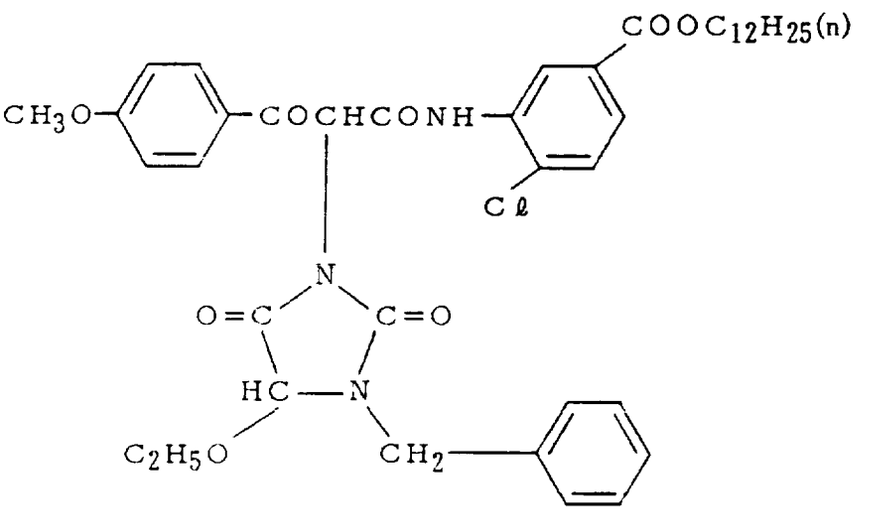
Ex Y－13



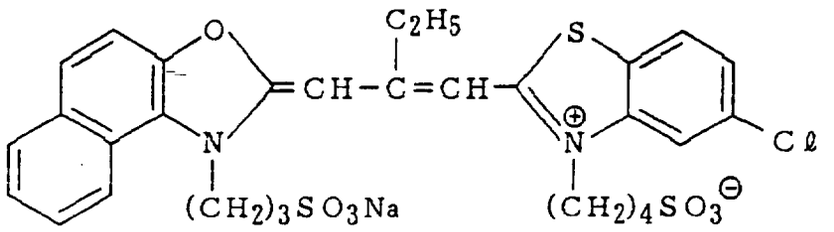
Ex M-14



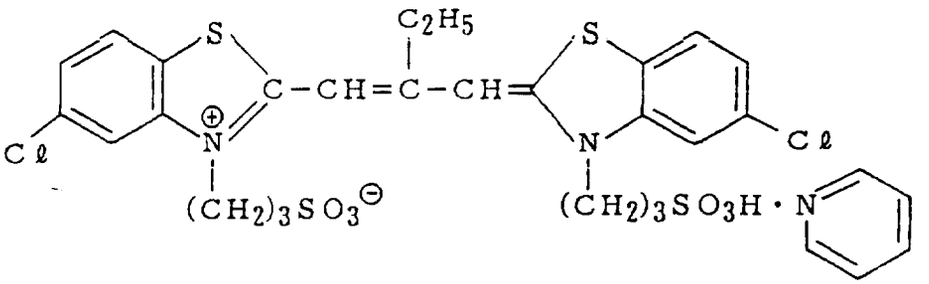
Ex Y-15



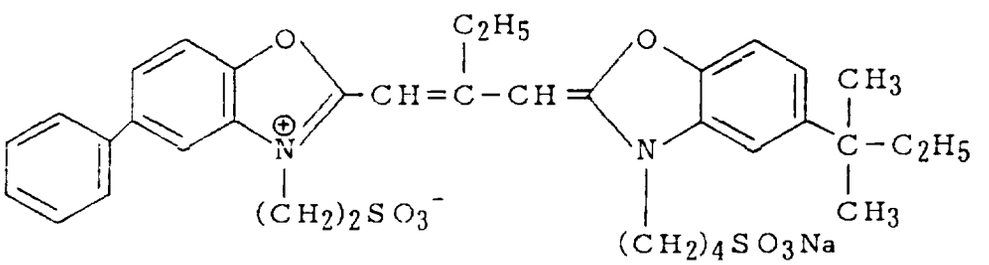
Ex S-1



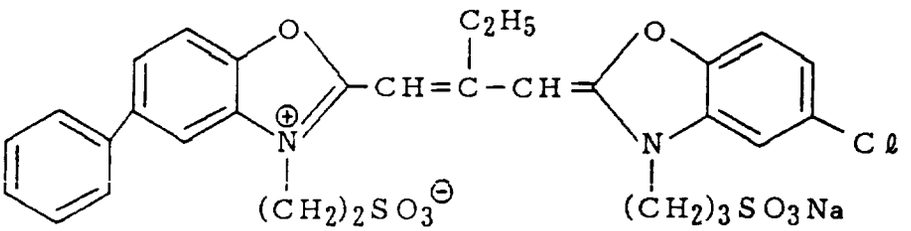
Ex S-2



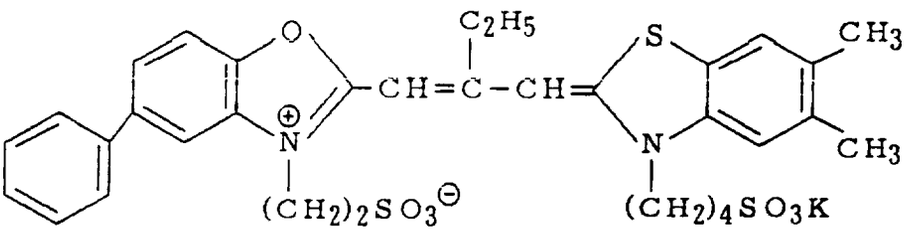
Ex S-3



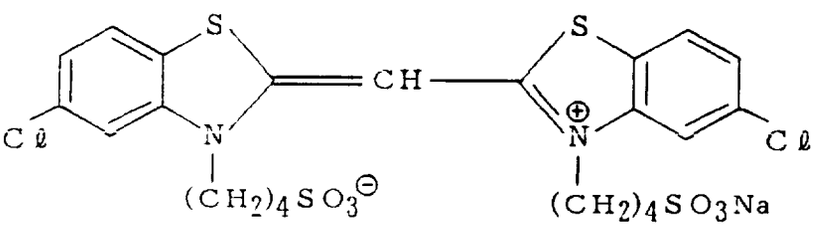
EXS-4



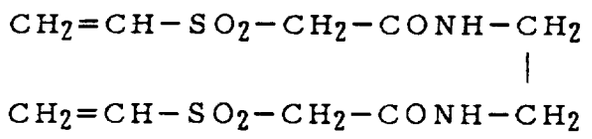
ExS-5



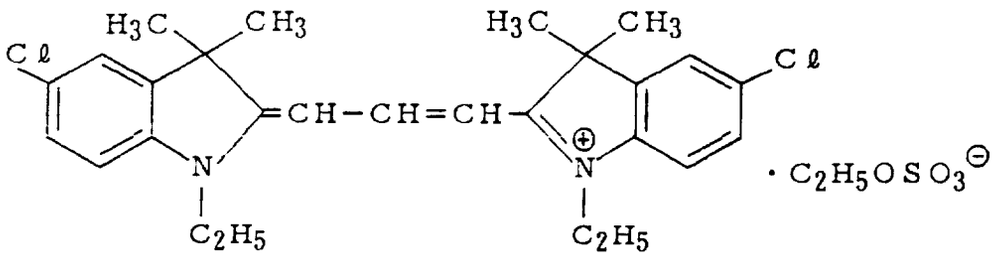
ExS-6



H-1



ExF-1



Claims

1. A silver halide color photographic light-sensitive material comprising at least one light-sensitive silver halide emulsion layer and at least one non-light-sensitive colloid layer on a support, said light-sensitive silver halide emulsion layer comprising silver halide grains containing a microscopically uniform silver halide localized region containing not less than 3 mol% of silver iodide, wherein said silver halide localized region has at most two lines indicating a microscopic silver iodide non-uniform distribution at an interval of 0.2 μm in a direction perpendicular to the lines in a transmission image of the grains obtained by using a cryo-transmission electron microscope and the number of the silver halide grains having such a silver halide localized region account for at least 60% of the number of all the grains in the emulsion, said light-sensitive silver halide emulsion layer or said non-light-sensitive colloid layer containing at least one development inhibitor releasing (DIR) compound which reacts with the oxidized form of a color developing agent to form a cleavage compound, said cleavage compound reacting with another molecule of the oxidized form of a color developing agent to form a development inhibitor or a precursor thereof.

2. The silver halide color photographic light-sensitive material according to claim 1, wherein the silver iodide content of the silver halide localized region is 5 mol% or more.

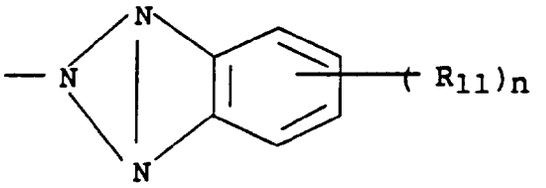
3. The silver halide color photographic light-sensitive material according to claim 1, wherein the total silver iodide content of the silver halide grains having the silver halide localized region is 2 mol% or more.

4. The silver halide color photographic light-sensitive material according to claim 1, wherein said at least one DIR compound is represented by the following formula:

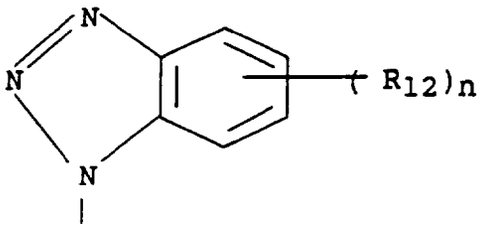
A(or B) -P-Z wherein A represents a coupling component which reacts with the oxidized form of a color developing agent to release -P-Z, B represents a redox component which undergoes oxidation-reduction reaction with the oxidized form of a color developing agent and alkali hydrolysis to release -P-Z, Z represents a development inhibitor or a precursor thereof, -P-Z represents a group which is cleaved from A or B and reacts with the oxidized form of a colour developing agent to release Z, and P represents a moiety which undergoes a bimolecular reaction with the oxidized form of a colour developing agent to release Z.

5. The silver halide color photographic light-sensitive material according to claim 1, wherein the development inhibitor or a precursor thereof in said at least one DIR compound is represented by the following formulas (Z-1) to (Z-9):

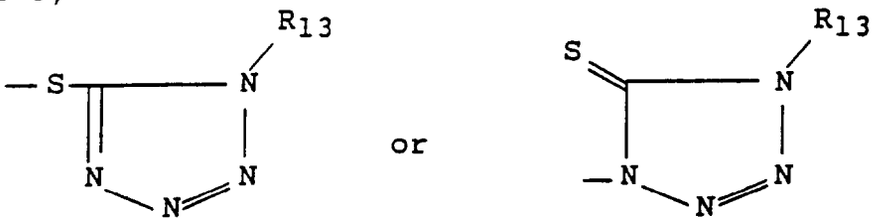
(Z-1)



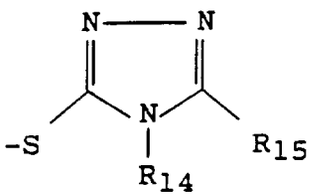
(Z-2)



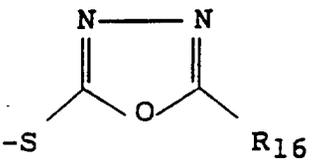
(Z-3)



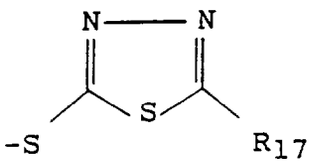
(Z-4)



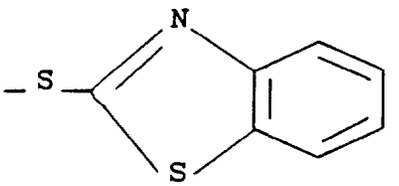
(Z-5)



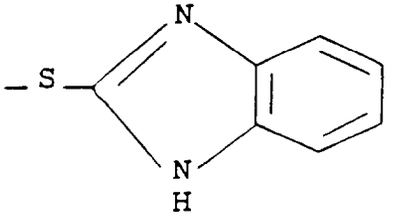
(Z-6)



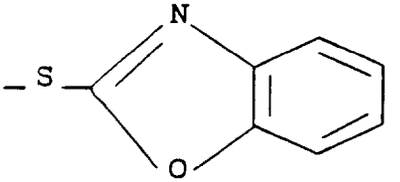
(Z-7)



(Z-8)



(Z-9)



wherein in the formulas (Z-1) and(Z-2), R_{11} and R_{12} each represents alkyl, alkoxy, acylamino, a halogen atom, alkoxycarbonyl, thiazolilideneamino, aryloxycarbonyl, acyloxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, sulfonamido, N-alkylcarbamoyloxy, ureido, hydroxy, alkoxycarbonylamino, aryloxy, alkylthio, arylthio, anilino, aryl, imido, a heterocyclic ring, cyano, alkylsulfonyl, or aryloxycarbo-

nylamino;

n represents 1 or 2, when n is 2, R_{11} and R_{12} may be the same or different, a total number of carbon atoms contained in n R_{11} and R_{12} is 0 to 20;
in the formulas (Z-3), (Z-4), (Z-5), and (Z-6), R_{13}, R_{14}, R_{15}, R_{16}, and R_{17} each represent alkyl, aryl, or a heterocyclic group;
in formulas (Z-1) and (Z-2), the number of carbon atoms contained in R_{11} and R_{12} is 1 to 20; and
in formulas (Z-3), (Z-4), (Z-5), and (Z-6), a total number of carbon atoms contained in R_{13} to R_{17} is 1 to 20.

Patentansprüche

1. Lichtempfindliches, farbphotographisches Silberhalogenidmaterial, umfassend mindestens eine lichtempfindliche Silberhalogenidemulsionsschicht und mindestens eine nicht lichtempfindliche Kolloidschicht auf einem Träger, wobei die lichtempfindliche Silberhalogenidemulsionsschicht Silberhalogenidkörner umfaßt, die einen mikroskopisch gleichförmigen lokalen Silberhalogenidbereich enthalten, welcher nicht weniger als 3 Mol% Silberiodid enthält, wobei der lokale Silberhalogenidbereich höchstens 2 Linien, die eine mikroskopisch ungleichförmige Silberiodidverteilung anzeigen, in einem Intervall von 0,2 µm in einer Richtung senkrecht zu den Linien in einem Transmissionsbild der Körner besitzt, erhalten unter Verwendung eines Tieftemperatur-Transmissionselektronenmikroskops, und die Anzahl der Silberhalogenidkörner mit solch einem lokalen Silberhalogenidbereich beträgt mindestens 60%, bezogen auf die Gesamtzahl aller Körner in der Emulsion, wobei die lichtempfindliche Silberhalogenidemulsionsschicht oder die nicht lichtempfindliche Kolloidschicht mindestens eine einen Entwicklungsinhibitor freisetzende Verbindung (DIR-Verbindung) enthält, welche mit der oxidierten Form eines Farbentwicklers reagiert, wobei eine Verbindung abgespalten wird, welche mit einem anderen Molekül der oxidierten Form eines Farbentwicklers reagiert, wobei ein Entwicklungsinhibitor oder ein Vorläufer davon gebildet wird.

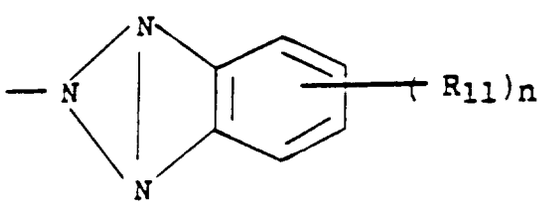
2. Lichtempfindliches, farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin der Silberiodidgehalt des lokalen Silberhalogenidbereichs 5 Mol% oder mehr beträgt.

3. Lichtempfindliches, farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin der gesamte Silberiodidgehalt der Silberhalogenidkörner mit dem lokalen Silberhalogenidbereich 2 Mol% oder mehr beträgt.

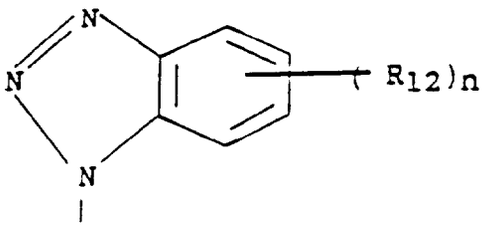
4. Lichtempfindliches, farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin die mindestens eine DIR-Verbindung durch die folgende Formel dargestellt wird:
A (oder B) -P-Z worin A ein Kupplungsbestandteil bedeutet, der mit der oxidierten Form eines Farbentwicklers reagiert, wobei -P-Z freigesetzt wird, B bedeutet ein Redoxbestandteil, der eine Redoxreaktion mit der oxidierten Form eines Farbentwicklers und eine Alkalihydrolyse eingeht, wobei -P-Z freigesetzt wird, Z bedeutet ein Entwicklungsinhibitor oder ein Vorläufer davon, -P-Z bedeutet eine Gruppe, die von A oder B abgespalten wird und mit der oxidierten Form eines Farbentwicklers reagiert, wobei Z abgespalten wird, und P bedeutet eine Komponente, die eine bimolekulare Reaktion mit der oxidierten Form eines Farbentwicklers eingeht, wobei Z freigesetzt wird.

5. Lichtempfindliches, farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin der Entwicklungsinhibitor oder ein Vorläufer davon in der mindestens einen DIR-Verbindung durch die folgenden Formeln (Z-1) bis (Z-9) dargestellt wird:

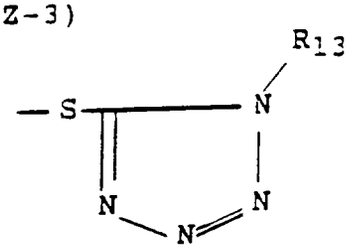
(Z-1)



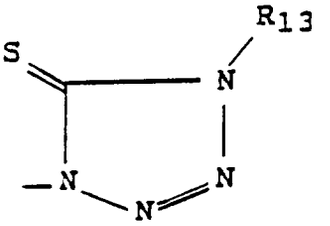
(Z-2)



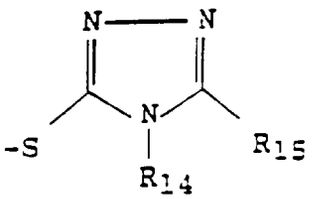
(Z-3)



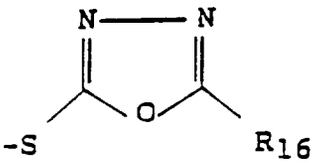
oder



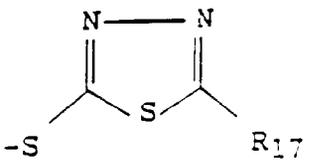
(Z-4)



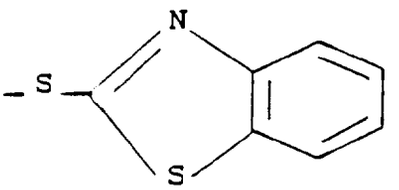
(Z-5)



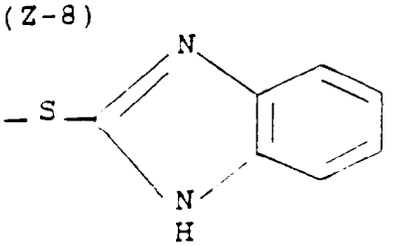
(Z-6)



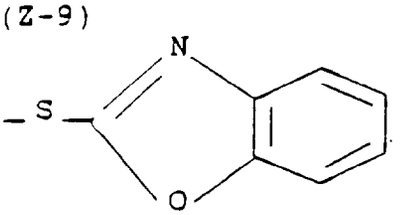
(Z-7)



(Z-8)



(Z-9)



worin, in den Formeln (Z-1) und (Z-2), R_{11} und R_{12} jeweils Alkyl, Alkoxy, Acylamino, ein Halogenatom, Alkoxycarbonyl, Thiazolilidenamino, Aryloxycarbonyl, Acyloxy, Carbamoyl, N-Alkylcarbamoyl, N,N-Dialkylcarbamoyl, Nitro, Amino, N-Arylcarbamoyloxy, Sulfamoyl, Sulfonamido, N-Alkylcarbamoyloxy, Ureido, Hydroxy, Alkoxycarbonylamino, Aryloxy, Alkylthio, Arylthio, Anilino, Aryl, Imido, einen heterocyclischen Ring, Cyano, Alkylsulfonyl oder Aryloxycarbonylamino bedeuten;

n bedeutet 1 oder 2, wenn n 2 ist, können R_{11} und R_{12} gleich oder verschieden sein, die Gesamtzahl der Kohlenstoffatome, enthaltend in n R_{11} und R_{12}, beträgt 0 bis 20;

in den Formeln (Z-3), (Z-4), (Z-5) und (Z-6) bedeuten R_{13}, R_{14}, R_{15}, R_{16} und R_{17} jeweils Alkyl, Aryl oder eine heterocyclische Gruppe;

in den Formeln (Z-1) und (Z-2) beträgt die Anzahl der Kohlenstoffatome, enthaltend in R_{11} und R_{12}, 1 bis 20; und

in den Formeln (Z-3), (Z-4), (Z-5) und (Z-6) beträgt die Gesamtzahl der Kohlenstoffatome, enthaltend in R_{13} bis R_{17}, 1 bis 20.

Revendications

1. Matériau photographique photosensible couleur à l'halogénure d'argent comprenant au moins une couche d'émulsion à l'halogénure d'argent photosensible et au moins une couche colloïdale non photosensible sur un support, ladite couche d'émulsion à l'halogénure d'argent photosensible comprenant des grains d'halogénure d'argent contenant une région localisée d'halogénure d'argent uniforme à l'échelle microscopique contenant au moins 3 % en mol d'iodure d'argent, dans lequel ladite région localisée d'halogénure d'argent possède au plus deux lignes indiquant une distribution microscopique non uniforme d'iodure d'argent à un intervalle de 0,2 µm dans une direction perpendiculaire aux lignes dans une image de transmission des grains obtenue en utilisant un microscope électronique de cryo-transmission et le nombre de grains d'halogénure d'argent possédant une telle région localisée d'halogénure d'argent représente au moins 60 % du nombre de tous les grains de l'émulsion, ladite couche d'émulsion à l'halogénure d'argent photosensible ou ladite couche colloïdale non photosensible contenant au moins un composé libérant un inhibiteur de développement (DIR) qui réagit avec la forme oxydée d'un agent développateur chromogène pour former un composé de coupure, ledit composé de coupure réagissant avec une autre molécule de la forme oxydée d'un agent développateur chromogène pour former un inhibiteur de développement ou un de ses précurseurs.

2. Matériau photographique photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel la teneur en iodure d'argent de la région localisée d'halogénure d'argent est supérieure ou égale à 5 % en mol.

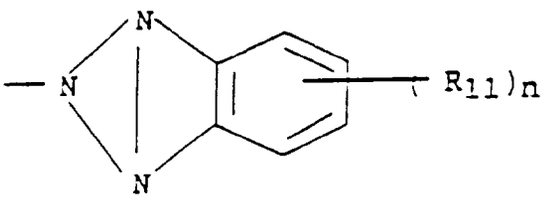
3. Matériau photographique photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel la teneur totale en iodure d'argent des grains d'halogénure d'argent possédant la région localisée d'halogénure d'argent est supérieure ou égale à 2 % en mol.

4. Matériau photographique photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel ledit composé DIR présent au moins au nombre de 1 est représenté par la formule suivante :

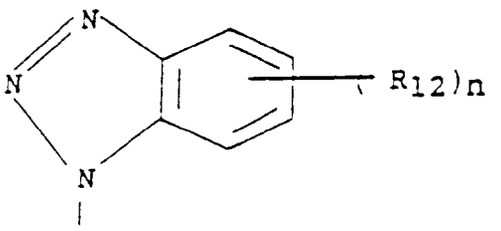
   A(ou B)-P-Z dans laquelle A représente un composant coupleur qui réagit avec la forme oxydée d'un agent développateur chromogène pour libérer -P-Z, B représente un composant redox qui subit une réaction d'oxydation-réduction avec la forme oxydée d'un agent développateur chromogène et une hydrolyse par un alcali pour libérer -P-Z, Z représente un inhibiteur de développement ou un de ses précurseurs, -P-Z représente un groupement qui est coupé de A ou B et qui réagit avec la forme oxydée d'un agent développateur chromogène pour libérer Z et P représente une fraction qui subit une réaction bimoléculaire avec la forme oxydée d'un agent développateur chromogène pour libérer Z.

5. Matériau photographique photosensible couleur à l'halogénure d'argent selon la revendication 1, dans lequel l'inhibiteur de développement ou un de ses précurseurs dans ledit composé DIR présent au moins au nombre de 1 est représenté par les formules (Z-1) à (Z-9) suivantes :

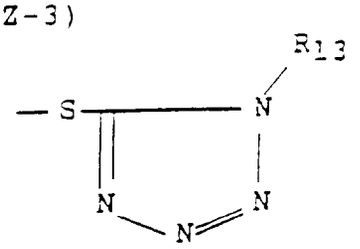
(Z-1)



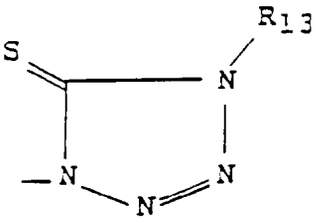
(Z-2)



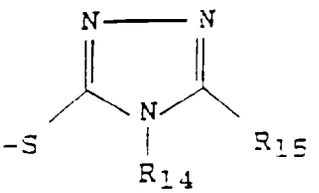
(Z-3)



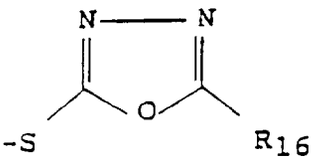
ou



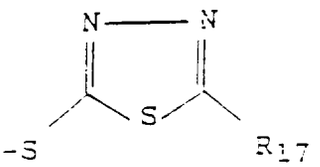
(Z-4)



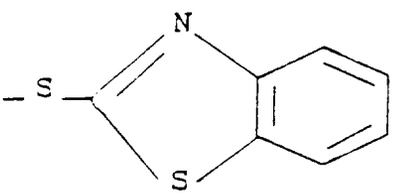
(Z-5)



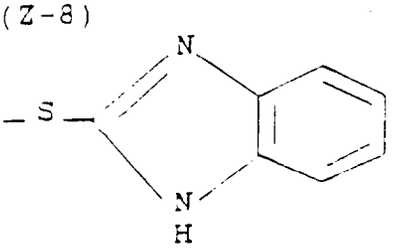
(Z-6)



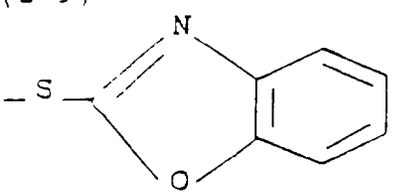
(Z-7)



(Z-8)



(Z-9)



où, dans les formules (Z-1) et (Z-2), R_{11} et R_{12} représentent chacun un alkyle, un alcoxy, un acylamino, un atome d'halogène, un alcoxycarbonyle, un thiazolylidéneamino, un aryloxycarbonyle, un acyloxy, un carbamoyle, un N-alkylcarbamoyle, un N,N-dialkylcarbamoyle, un nitro, un amino, un N-arylcarbamoyloxy, un sulfamoyle, un sulfonamido, un N-alkylcarbamoyloxy, un uréido, un hydroxy, un alcoxycarbonylamino, un aryloxy, un alkylthio, un arylthio, un anilino, un aryle, un imido, un noyau hétérocyclique, un cyano, un alkylsulfonyle ou un aryloxycarbonylamino;

n représente 1 ou 2 ; lorsque n représente 2, R_{11} et R_{12} peuvent être identiques ou différents ; le nombre total d'atomes de carbone contenus dans n R_{11} et R_{12} est compris entre 0 et 20 ;

dans les formules (Z-3), (Z-4), (Z-5) et (Z-6), R_{13}, R_{14}, R_{15}, R_{16} et R_{17} représentent chacun un alkyle, un aryle ou un groupement hétérocyclique;

dans les formules (Z-1) et (Z-2), le nombre d'atomes de carbone contenus dans R_{11} et R_{12} est compris entre 1 et 20 ; et

dans les formules (Z-3), (Z-4), (Z-5) et (Z-6), le nombre total d'atomes de carbone contenus dans R_{13} à R_{17} est compris entre 1 et 20.

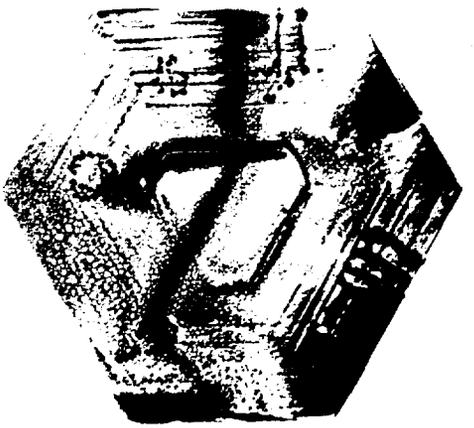


FIG. 1

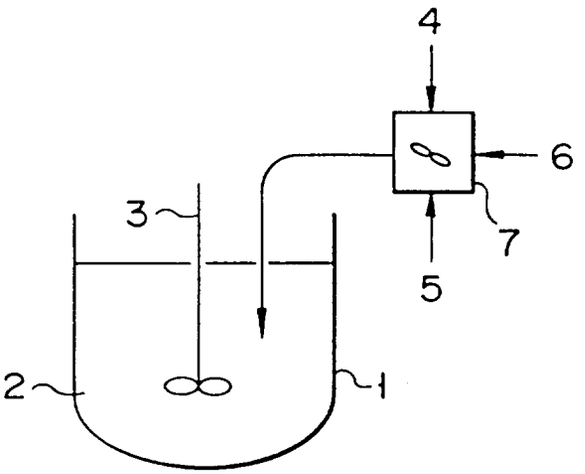


FIG. 2

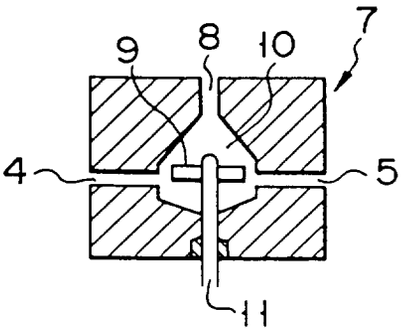


FIG. 3

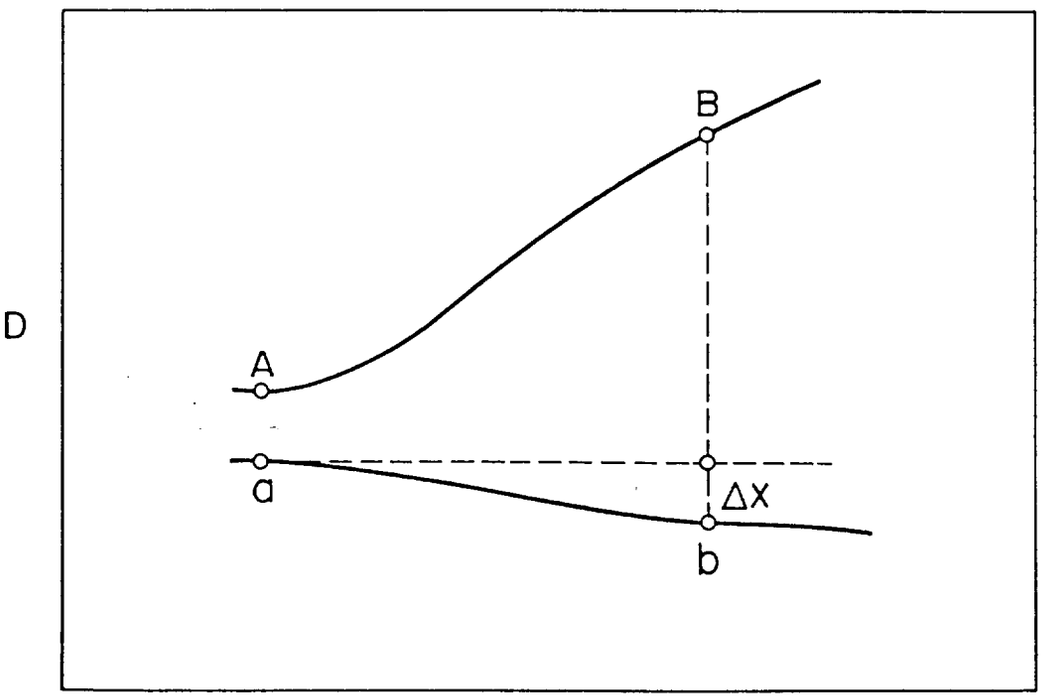
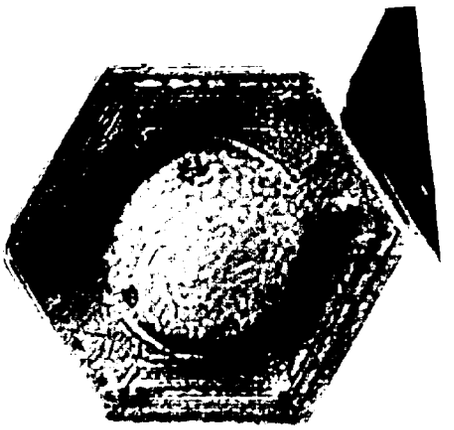
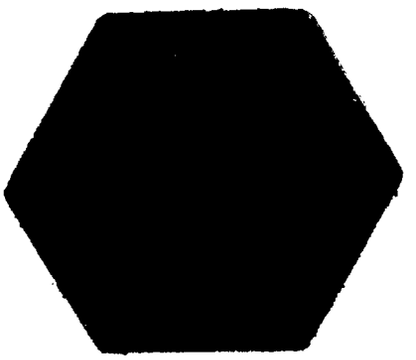


FIG. 5



(I-C)

FIG. 4A



(I-D)

FIG. 4B



(I-E)

FIG. 4C

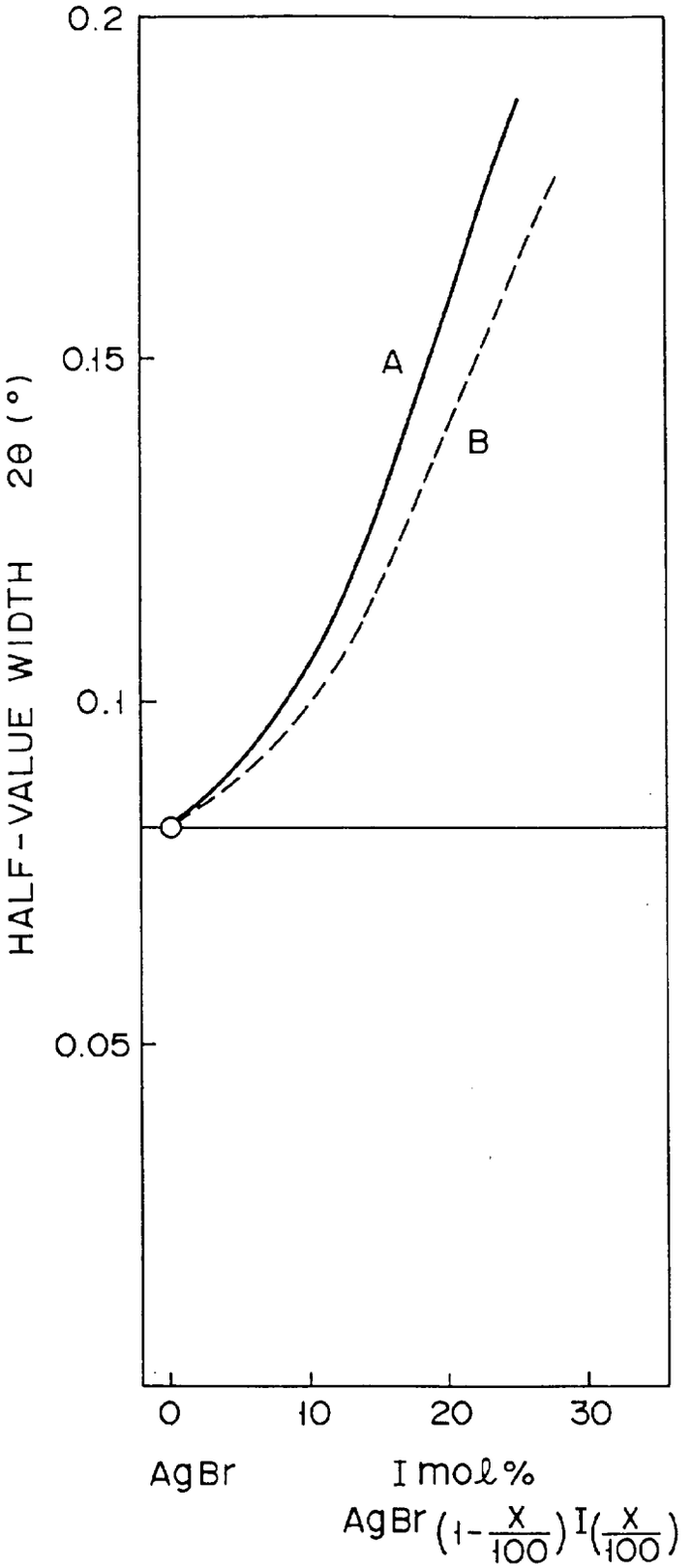

0.2
0.15
0.1
0.05
HALF-VALUE WIDTH 2θ (°)
A
B
0
10
20
30
AgBr
I mol%
AgBr (1-X/100) I(X/100)

FIG. 6