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(54) Silver halide color photographic material and method for producing of color image using the same.

(57) A silver halide color photographic material comprising a support and formed thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one blue-sensitive silver halide emulsion layer, wherein gradients γ_R^P , γ_G^P and γ_B^P in monochromatic exposure of each wavelength giving peak sensitivities are

$$0.80 < \gamma_R^P$$

$$0.80 < \gamma_G^P$$

$$0.65 < \gamma_B^P$$

and gradients γ_R , γ_G and γ_B in standard white light source exposure are

$$\gamma_R < 0.65$$

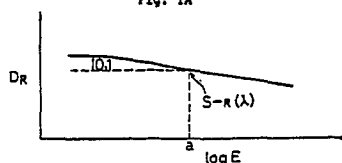
$$\gamma_G < 0.65$$

$$\gamma_B < 0.75,$$

and a method for producing a color image using the same.

The photographic material has a high saturation and excellent color and contrast reproducibility.

Fig. 1A



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SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL AND METHOD FOR PRODUCTION OF COLOR IMAGE USING THE SAME

FIELD OF THE INVENTION

5 This invention relates to a color photographic material, and more specifically to a color photographic material having high saturation and excellent color reproducibility and gradation reproducibility, and a method for production of a color image using the same.

BACKGROUND OF THE INVENTION

15 It has been known to utilize an interlayer inhibiting effect as means for improving color reproducibility in color photographic materials. For example, in the case of a color negative photographic material, by imparting a development inhibiting effect to a red-sensitive layer from a green-sensitive layer, coloration of the red-sensitive layer in white light exposure can be inhibited as compared with that in the case of red light exposure. Since a color negative paper system is balanced in gradation so that when it is exposed by white light, the color is reproduced in gray on a color print, the aforesaid effect gives a cyan color of a higher density in red exposure than in the case of gray exposure. Consequently, a red color of a higher degree of saturation with inhibited cyan coloration can be reproduced on the print. Likewise, the development inhibiting effect from a red-sensitive layer to a green-sensitive layer gives a reproduction of green having a high degree of saturation.

20 One known method of enhancing the interlayer effect involves using an iodine ion released from the silver halide emulsion during development. According to this method, the silver iodide content of a layer which imparts the interlayer effect is increased and that of a layer which receives this effect is decreased. Another method of enhancing the interlayer effect is to add a coupler which reacts with the oxidation product of a developing agent in a p-phenylenediamine-type color developer to release a development inhibitor, as disclosed in JP-A-50-2537. ("JP-A" as used herein means an "unexamined published Japanese patent application". Foreign patents corresponding to Japanese patent publications are shown hereinafter.) Still another method of enhancing the interlayer effect is called "automatic masking" whereby a colored coupler is added to a colorless coupler to mask the unwanted absorption of a formed dye from the colorless coupler. The method using the colored coupler gives masking to a greater extent than the unwanted absorption of the colorless coupler are masked by increasing the amount of the colored coupler added, and can impart the same effect as the interlayer effect.

35 These methods have the defect that when the saturations of the primary colors, red, green and blue are increased, a yellowish to cyan-like green color is not faithful. As a measure to remedy this defect, the technique disclosed in JP-A-61-34541 was proposed. This technique contemplates the achievement of clear and faithful color reproduction by a silver halide color photographic material comprising a support and formed thereon, at least one blue-sensitive silver halide emulsion layer containing a color coupler which forms yellow, at least one green-sensitive silver halide emulsion layer containing a color coupler which forms magenta and at least one red-sensitive silver halide emulsion layer containing a color coupler which forms cyan; wherein

40 the center of the sensitivity wavelength ($\bar{\lambda}_G$) of the spectral sensitivity distribution of the green-sensitive layer is $520 \text{ nm} \leq \bar{\lambda}_G \leq 580 \text{ nm}$,
the center of the wavelength ($\bar{\lambda}_R$) of the distribution of the magnitude of the interlayer effect which at least one said red-sensitive silver halide emulsion layer receives from another layer in a range of 500 nm to 600 nm is $500 \text{ nm} \leq \bar{\lambda}_R \leq 560 \text{ nm}$, and
 $\bar{\lambda}_G - \bar{\lambda}_R \leq 5 \text{ nm}$.

50 The center of the wavelength $\bar{\lambda}_R$ of the wavelength distribution of the magnitude of the interlayer effect which the red sensitive silver halide emulsion layer receives from another layer in a range of 500 nm to 600 nm is determined by the following procedure.

(1) A uniform exposure is given to the photographic material to fog it using a red filter which permits passage of wavelengths above specific wavelength to which the red-sensitive layer which forms cyan at wavelengths above 600 nm is sensitive but the other layers are not sensitive, or using an interference filter which permits passage, of only the specific wavelength, thereby uniformly fogging the red-sensitive layer which forms a cyan color to a suitable value.

(2) When spectral exposure is then imparted, the interlayer effect of development inhibition acts on the fogged emulsion from the blue-sensitive layer and the green-sensitive layer to give a reversal image (see Fig. 1A).

(3) The spectral sensitivity distribution $S_R(\lambda)$ of the reversal photographic material is determined from the reversal image. $[S_R(\lambda)]$ for a given λ (wavelength) can be determined relatively from point a in Fig. 1A]

(4) The center of the wavelength ($\bar{\lambda}_R$) of the interlayer effect is calculated from the following equation.

$$\bar{\lambda}_R = \frac{\int_{500 \text{ nm}}^{600 \text{ nm}} \lambda \cdot S_R(\lambda) d\lambda}{\int_{500 \text{ nm}}^{600 \text{ nm}} S_R(\lambda) d\lambda}$$

The center of the sensitivity wavelength $\bar{\lambda}_G$ is given by the following equation.

$$\bar{\lambda}_G = \frac{\int_{500 \text{ nm}}^{600 \text{ nm}} \lambda \cdot S_G(\lambda) d\lambda}{\int_{500 \text{ nm}}^{600 \text{ nm}} S_G(\lambda) d\lambda}$$

$S_G(\lambda)$ is the spectral sensitivity distribution curve, and $S_G(\lambda)$ at a given λ can be determined from point b of Fig. 1B as a relative value.

When all objects existing in nature were photographed using the above-described photographic material and the images were printed on commercial color prints, it was found that the photographic material was sufficient for reproduction of conspicuous colors as in a color chart, but this improvement is still insufficient for subtle reproduction of skin colors which are most important colors. A further development in technique is necessary in order to depict accurately the continuity of the highlights and shadows of colors of a human face and skin colors of white, black and yellow human species. Furthermore, reproduction of hair colors like skin colors is also important. Reproduction of fair or red hairs in black at a shadow portion is most disliked because the black shadow portion is mistaken for dyed hair. The technique of the above-discussed invention is not sufficient, and a new technique is required.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a color photographic material having high saturation and excellent color reproducibility and gradation reproducibility.

The present inventors worked extensively and have found that when the gradations of the blue-, green, and red-sensitive silver halide emulsion layers of a photographic material meet certain conditions in a white light source and a spectrum light source, respectively, the object of the present invention can be achieved.

Specifically, according to this invention, the foregoing problem is solved by a silver halide color photographic material comprising a support and formed thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one blue-sensitive silver halide emulsion layer, wherein gradients γ_R^P , γ_G^P and γ_B^P in monochromatic exposure of wavelengths giving peak sensitivities are

$$\begin{aligned} 0.80 &< \gamma_R^P \\ 0.80 &< \gamma_G^P \\ 0.65 &< \gamma_B^P, \end{aligned}$$

and maximum gradients γ_R , γ_G and γ_B in standard white light source exposure are

$$\begin{aligned}\gamma_R &< 0.65 \\ \gamma_G &< 0.65 \\ \gamma_B &< 0.75.\end{aligned}$$

5

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is the characteristic curve of a reversal image obtained as a result of the red-sensitive layer receiving the interlayer effect from the green-sensitive layer at a wavelength λ .

Fig. 1B is the characteristic curve of the green-sensitive layer at a wavelength λ .

Fig. 1C shows a method of determining the magnitude of the interlayer effect. Fig. 1C shows the interlayer effect of color sensitivity Y on color sensitivity X. The density decrease of color sensitivity X which decreases during movement toward a higher exposure by 1.0 of log E from the sensitivity point (the logarithm of the amount of exposure which gives a density of fog + 0.2) of color sensitivity Y is defined as IE(X/Y).

Fig. 2 shows the equivalent energy spectra of typical samples. The ordinate shows the logarithm of the reciprocal of the relative sensitivity. The curves arranged in the order from that having smaller values, i.e. higher sensitivities show sensitivities at a density of fog + 0.4, fog + 0.6, fog + 0.8, and fog + 1.0, respectively. The circular marks show points which give peaks. The averages of these are calculated as 413 nm, 543 nm and 621 nm, respectively.

Fig. 3 shows absorption spectra of blue, green and red optical filters using in density measurement.

25

DETAILED DESCRIPTION OF THE INVENTION

The present inventors also found that by providing some restrictions on the 4 directions of the interlayer effect in addition to the above conditions, more favorable color reproduction can be obtained.

Specifically, with regard to the magnitude IE(X/Y) of the interlayer effect defined in Fig. 1C, the following conditions are set down.

$$0.15 < \text{IE (R/G)}$$

$$0.15 < \text{IE (G/R)}$$

$$0.15 < \text{IE (G/B)}$$

$$\text{IE(R/B)/IE(G/B)} < 1.0.$$

IE(X/Y) above represents the magnitude of the interlayer effect of Y on X.

This effect is most favorable in the structure shown in JP-A-61-34541 which has a donar layer for giving the effect. It has been ascertained however that with an ordinary layer structure, the same effect exists.

A preferred range of γ_R^P , γ_G^P , and γ_B^P is as follows:

$$0.90 < \gamma_R^P < 1.15$$

$$0.90 < \gamma_G^P < 1.10$$

$$0.70 < \gamma_B^P < 1.2,$$

A preferred range of γ_R , γ_G and γ_B is as follows:

$$0.4 < \gamma_R < 0.60$$

$$0.4 < \gamma_G < 0.60$$

$$0.4 < \gamma_B < 0.65.$$

A silver halide color negative film is required to have a broad exposure latitude, and variations in color reproducibility according to the amount of exposure are undesirable. It is generally desirable therefore that the spectral sensitivity distributions of the same color developing layers coincide with each other. But subtle differences in spectral sensitivity distribution may arise depending upon the halogen composition of the emulsion, the state of adsorption of sensitizing dyes, and the absorptions of diffusion-resistant dyes and a colored coupler in the coating composition. Accordingly, gradations may vary according to wavelengths. There is also the case where the spectral sensitivity distribution is intentionally changed. For example, if a high-sensitivity emulsion layer of a red-sensitive layer is set at a longer wavelength than the spectral sensitivity distribution of its low-sensitivity emulsion layer, the red-sensitive layer as a whole becomes a soft gradation on the long wavelength side and a hard gradation on the short wavelength side. If at this time, the low-sensitivity layer is a layer contributing greatly to the color density, the gradation at the peak wavelength of the low-sensitivity emulsion contributes greatly to color reproducibility.

The wavelength which gives a peak sensitivity is defined as follows:

The wavelength which gives the peak sensitivity of a red-sensitive silver halide emulsion layer is obtained by determining the wavelength at which the spectral sensitivity distribution of the silver halide emulsion layer becomes highest at varying densities, the fog +0.4, 0.6, 0.8 and 1.0, and calculating an arithmetic mean of these wavelengths. The spectral sensitivity distribution is given by the reciprocal of the amount of exposure which gives the density of (fog + a given density) of the silver halide emulsion layer having sensitivity in the range of from 550 nm to 700 nm and containing a color coupler which couples with the oxidation product of the developing agent to develop cyan.

Likewise, the wavelength which gives the peak sensitivity of a green-sensitive silver halide emulsion layer is obtained by determining the wavelength at which the spectral sensitivity distribution of the silver halide emulsion layer becomes highest at varying densities, the fog +0.4, 0.6, 0.8 and 1.0, and calculating an arithmetic mean of these wavelengths. The spectral sensitivity distribution is given by the reciprocal of the amount of exposure which gives the density of (fog + a given density) of the silver halide emulsion layer having sensitivity in the range of from 480 nm to 620 nm and containing a color coupler which couples with the oxidation product of the developing agent to develop magenta.

Likewise, the wavelength which gives the peak sensitivity of a blue-sensitive silver halide emulsion layer is obtained by determining the wavelength at which the spectral sensitivity distribution of the silver halide emulsion layer becomes highest at varying densities, the fog +0.4, 0.6, 0.8 and 1.0, and calculating an arithmetic mean of these wavelengths. The spectral sensitivity distribution is given by the reciprocal of the amount of exposure which gives the density of (fog + a given density) of the silver halide emulsion layer having sensitivity in the range of from 400 nm to 520 nm and containing a color coupler which couples with the oxidation product of the developing agent to develop yellow.

Examples of wavelengths obtained by the above methods are shown in Fig. 2.

In the present invention, the gradient at a wavelength which gives the peak sensitivity is determined by the following procedure.

A test photographic material is exposed through a wedge using a metal vapor-deposited interference filter (e.g., Model MIF-W, made by Japan Vacuum Optical Co., Ltd.) having the peak wavelengths obtained by the above method, and subjected to a designated development. The density of the developed photographic material is measured through a red, a green and a blue filter having the absorption characteristics shown below and in Figure 3.

<u>Filter</u>	<u>Maximum Wavelength</u> (nm)	<u>Half Width</u> (nm)
Blue	434	9
Green	550	8
Red	690	52

On a graph having the logarithm of the amount of exposure on the abscissas and the density on the ordinates, values giving densities, the fog +0.4, 0.6, 0.8 and 1.0, are plotted. These points are approximated to a straight line by the method of least square. Then $\tan \theta$ values with respect to the angle θ from the abscissa are defined as γ_R^p , γ_G^p , and γ_B^p of this photographic material.

Likewise, the gradients in a standard white light source are determined by the following procedure.

A photographic material is exposed through a wedge to a standard white light source, for example, a light source having an energy distribution of 5,500° K of black body radiation if the photographic material is of the daylight type. The exposed photographic material is subjected to a designated development, and the density of the developed photographic material is measured through a red, a green and blue filter having the absorption characteristics shown in Fig. 3. On a graph having the logarithm of the amount of exposure on the abscissa and the density on the ordinates, values giving densities, fog +0.4, 0.6, 0.8 and 1.0, are plotted. These points are approximated to a straight line by the method of least square. The $\tan \theta$ values with respect to the angle θ from the abscissa are defined as γ_R , γ_G and γ_B of this photographic material.

When the silver halide color photographic material of this invention is a color negative film, those commercially available as color papers giving prints can all be used.

The preferred gradient of color paper is about 2.7 ± 0.1 in terms of colorimetric density (for the colorimetric density, see, for example, Fundamentals of Photographic Engineering, Silver Halide Photog-

raphy, edited by Japan Society of Photography, page 387).

Should the average gradient of color papers be increased by α times in future for some reason, the gradients in this invention may be set as follows:-

Namely, the gradients of the wavelengths giving the peak sensitivities in monochromatic exposure are
 5 set at

$$\frac{0.80}{\alpha} < \gamma_R^P$$

$$10 \quad \frac{0.80}{\alpha} < \gamma_G^P$$

$$15 \quad \frac{0.65}{\alpha} < \gamma_B^P$$

20 and the gradients in a standard white light source exposure are set:

$$\gamma_R < \frac{0.65}{\alpha}$$

$$25 \quad \gamma_G < \frac{0.65}{\alpha}$$

$$\gamma_B < \frac{0.75}{\alpha}$$

30 The preferred ranges of γ_R^P , γ_G^P , and γ_B^P are set:

$$35 \quad \frac{0.90}{\alpha} < \gamma_R^P < \frac{1.15}{\alpha}$$

$$\frac{0.90}{\alpha} < \gamma_G^P < \frac{1.10}{\alpha}$$

$$40 \quad \frac{0.70}{\alpha} < \gamma_B^P < \frac{1.2}{\alpha}$$

and the preferred ranges of γ_R , γ_G and γ_B are set:

$$45 \quad \frac{0.4}{\alpha} < \gamma_R < \frac{0.60}{\alpha}$$

$$50 \quad \frac{0.4}{\alpha} < \gamma_G < \frac{0.60}{\alpha}$$

$$\frac{0.4}{\alpha} < \gamma_B < \frac{0.65}{\alpha}$$

55 The present invention has succeeded in enhancing color reproducibility and contrast reproducibility by setting certain restrictions on the gradients of red-, green- and blue-sensitive silver halide emulsion layers to certain spectral lights and to white light, and quite differs from technique of obtaining an effect in color

reproduction by specifying the spectral sensitivity and the magnitude of the interlayer effect which is disclosed in JP-A-62-160447.

This means that by employing whatever combinations of the spectral sensitivity and the interlayer effect, good results cannot be obtained if the gradations of red-, green- and blue-sensitive silver halide emulsion layers to specific spectral lights and to white light in this invention are not satisfied. This will be clarified in working examples to be given later on.

The present invention pertains to a photographic material which has a high gradient when no interlayer inhibiting effect is received from another layer and a low gradient when this effect is received. Desirably, the silver halide to be coated should have excellent granularity irrespective of the presence of the interlayer inhibiting effect. Thus, it is preferred to use double-structure grains or multi-structure grains having high quantum sensitivity. For the same reasons, it is preferred to use flat tabular grains having a high color sensitization ratio.

Use of an emulsion having a high gradation in the same amount of coating is preferred in view of the cost, the increase of the rate of desilvering in processing and the increase of the sharpness of the image as a result of reduced optical scattering. Accordingly, the silver halide grains used in this invention preferably contain from 0 to 15 mol%, more preferably not more than 10 mol%, most preferably not more than 8 mol%, on an average of silver iodide.

When silver halide containing at least 8 mol% of silver iodide is used in any one layer of the photographic material of this invention, the content of silver iodide on the surface of silver halide grains is from 0 to 6 mol%, preferably not more than 4 mol%, for the same reason.

Now, means for controlling the interlayer effect used in this invention will be described.

Usually, development of a given layer is inhibited or the dye formed is masked when another color-sensitive layer(s) exposed is developed. In the present invention, this effect is referred to as a plus interlayer effect. Conversely, when the other color-sensitive layer(s) exposed is developed, the development of the given layer is promoted or the color density of the given layer looks as it is increased because of the turbidity of the color formed of the other layer, this effect is referred to as a minus interlayer effect.

The following methods, for example, are available for imparting the plus interlayer effect.

A masking technique using colored couplers as described in U.S. Patents 2,983,808 and 3,034,892.

A method involving the use of DIR compounds having a great interlayer effect as described in JP-A-57-151944, JP-A-56-114946 and JP-A-54-145135.

A method involving including a DIR compound into a non-photosensitive layer as described in JP-A-61-43745.

A method involving skillfully selecting the properties of a DIR compound as described in JP-A-62-54244.

A method in which an emulsion is monodispersed to reduce adsorption of an inhibiting substance by a fine particulate emulsion as described in JP-A-58-100847.

When the pyrazolotriazole magenta coupler described in JP-A-61-0222342 is used in a green sensitive silver halide emulsion layer, the interlayer effect on a substantially blue-sensitive layer can be increased because there is no subsidiary absorption of yellow. Furthermore, when the 5-amide naphthol-type cyan coupler described in JP-A-61-153460 is used in a blue-sensitive layer, the interlayer effect on a green-sensitive effect can be increased because there is little subsidiary absorption of magenta.

Means for increasing the gradient γ^P at a wavelength which gives a peak sensitivity will be specifically described without any limitation thereby.

The simplest method is to increase the amount of the silver halide or the coupler coated. Increasing the developability of the silver halide, for example, decreasing of the content of silver iodide whose development inhibition is large, and including silver chloride having a high rate of development are also available. Likewise, there is a method in which the amount of a development inhibitor releasing compound (DIR compound) is decreased.

The above-cited methods increase not only γ^P but also γ in white light exposure. Accordingly, means for confining γ within the range specified by this invention become necessary. Examples of such means are listed below.

1. The amount of a coupler which forms a dye having an absorption at the same wavelength as the color developed of an emulsion layer desired to be inhibited is reduced. For example, in a working example of this invention, γ_R is decreased by reducing the amounts of the cyan couplers ExC-1 and ExC-4 in the 12th layer (blue-sensitive layer). Furthermore, γ_B can be decreased by replacing the 5-pyrazolone-type magenta coupler used in a green-sensitive layer by a pyrazole-type magenta coupler having a little subsidiary absorption of yellow.

2. Automasking by colored couplers is strengthened.

For example, in the working example of this invention, γ_B can be decreased by increasing the amount of the yellow colored magenta coupler EXM-7 in the 7th layer.

Likewise, γ_G can be decreased by increasing the amount of the magenta colored cyan coupler ExC-3 in the third layer.

5 3. The interlayer development inhibiting effect is increased.

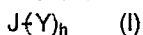
For example, γ_R and γ_B can be decreased by increasing the amount of the DIR coupler EXM-10 in the 10th layer in the example of this invention. Likewise, γ_G and γ_B can be decreased by increasing the amount of the coupler ExC-2 in the third layer.

10 The inclusion of at least one nondiffusible coupler which releases a diffusible development inhibitor or its precursor only in one of the blue-sensitive, green-sensitive and blue-sensitive layers is effective. But to obtain better color reproducibility, it is preferred to include them in two or more layers. It is also possible to include the diffusible DIR compound into a layer containing no silver halide or having no color sensitivity so long as it substantially couples with the oxidation product of the color developing agent diffused from another layer to release a releasing group during color development.

15 Alternatively, it is possible to divide a color-sensitive layer into two or more layers and include the diffusible DIR compound into one or more layers without including it in the remained layers. The sensitivities of the layers may differ from each other, for example, one being a more-sensitive layer and another, a less-sensitive layer. Or they may not be completely the same color sensitivity.

20 To change the degree of the interlayer inhibiting effect, it is possible to properly change the iodine content of the emulsion, or to add a colored coupler to the emulsion, thereby masking an unwanted absorption of a colored dye. There can also be used a method in which the interlayer inhibiting effect is set off by intentionally mixing a colored dye having different color from the color to which the layer is sensitive and thus increasing color turbidity.

25 Nondiffusible couplers which release a diffusible development inhibitor or its precursor during coupling with a color developing agent in this invention are represented by the following formula.



30 wherein J represents a coupler component, h represents 1 or 2, and Y is a group which is bonded to the coupling site of the coupler component J and split off upon reaction with an oxidation product of a color developing agent, to produce a development inhibitor having high diffusibility or a compound which can release a development inhibitor having high diffusibility (preferably having a diffusibility, measured by the method to be described hereinbelow, of at least 0.4).

Y in general formula (I) above preferably includes the following groups of general formulae (II) to (V).

35

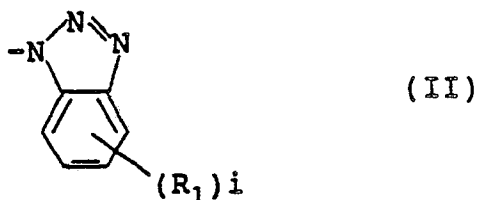
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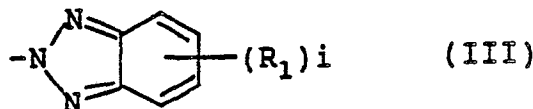
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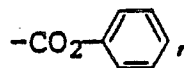
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In the formulae, W represents -S-, -O-, or -N(R₃)-, R₁, R₂, R₃ and R₄ each represents a substituent selected so that they each has a diffusibility of at least 0.4, and i represents an integer of from 1 to 4. R₁ group(s) may be substituted at any position(s) on the ring.

Examples of R₁ include a lower alkyl group having from 1 to 4 carbon atoms (preferably, the total number of carbon atoms in R₁ group(s) is 2, for example, R₁ is CH₃ and i=2), and a halogen atom, for example, Cl and Br and i=1 or 2, preferably R₁ is Br and i=1. Furthermore, examples of R₁ include -NHCOR' (R' has 3 to 7 carbon atoms), -NHSO₂R' (R' has 4 to 8 carbon atoms), -OR' (R' has 2 to 5 carbon atoms), -R' (1-3 carbon atoms),



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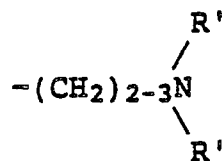
and -CO₂R' (R' has 2 to 6 carbon atoms); R' herein represents a substituted or unsubstituted chain, cyclic or branched aliphatic hydrocarbon group, i is preferably 1. When i is 2 or more, groups represented by R₁ may be the same or different from each other.

R₂ represents a substituted or unsubstituted alkyl group having from 1 to 4 carbon atoms in the alkyl moiety. Examples of the substituent include a sulfo group, a carboxyl group, a hydroxyl group, an alkoxy group, a halogen atom, an alkyl, aryl or heterocyclic ring, sulfonyl group, a nitro group, an amino group, or an aryl group. Examples of an alkyl group include an ethyl group and propyl group.

R₂ further represents a substituted or unsubstituted phenyl group. Examples of substituents include a sulfo group, an alkoxycarbonyl group, a carboxyl group, a hydroxyl group, an alkoxy group, a halogen atom, a cyano group, a nitro group, an amino group, an alkyl group, a carbamoyl group and a ureido group. These substituents preferably substituted at m- or p-position of the phenyl group.

Examples of the substituted phenyl group include a hydroxyphenyl group, an aminophenyl group, a sulfamoylphenyl group, a carboxyphenyl group, a methoxycarbonylphenyl group, a 3-methoxyphenyl group, a 3-carbamoylphenyl group and a 3-ureidophenyl group.

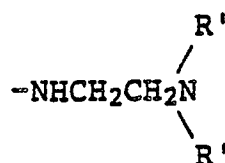
R₂ also represents (CH₂)₂₋₃COOR' (R' has 2 to 3 carbon atoms),



(the two R' groups may be identical or different and have 2 to 3 carbon atoms), and $-(\text{CH}_2)_2\text{OCH}_3$. R' is as defined above with regard to R₁.

Examples of R₃ are a hydrogen atom and alkyl groups as defined the alkyl group represented by R₂.

Examples of R₄ are an amino group, $-\text{NHCOR}'$ (R' represents an alkyl group having from 1 to 6 carbon atoms),



(the two R's are identical or different and each represents a methyl or ethyl group), a methyl group, an ethyl group, a propyl group, $-(\text{CH}_2)_2-\text{COOH}$ and $-(\text{CH}_2)_2-\text{SO}_3\text{H}$.

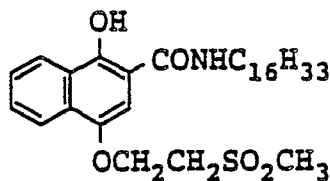
The diffusibility of the development inhibitor is evaluated by the following method.

A photographic material (sample B) was prepared by forming the following two layers on a transparent support.

First layer: red-sensitive silver halide emulsion layer

An emulsion obtained by rendering a silver iodobromide emulsion (silver iodide 5 mol%, average size 0.4μ) red-sensitive using 6×10^{-5} , per mole of silver, of sensitizing dye I in Example 1, and a gelatin coating solution containing 0.0015 mole, per mole of silver, of coupler X were coated so that the amount of silver coated was 1.8 g/m^2 (coating thickness 2μ).

Coupler X



Second layer:

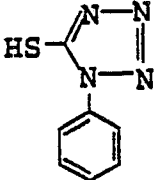
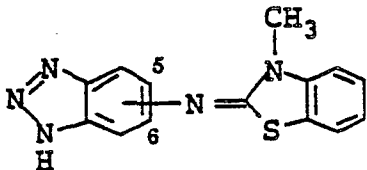
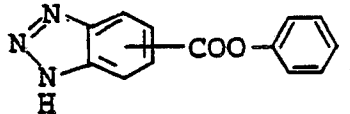
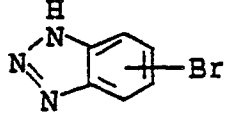
A gelatin layer (the amount of silver coated 2 g/m^2 , coating thickness 1.5μ) containing the same silver iodobromide emulsion as used in the first layer (having no red-sensitivity) and polymethyl methacrylate particles (diameter about 1.5μ).

Another gelatin hardener or a surface-active agent is incorporated in each of these layers.

A photographic material having the same structure as the sample B except that the silver iodobromide was not contained in the second layer was prepared as sample A.

The samples A and B were each exposed to red light through a wedge, and processed in accordance with the processing recipe in Example 1 except that the developing time was changed to 2 minutes and 10 seconds. As development inhibitor was added to the developing solution so that the density of sample A

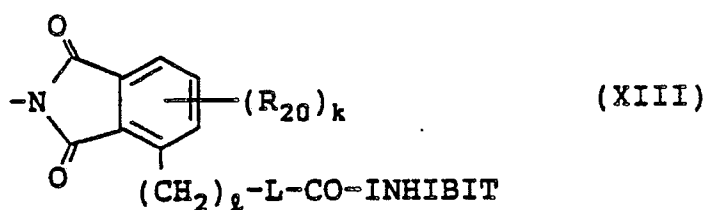
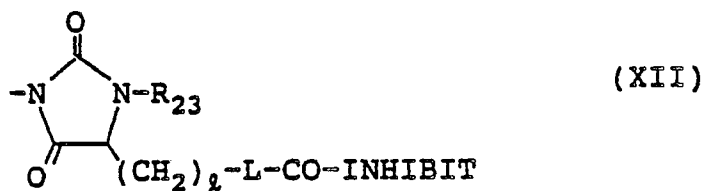
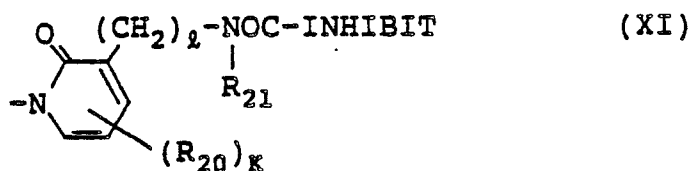
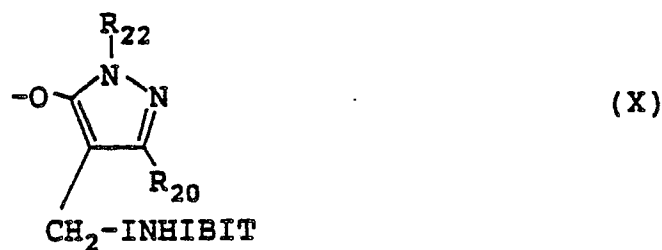
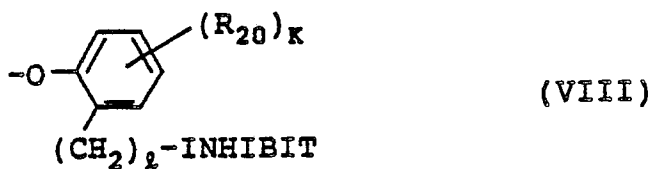
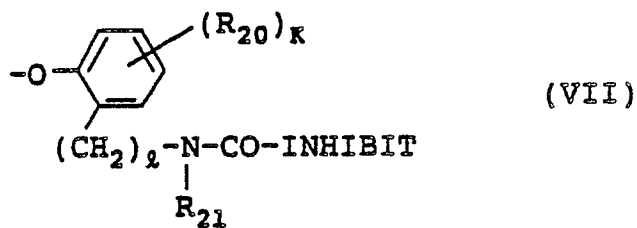
decreased to 1/2. The decrease of the density of sample B at this time was used as a measure of the diffusibility of the silver halide emulsion coating. The results are shown below.

Development inhibitor	Amount of added to the developer	Degree of decrease of density		Diffusi- bility (=B/A)
		Sample A	Sample B	
	$0.75 \times 10^{-4} M$	50	10	0.2
 (A mixture of 5- or 6-substituted compounds)	0.5×10^{-4}	50	15	0.3
 (A mixture of 5- or 6-substituted compounds)	2×10^{-4}	52	37	0.74
	2.5×10^{-4}	51	45	0.9

In general formula (I), Y further represents the following general formula (VI):
-TIME-INHIBIT (VI)

In the formula, the TIME group is a group which is bonded to the coupling site of the coupler and can be cleaved by reaction with a color developing agent, and which after being cleaved from the coupler, can release the INHIBIT group under moderate control; and the INHIBIT group forms a development inhibitor.

In general formula (VI), the TIME-INHIBIT group is preferably one of those represented by the following general formulae (VII) to (XIII).



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In general formulae (VII) to (XIII), R_{20} represents a hydrogen or halogen atom, or an alkyl, alkenyl, aralkyl, alkoxy, alkoxy carbonyl, anilino, acylamino, ureido, cyano, nitro, sulfonamide, sulfamoyl, carbamoyl,

aryl, carboxyl, sulfo, hydroxyl or alkanesulfonyl group. These groups preferably have from 1 to 20 carbon atoms.

In general formulae (VII), (VIII), (IX), (XI) and (XIII), k represents 1 or 2.

In general formulae (VII), (XI), (XII) and (XIII), l represents an integer from 0 to 2.

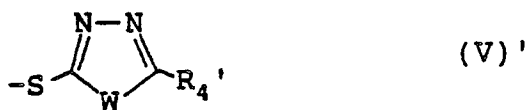
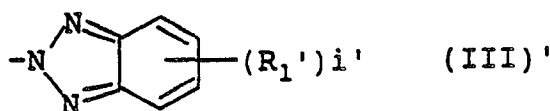
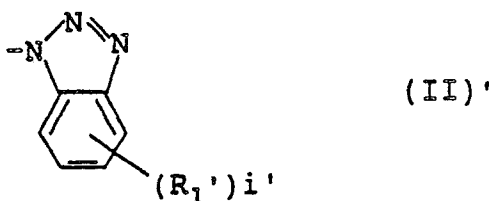
In general formulae (VII), (X) and (XI), R_{23} represents an alkyl, alkenyl, aralkyl, cycloalkyl or aryl group. These groups preferably have from 1 to 20 carbon atoms.

In general formulae (XII) and (XIII), L represents an oxygen atom, or a group of the formula



in which R_{24} represents a hydrogen atom or a lower alkyl group, preferably having from 1 to 5 carbon atoms.

Preferably, the INHIBIT group is represented by general formulae (II)', (III)', (IV)' and (V)'.



In the formulae, W represents $-S-$, $-O-$, or $-N(R_3)-$, R_1' , R_2' , R_3' and R_4' each represents a substituent selected so that they each has a diffusibility of at least 0.4, and i' represents an integer of from 1 to 4. R_1' group(s) may be substituted at any position(s) on the ring.

R_1' represents a halogen atom or an alkyl, alkoxy, acylamino, alkoxycarbonyl, thiazolydenamino, aryloxycarbonyl, acyloxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, N-alkylcarbamoyloxy, hydroxyl, alkoxycarbonylamino, alkylthio, arylthio, aryl, heterocyclic, cyano, alkylsulfonyl or aryloxycarbonylamino group.

In general formulae (II)' and (III)', i' represents 1 or 2, and when i' is 2, two or more R_1' groups may be identical or different, and i' R_1' groups may contain 0 to 32 carbon atoms in total.

In general formula (IV)', R_2' represents an alkyl, aryl or heterocyclic group.

In general formula (V)', R_3' represents a hydrogen or halogen atom, or an alkyl, aryl or heterocyclic group; and R_4' represents a hydrogen or halogen atom or an alkyl, aryl, acylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkanesulfonamide, cyano, heterocyclic, alkylthio or amino group.

When R_1' , R_2' , R_3' or R_4' represents an alkyl group, it may be substituted or unsubstituted and linear

or cyclic. Examples of substituents on such alkyl groups include halogen atoms, and nitro, cyano, aryl, alkoxy, aryloxy, alkoxycarbonyl, aryloxy carbonyl, sulfamoyl, carbamoyl, hydroxyl, alkanesulfonyl, arylsulfonyl, alkylthio and arylthio groups.

When R_1' , R_2' , R_3' or R_4' represents an aryl group, the aryl group may be substituted. Examples of substituents on the aryl group include halogen atoms and alkyl, alkenyl, alkoxy, alkoxycarbonyl, nitro, amino, sulfamoyl, hydroxyl, carbamoyl, aryloxy carbonylamino, alkoxycarbonylamino, acylamino, cyano and ureido groups.

When R_1' , R_2' , R_3' or R_4' represents a heterocyclic group, it represents a 5- or 6-membered monocyclic or fused ring group containing at least one of a nitrogen, oxygen and sulfur atoms as a hetero atom. It may be substituted by a substituent selected, for example, from pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, thiazolyl, triazolyl, benzotriazolyl, imido and oxazine group and these groups may be substituted with at least one of the substituents listed above with regard to the aryl group.

In general formula (IV), the number of carbon atoms contained in R_2' is 1 to 32.

In general formula (V), the total number of carbon atoms contained in R_3' and R_4' is 1 to 32.

When R_{20} and R_{23} represent an alkyl group, it is substituted or unsubstituted and linear or cyclic. The same substituents as listed above with regard to the alkyl groups R_1' to R_4' above may be cited as examples of substituents in this case.

R_{21} , R_{22} and R_{23} each represent a hydrogen atom or a lower alkyl group.

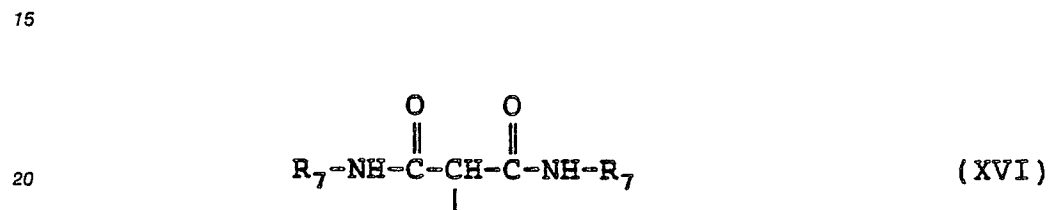
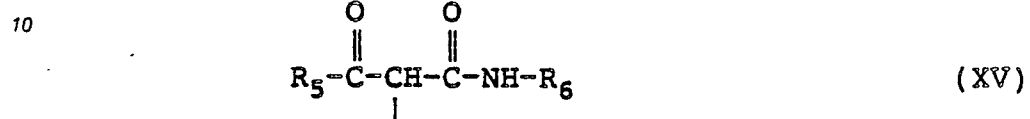
Examples of the yellow image-forming coupler residue represented by J in general formula (I) include coupler residues of the pivaloyl acetanilide, benzoyl acetanilide, malonic diester, malondiamide, dibenzoyl methane, benzothiazolyl acetamide, malonic ester monoamide, benzothiazolyl acetate, benzoxazolyl acetamide, benzoxazolyl acetate, benzimidazolyl acetamide and benzimidazolyl acetate types; coupler residues derived from hetero ring-substituted acetamides or hetero ring-substituted acetates disclosed in U.S. Patent 3,841,880; coupler residues derived from acylacetamides described in U.S. Patent 3,770,446, British Patent 1,459,171, West German Patent (OLS) 2,503,009, JP-A-50-139738 or Research Disclosure No. 15737; and heterocyclic type coupler residues described in U.S. Patent 4,046,574.

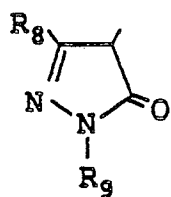
Coupler residues having a 5-oxo-2-pyrazoline ring, a pyrazolo[1,5-a]benzimidazole ring or a cyanoacetophenone-type coupler residue are preferred as the magenta image-forming coupler residue represented by J.

Couplers having a phenol ring or an α -naphthol ring are preferred as the cyan image-forming coupler residue represented by J.

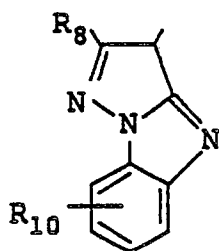
Even if the coupler does not substantially forms a dye after it has coupled with the oxidation product of a developing agent and released a development inhibitor, its effect as a DIR coupler remains the same. Examples of coupler residues of this type represented by J are the couplers described in U.S. Patents 4,052,213, 4,088,491, 3,632,345, 3,958,993 and 3,961,959.

In general formula (I), J preferably represents general formulae (XIV), (XV), (XVI), (XVII), (XVIII), (XIX), (XX), (XXI) and (XXII).

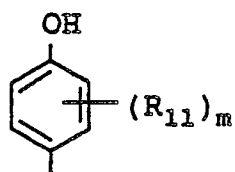




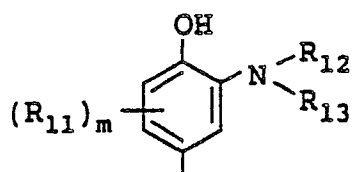
(XVII)



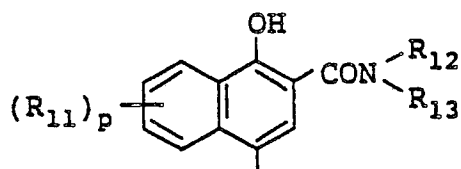
(XVIII)



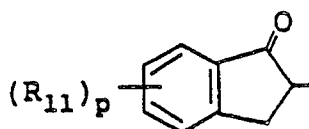
(XIX)



(XX)



(XXI)



(XXII)

In the formulae, R_5 represents an aliphatic hydrocarbon group, an aromatic hydrocarbon group, an alkoxy group, or a heterocyclic group, and R_6 and R_7 represent an aromatic hydrocarbon group, an aliphatic hydrocarbon group or a heterocyclic group.

The aliphatic hydrocarbon group represented by R_5 has 1 to 22 carbon atoms and is substituted or
 5 unsubstituted and linear or cyclic. Preferred substituents on the alkyl groups are alkoxy, aryloxy, amino, and acylamino groups and halogen atoms which themselves may be further substituted with these groups. Specific examples of useful aliphatic hydrocarbon groups R_5 , R_6 and R_7 are isopropyl, isobutyl, tert-butyl, isoamyl, tert-amyl, 1,1-dimethylbutyl, 1,1-dimethylhexyl, 1,1-diethylhexyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, 2-methoxyisopropyl, 2-phenoxyisopropyl, 2-p-tert-butylphenoxyisopropyl, α -aminoisopropyl, α -
 10 (diethylamino)isopropyl, α -(succinimido) isopropyl, α -(phthalimido)isopropyl, and α -(benzenesulfonamido)-isopropyl groups.

When R_5 , R_6 or R_7 represents an aromatic hydrocarbon group (particularly, a phenyl group), the aromatic hydrocarbon group may be substituted. The aromatic hydrocarbon group (e.g., phenyl) may be substituted by, for example, an alkyl, alkenyl, alkoxy, alkoxycarbonyl, alkoxycarbonylamino, aliphatic amido,
 15 alkylsulfamoyl, alkylsulfonamido, alkylureido or alkyl-substituted succinimido group having not more than 32 carbon atoms. The phenyl group may also be substituted by, for example, an aralkyl, aryloxy, aryloxycarbonyl, arylcarbamoyl, arylamido, arylsulfamoyl, arylsulfonamido or arylureido group. The aryl moiety of these substituents may further be substituted by at least one alkyl group having 1 to 22 carbon atoms in total.

20 The phenyl group represented by R_5 , R_6 and R_7 may further be substituted by an amino (which may be substituted by an alkyl group having 1 to 6 carbon atoms), hydroxyl, carboxyl, sulfo, nitro, cyano or thiocyno group or a halogen atom.

Furthermore, R_5 , R_6 and R_7 may represent a substituent resulting from fusion of the phenyl group with another ring, such as a naphthyl, quinolyl, isoquinolyl, chromanyl, coumaranyl or tetrahydronaphthyl group.
 25 These substituents may further be substituted with a substituent disclosed above as examples of substituents for the phenyl group.

When R_5 represents an alkoxy group, its alkyl moiety represents a C_1 to C_{40} , preferably C_1 to C_{22} , linear or branched alkyl group, an alkenyl group, a cycloalkyl group or a cycloalkenyl group, which may be substituted by, for example, a halogen atom, an aryl group or an alkoxy group.

30 When R_5 , R_6 or R_7 represents a heterocyclic group, the heterocyclic group is bonded to the nitrogen atom of the amido group or the carbon atom of the carbonyl group of the acyl group in the α -acylacetamido via one of the carbon atoms forming the ring. Examples of such heterocyclic rings are thiophene, furane, pyrane, pyrrole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, indolidine, imidazole, thiazole, oxazole, triazine, thiadiazine and oxazine rings. They may further be substituted with a substituent disclosed above
 35 as examples of the substituted aromatic hydrocarbon group.

In general formula (XVII), R_8 represents a linear or branched alkyl group having 1 to 40 carbon atoms, preferably 1 to 22 carbon atoms, (such as a methyl, isopropyl, tert-butyl, hexyl or dodecyl group), an alkenyl group (such as an allyl group), a cycloalkyl group (such as a cyclopentyl, cyclohexyl or norbornyl group), an aralkyl group (such as a benzyl or β -phenylethyl group), or a cycloalkenyl group (such as a
 40 cyclopentenyl or cyclohexenyl group), which may be substituted by, for example, a halogen atom, or a nitro, cyano, aryl, alkoxy, aryloxy, carboxyl, alkylthiocarbonyl, arylthiocarbonyl, alkoxycarbonyl, aryloxycarbonyl, sulfo, sulfamoyl, carbamoyl, acylamino, diacylamino, ureido, urethane, thiourethane, sulfonamido, heterocyclic, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio alkylamino, dialkylamino, anilino, N-arylanilino, N-alkylanilino, N-acylanilino, hydroxyl or mercapto group.

45 Furthermore, R_8 may represent an aryl group such as a phenyl or α - or β -naphthyl group. The aryl group may contain at least one substituent. Examples of the substituent include halogen atoms, and alkyl, alkenyl, cycloalkyl, aralkyl, cycloalkenyl, nitro, cyano, aryl, alkoxy, aryloxy, carboxyl, alkoxycarbonyl, aryloxycarbonyl, sulfo, sulfamoyl, carbamoyl, acylamino, diacylamino, ureido, urethane, sulfonamido, heterocyclic, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylamino, dialkylamino, anilino, N-alkylanilino, N-
 50 arylanilino, N-acylanilino, hydroxyl and mercapto groups. More preferred as R_8 is a phenyl group in which at least one ortho position is substituted by, for example, an alkyl group, an alkoxy group, or a halogen atom because it reduces coloration of the coupler remaining in the film under the action of light or heat.

R_8 may also represent a heterocyclic group, for example, a 5- or 6-membered heterocyclic or fused heterocyclic group containing at least one of nitrogen, oxygen and sulfur atoms as hetero atoms, such as a
 55 pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl or naphthoxazolyl group. A heterocyclic group substituted by the substituents listed above for the aryl group, or an aliphatic or aromatic acyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkylcarbamoyl group, an arylcarbamoyl group, an alkylthiocarbamoyl group or an arylthiocarbamoyl group.

In the formulae, R_8 represents a hydrogen atom, a C_1 to C_{40} , preferably C_1 to C_{22} , linear or branched alkyl or alkenyl, cycloalkyl, aralkyl or cycloalkenyl group (which may be substituted by the substituents listed above with regard to R_9), an aryl or heterocyclic group (which may have the substituents listed above with regard to R_9), an alkoxycarbonyl group (such as a methoxycarbonyl, ethoxycarbonyl or stearyloxycarbonyl group), an aryloxycarbonyl group (such as a phenoxycarbonyl or naphthoxycarbonyl group), an aralkyloxycarbonyl group (such as a benzyloxycarbonyl group), an alkoxy group (such as a methoxy, ethoxy or heptadecyloxy group), an aryloxy group (such as a phenoxy or tolyloxy group), an alkylthio group (such as an ethylthio or dodecylthio group), an arylthio group (such as a phenylthio or α -naphthyl group), a carboxyl group, an acylamino group (such as an acetylamino or 3-[(2,4-di-tert-amylphenoxy)acetamido]-benzamido group), a diacylamino group, an N-alkylacylamino group (such as an N-methylpropionamido group), an N-arylacylamino group (such as an N-phenylacetamido group), a ureido group (such as a ureido, N-aryluureido or N-alkylureido group), a urethane group, a thiourethane group, an arylamino group (such as a phenylamino, N-methylanilino, diphenylamino, N-acetylanilino or 2-chloro-5-tetradecaneanilino group), a dialkylamino group (such as a dibenzylamino group), an alkylamino group (such as an n-butylamino, methylamino or cyclohexylamino group), a cycloamino group (such as a piperidino or pyrrolidino group), a heterocyclic amino group (such as a 4-pyridylamino or 2-benzoxazolylamino group), an alkylcarbonyl group (such as a methylcarbonyl group), an arylcarbonyl group (such as a phenylcarbonyl group), a sulfonamido group (such as an alkylsulfonamido or arylsulfonamido group), a carbamoyl group (such as an ethylcarbamoyl, dimethylcarbamoyl, N-methylphenylcarbamoyl or N-phenylcarbamoyl group), a sulfamoyl group (such as an N-alkylsulfamoyl, N,N-dialkylsulfamoyl, N-arylsulfamoyl, N-alkyl-N-arylsulfamoyl or N,N-diaryl-sulfamoyl group), a cyano group, a hydroxyl group, a mercapto group, a halogen atom, or a sulfo group.

In the formulae, R_{10} represents a hydrogen atom, or a C_1 to C_{32} , preferably C_1 to C_{22} , linear or branched alkyl or alkenyl, cycloalkyl, aralkyl or cycloalkenyl group which may have the substituents listed above with regard to R_9 .

R_{10} may also represent an aryl or heterocyclic group which may have the substituents listed above with regard to R_9 .

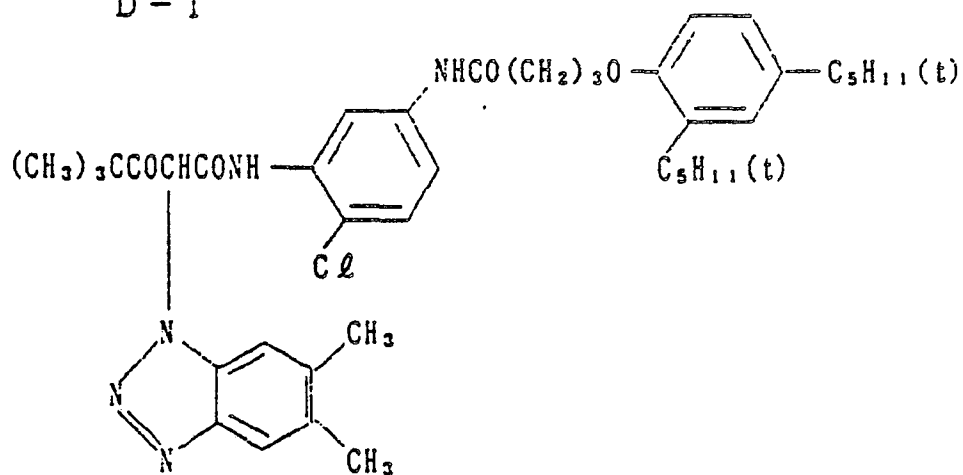
Furthermore, R_{10} may represent a halogen atom, or a cyano, alkoxy, aryloxy, carboxyl, alkoxycarbonyl, aryloxycarbonyl, acyloxy, sulfo, sulfamoyl, carbamoyl, acylamino, diacylamino, ureido, urethane, sulfonamido, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkyl amino, dialkylamino, anilino, N-arylanilino, N-alkylanilino, N-acetylanilino, hydroxyl or mercapto group.

Each of R_{11} , R_{12} and R_{13} represents groups which are used in ordinary 4-equivalent phenol or α -naphthol couplers. Specifically, R_{11} represents a halogen atom, an aliphatic hydrocarbon group, an acylamino group, $-O-R_{14}$ or $S-R_{14}$ (in which R_{14} represents an aliphatic hydrocarbon group). When two or more R_{11} groups exist in the same molecule, they may be different, and the aliphatic hydrocarbon group may be substituted. R_{12} and R_{13} may represent groups selected from aliphatic hydrocarbon groups, aryl groups and heterocyclic groups. Alternatively, one of them may be a hydrogen atom. These groups may have a substituent. Furthermore, taken together, R_{12} and R_{13} may form a nitrogen-containing heterocyclic ring. m is an integer of 0 to 4; n is an integer of 0 to 3; and p is an integer of 0 to 5. The aliphatic hydrocarbon groups may be saturated or unsaturated, and linear, branched or cyclic. Preferably, they are alkyl groups (such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, isobutyl, dodecyl, octadecyl, cyclobutyl and cyclohexyl groups) or alkenyl groups (such as allyl and octenyl groups). The aryl groups are phenyl and naphthyl groups. Typical examples of the heterocyclic group are pyridinyl, quinolyl, thienyl, piperidyl and imidazolyl groups. Substituents which may be introduced into the aliphatic hydrocarbon groups, aryl groups and heterocyclic groups include, for example, halogen atoms, and nitro, hydroxyl, carboxyl, amino, substituted amino sulfo, alkyl, alkenyl, aryl, heterocyclic (as listed above with regard to R_{12} and R_{13}), alkoxy, aryloxy, arylthio, arylazo, acylamino, carbamoyl, ester, acyl, acyloxy, sulfonamide, sulfamoyl, alkyl or aryl sulfonyl and morpholino groups.

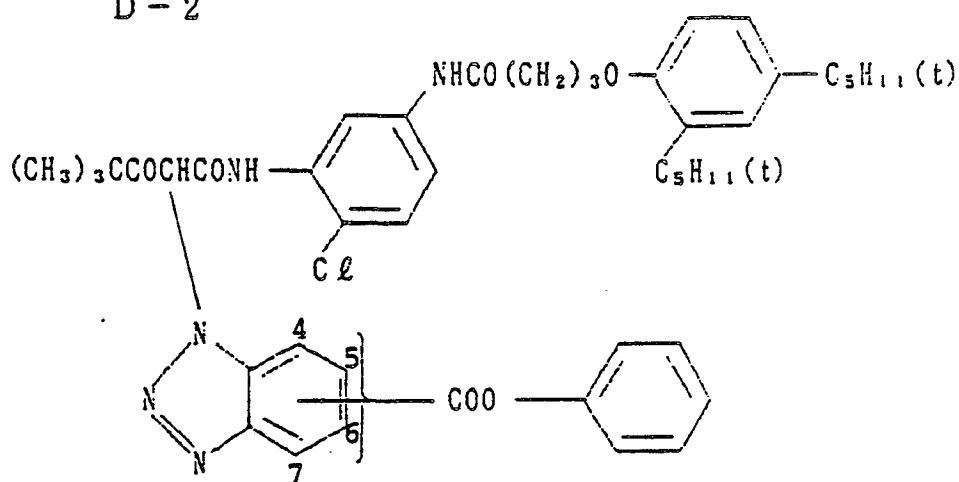
The substituents R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} , R_{11} , R_{12} and R_{13} of the couplers represented by general formulae (XIV) to (XXII) may be bonded to each other, or any of them becomes a divalent group to form symmetric or asymmetric compound couplers.

Examples of preferred diffusible DIR compounds used in this invention are shown below.

D - 1

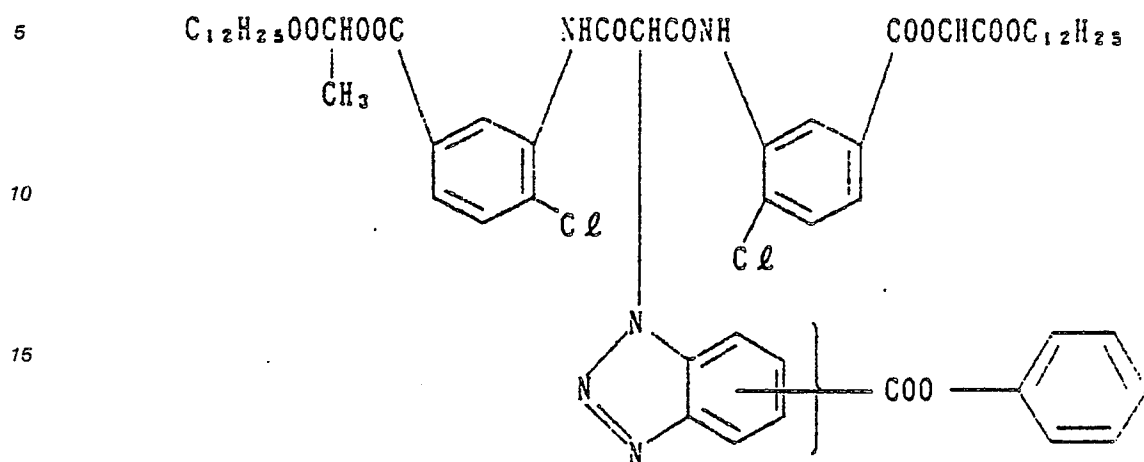


D - 2

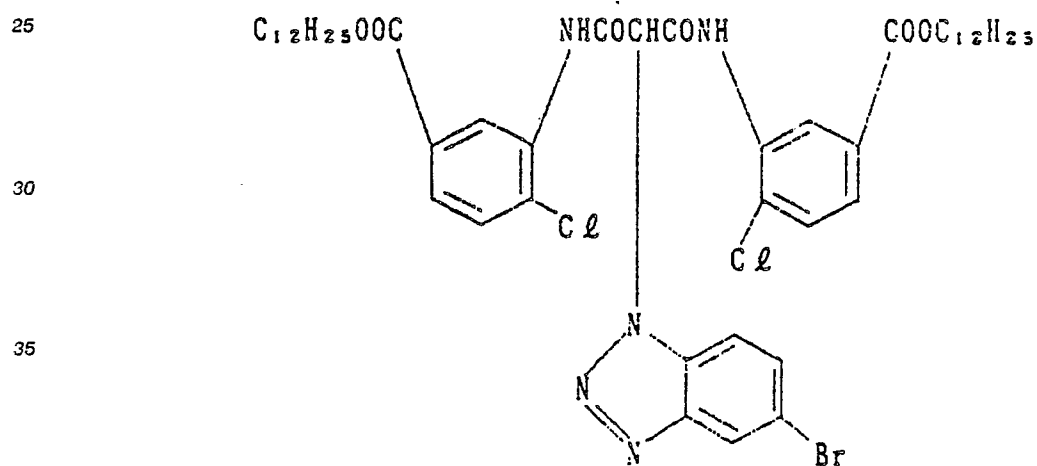


(a compound substituted at
4-, 5-, 6- or 7- position
or a mixture thereof:
the same hereinafter)

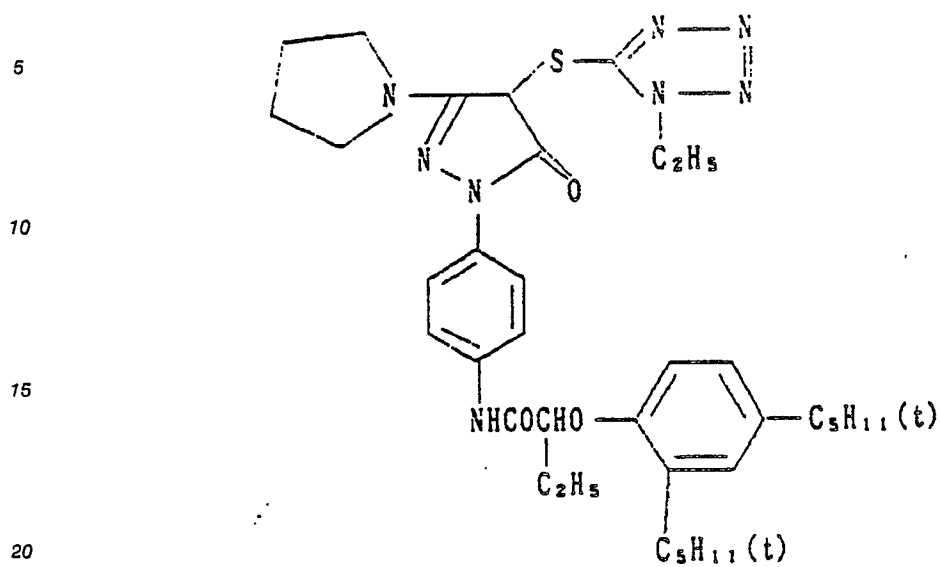
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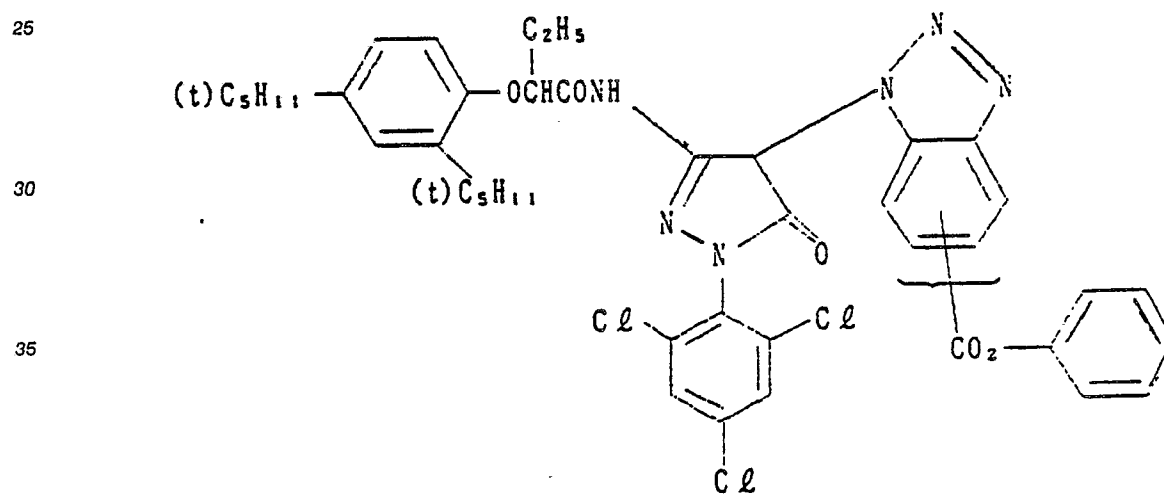
D - 4



D - 5



D - 6



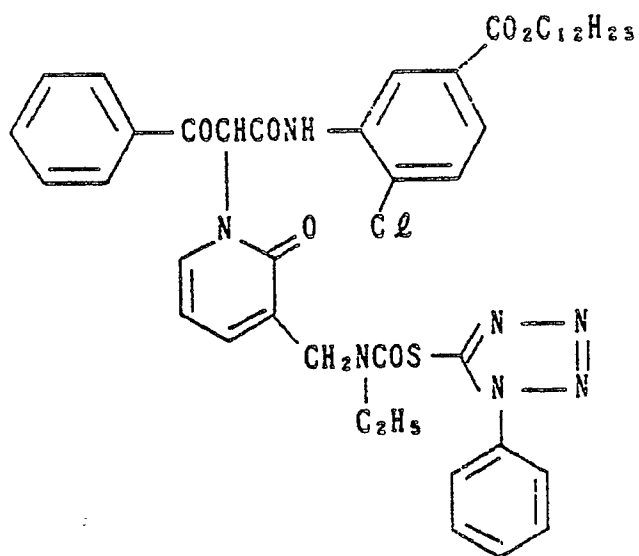
D - 7

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D - 8

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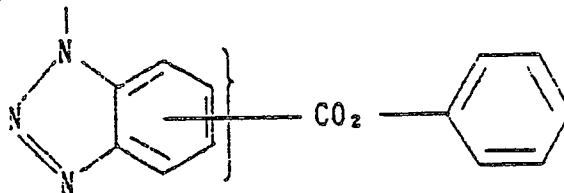
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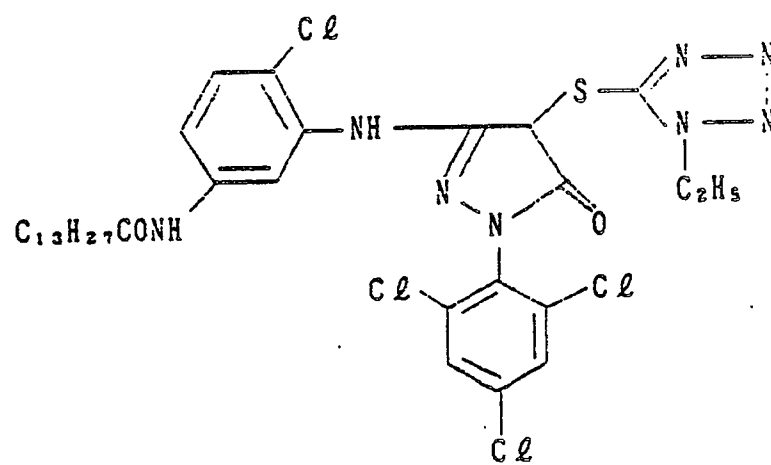
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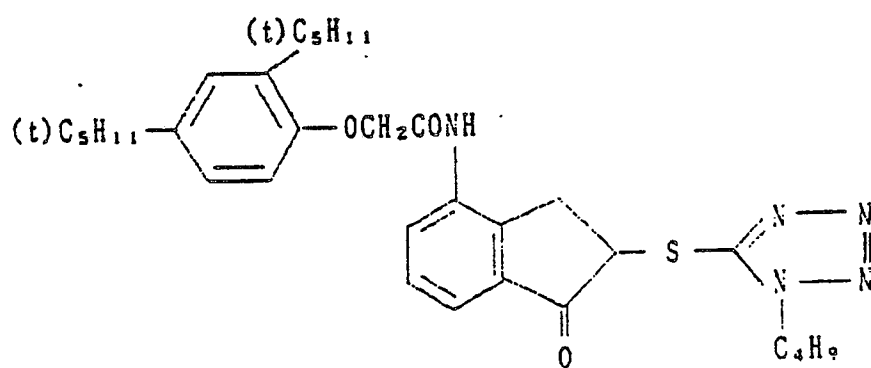
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C₁₂H₂₅OOCC₁₂H₂₅

D - 9

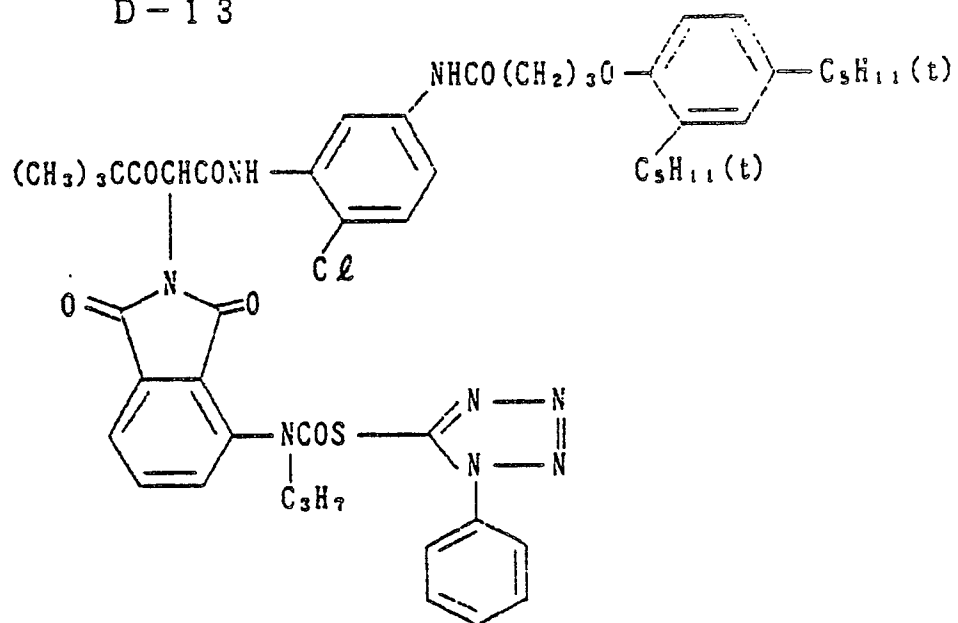


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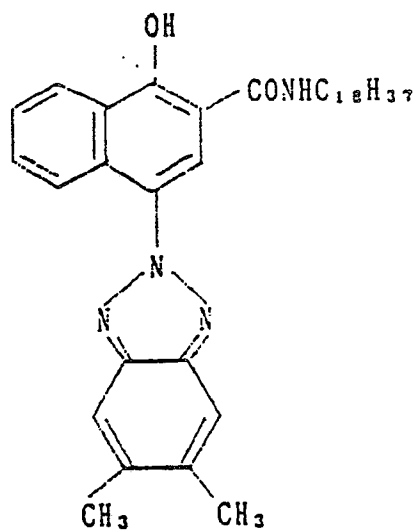




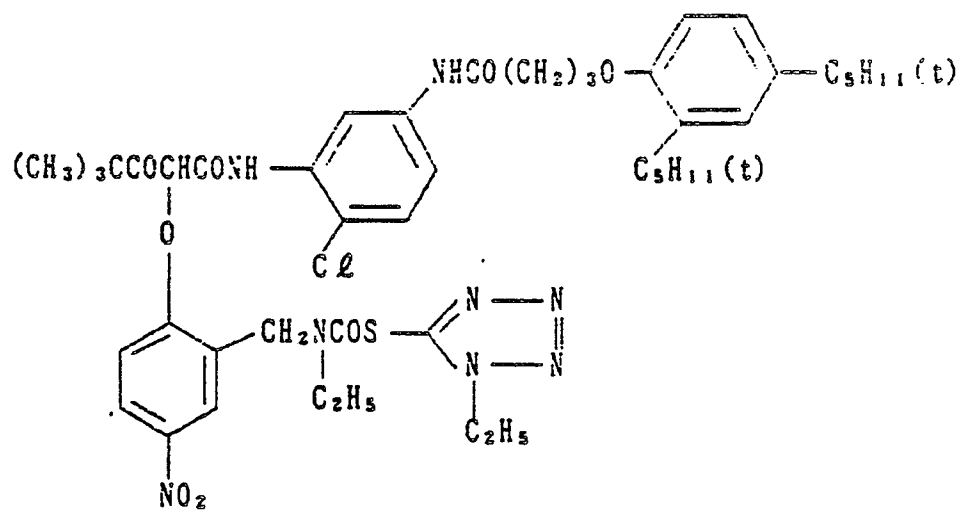
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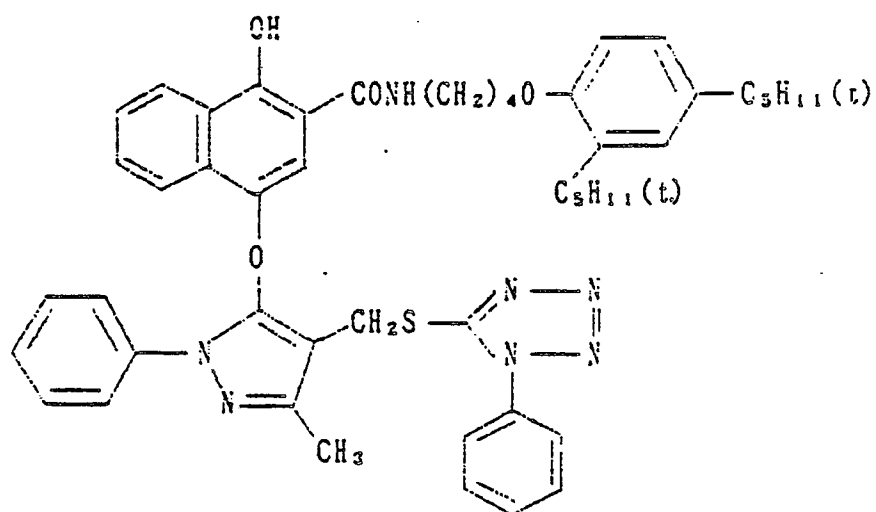
D - 1 4



D - 1 5



D - 1 6



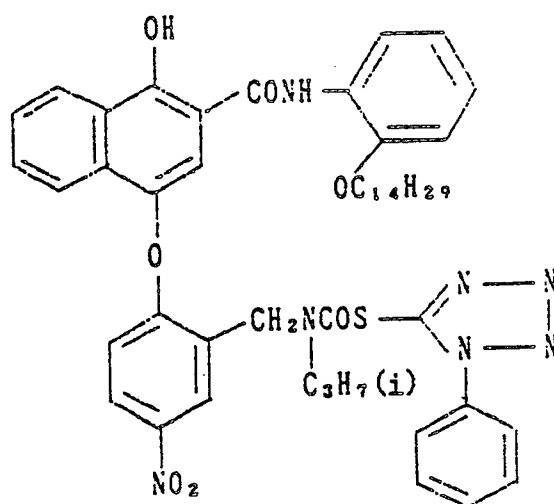
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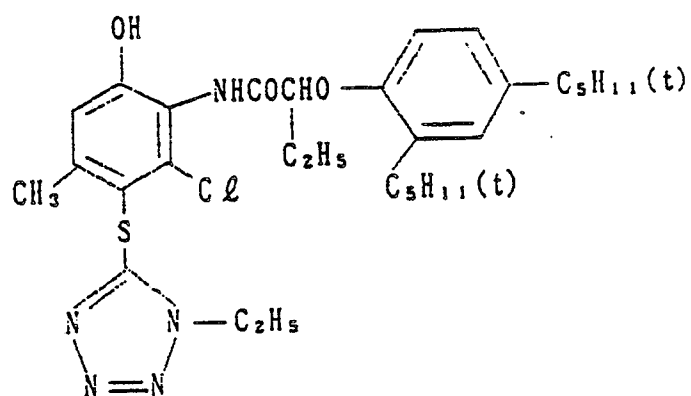
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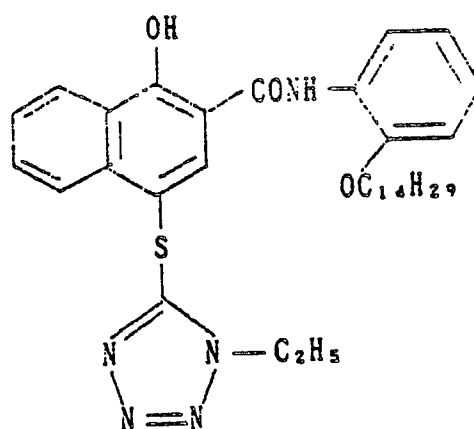
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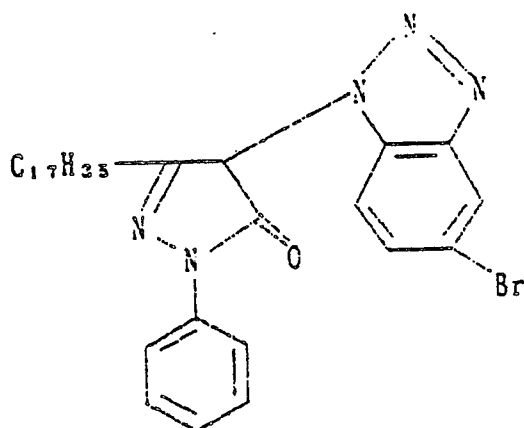
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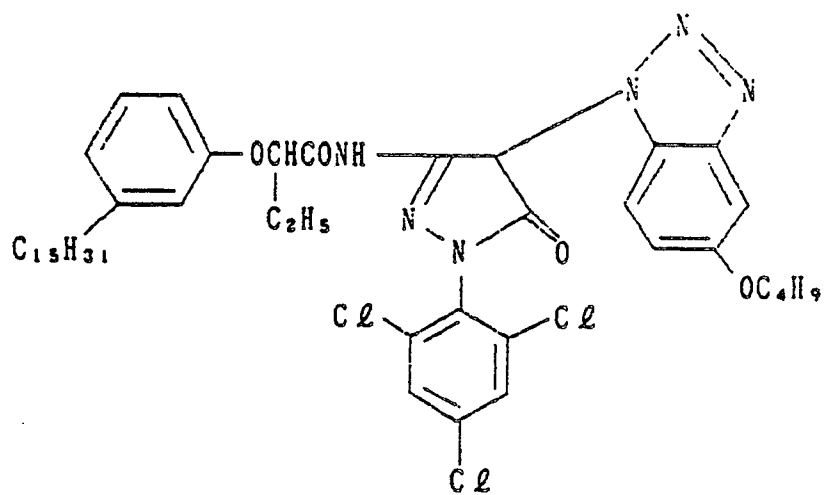
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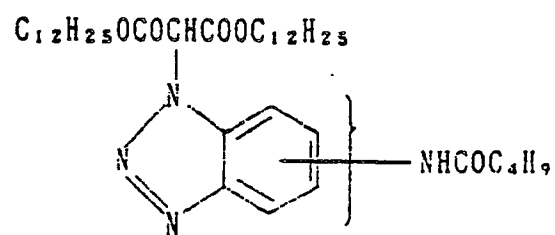
D - 2 0



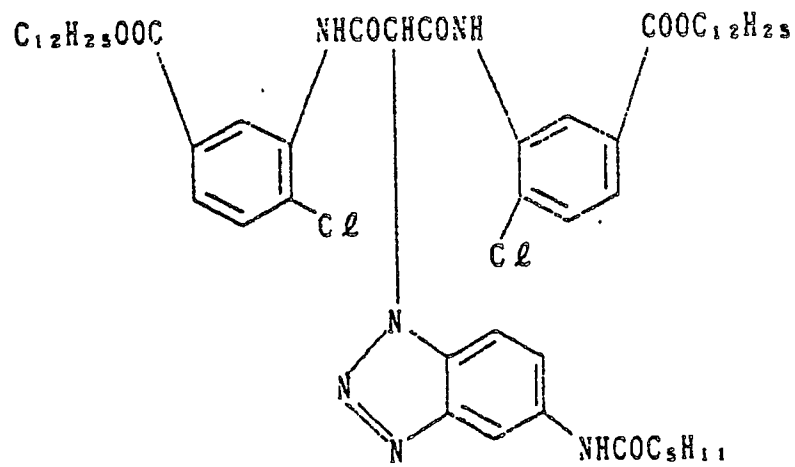
D - 2 1



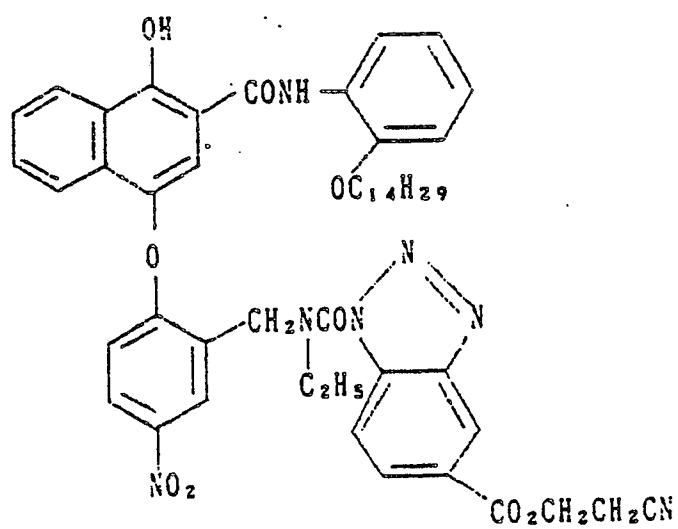
D - 2 2



D - 2 3



D - 2 4



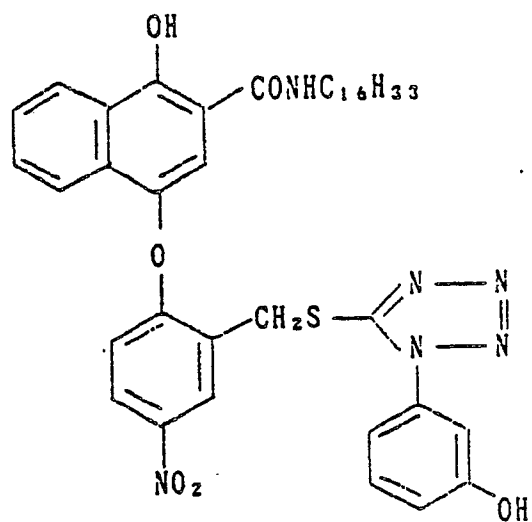
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D - 2 6

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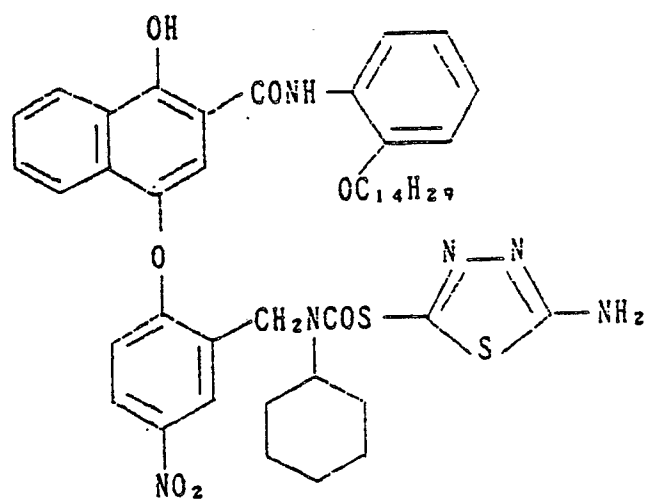
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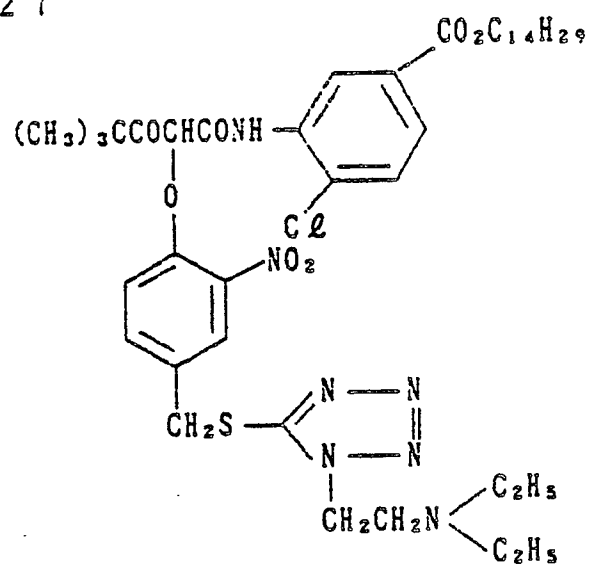
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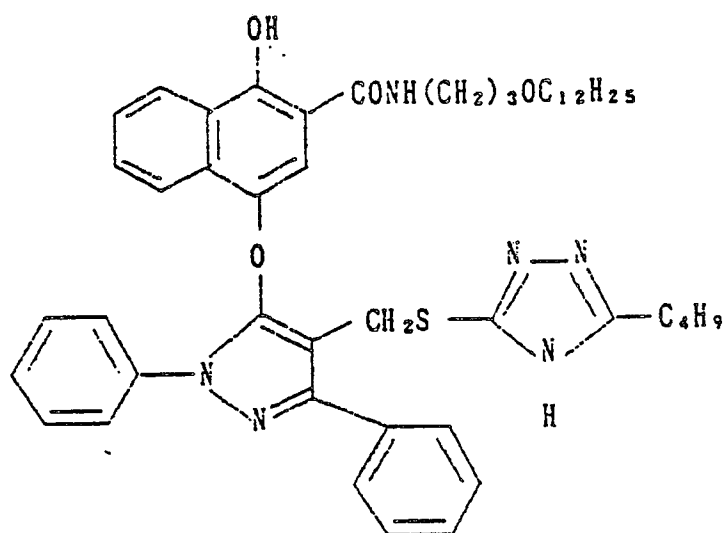
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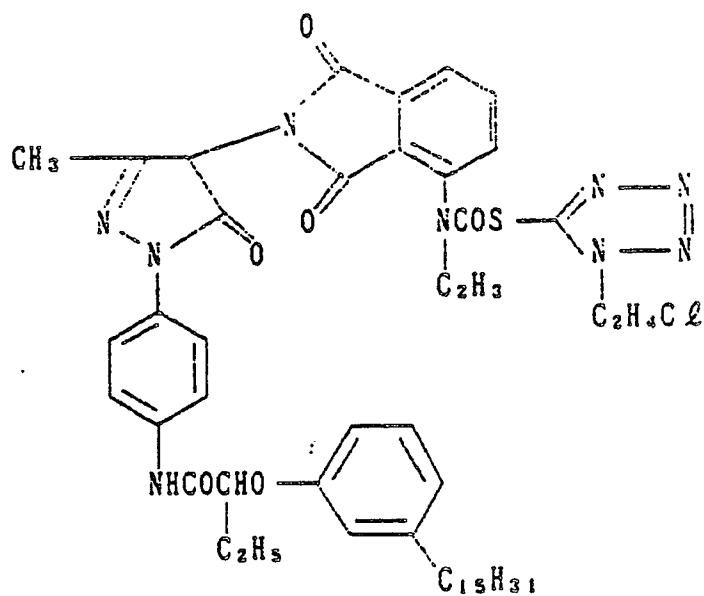
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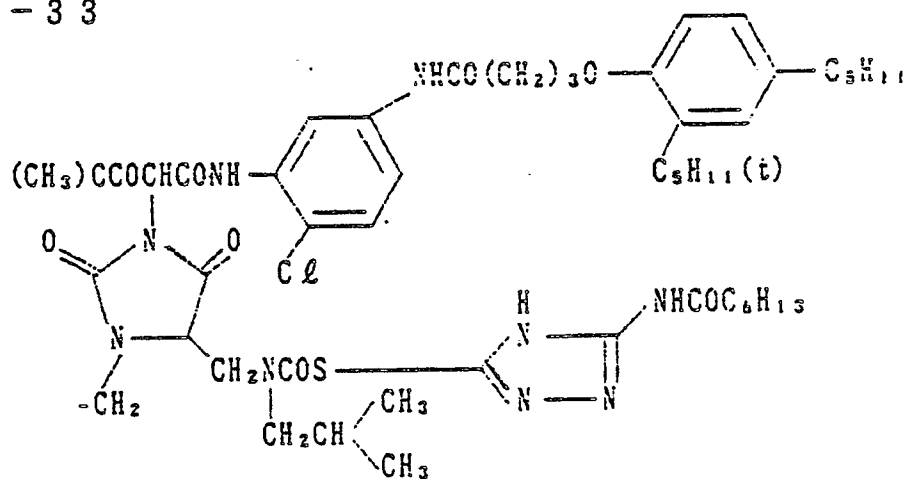
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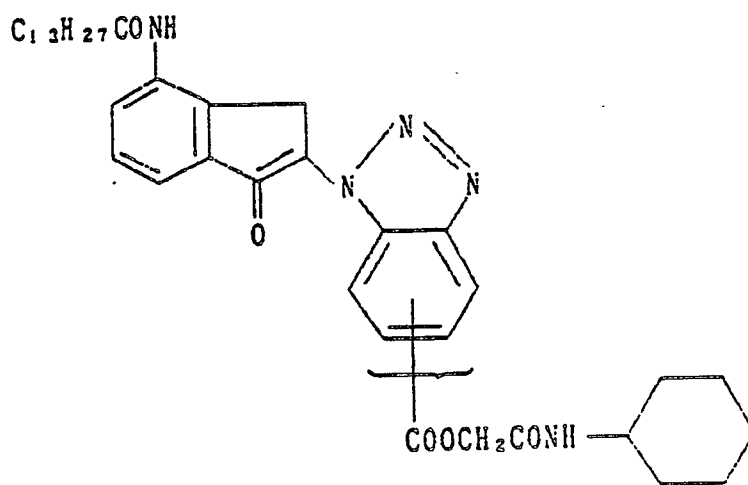
D - 3 2



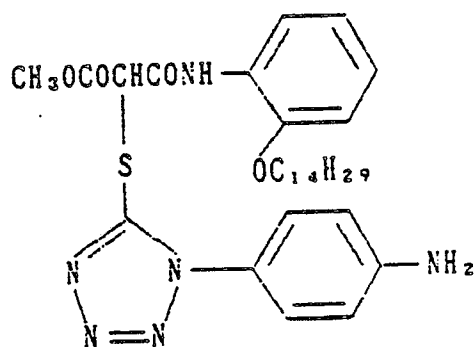
D - 3 3

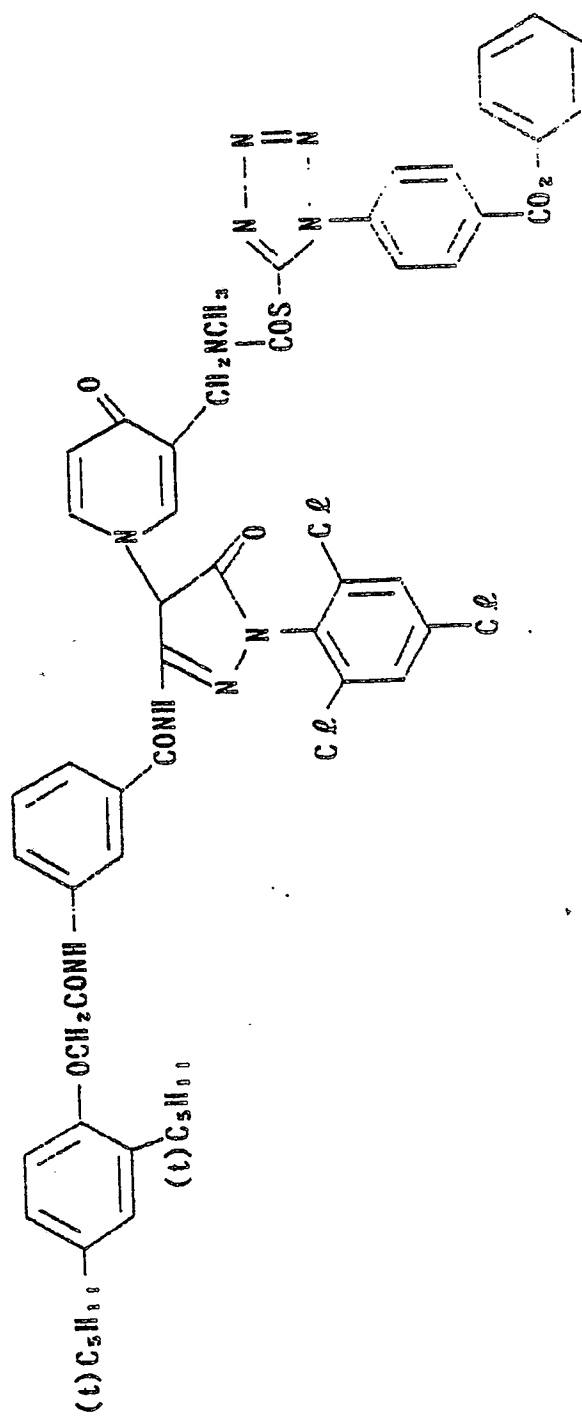


D - 3 4

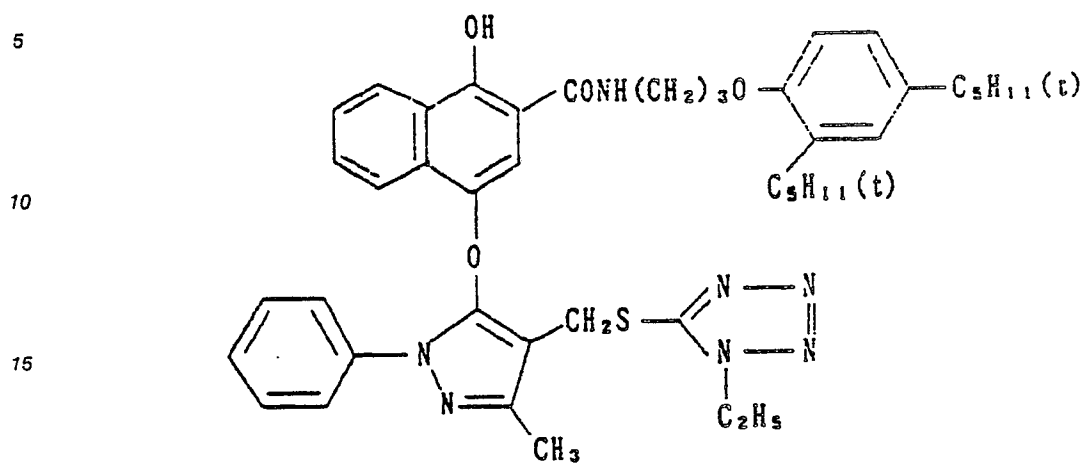


D - 3 5

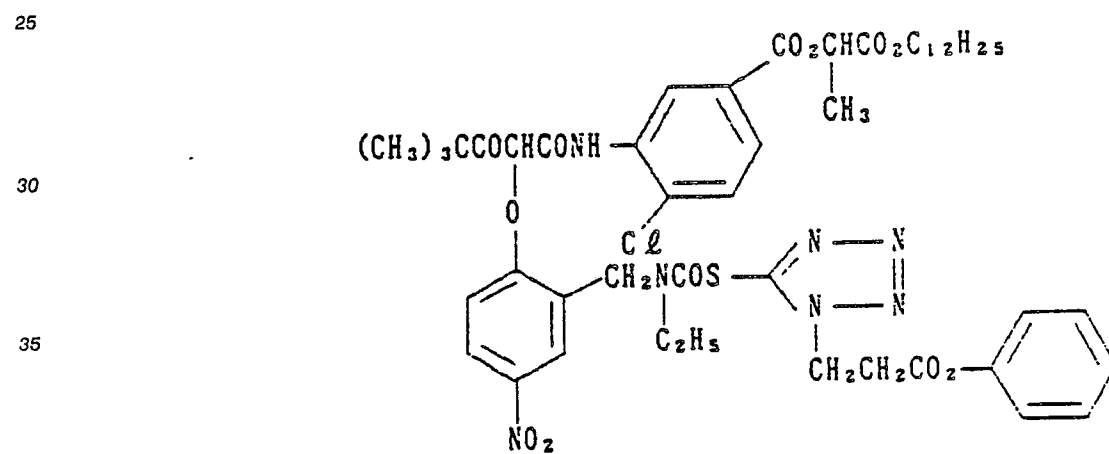




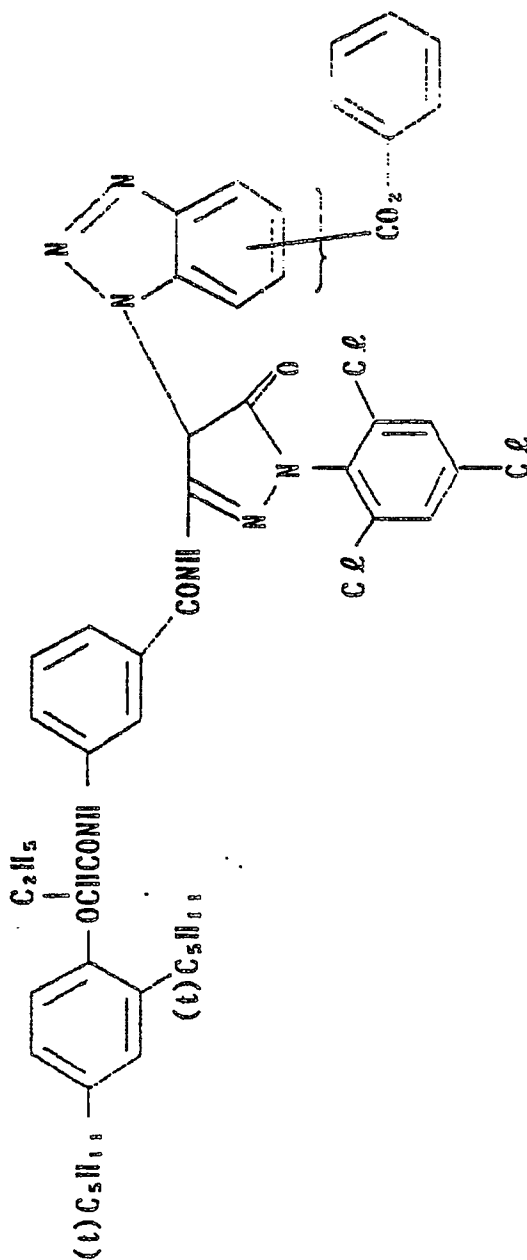
D - 3 7



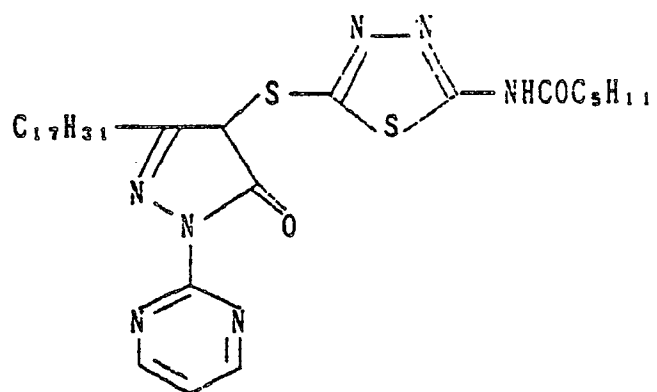
D - 3 8



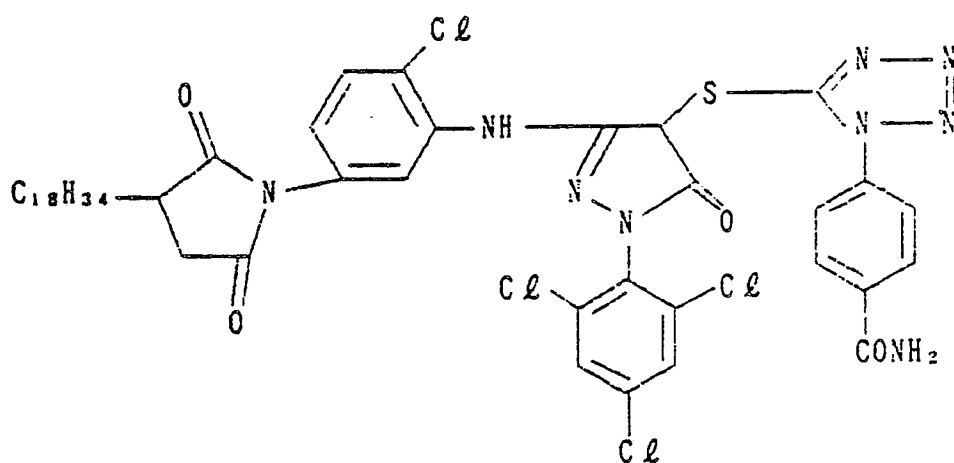
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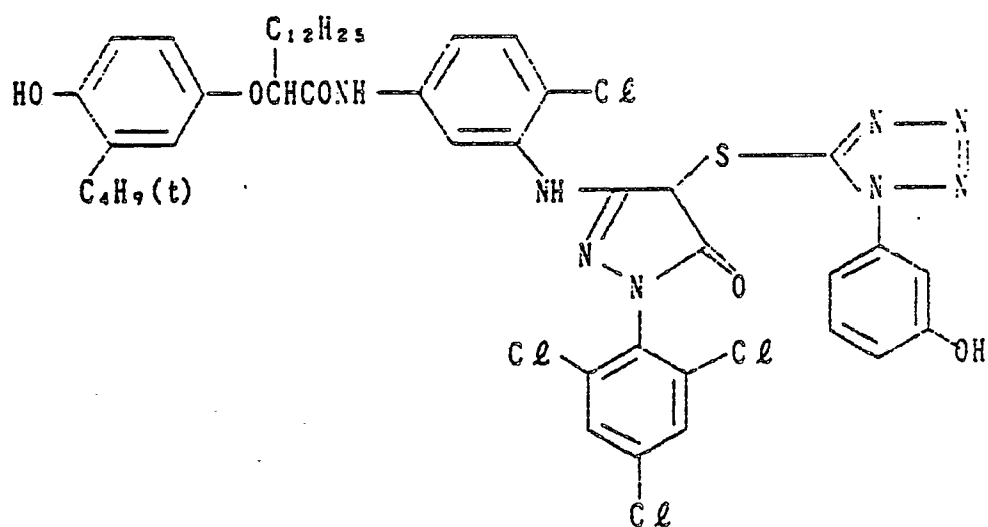
D - 4 0



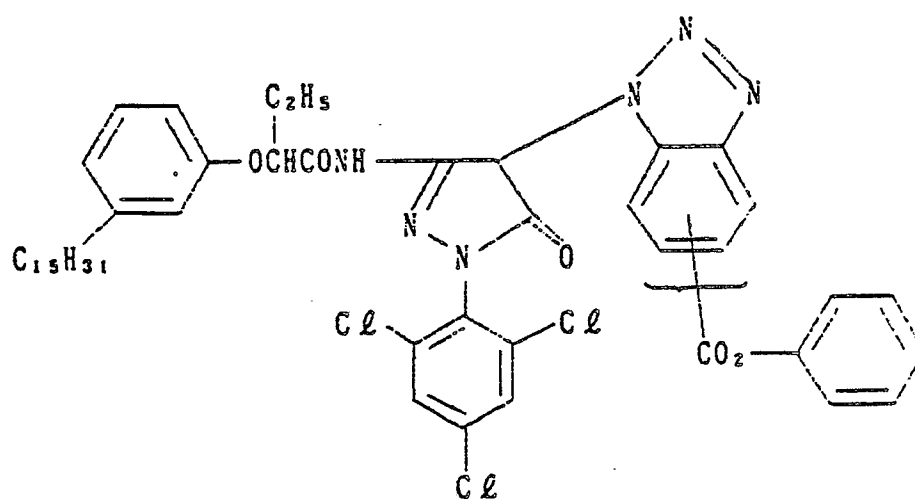
D - 4 1



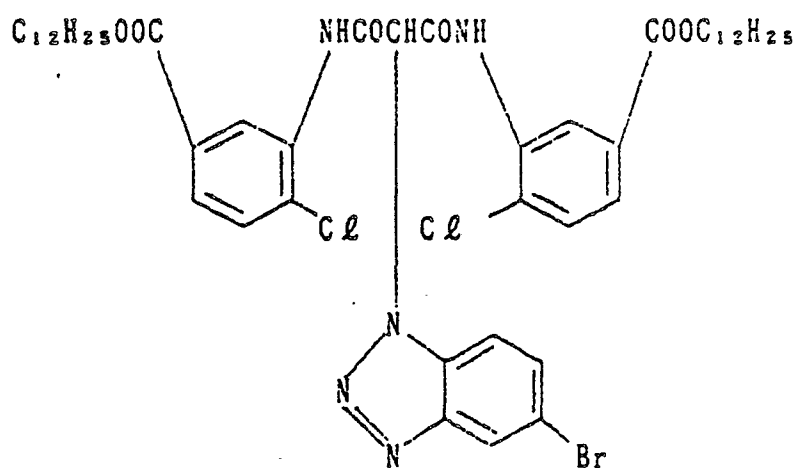
D - 4 2



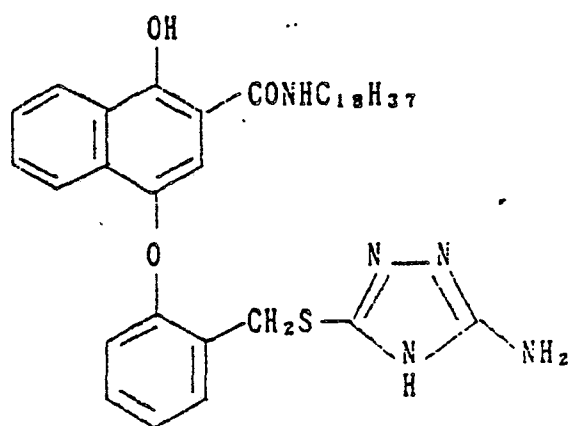
D - 4 3



D - 4 4

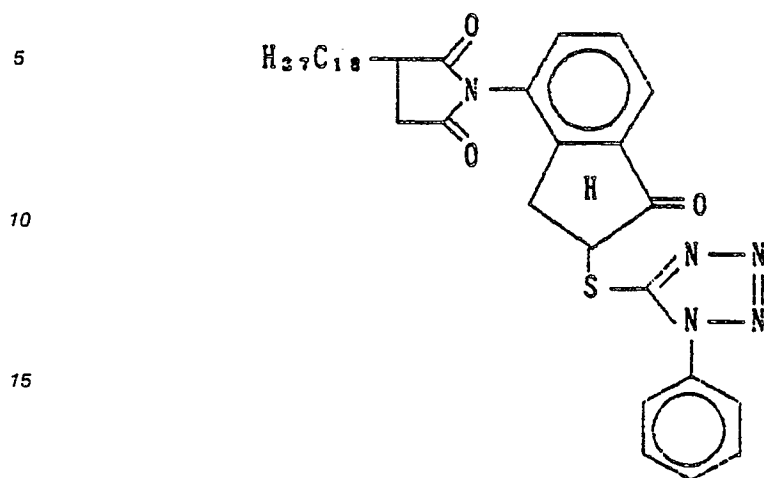


D - 4 5

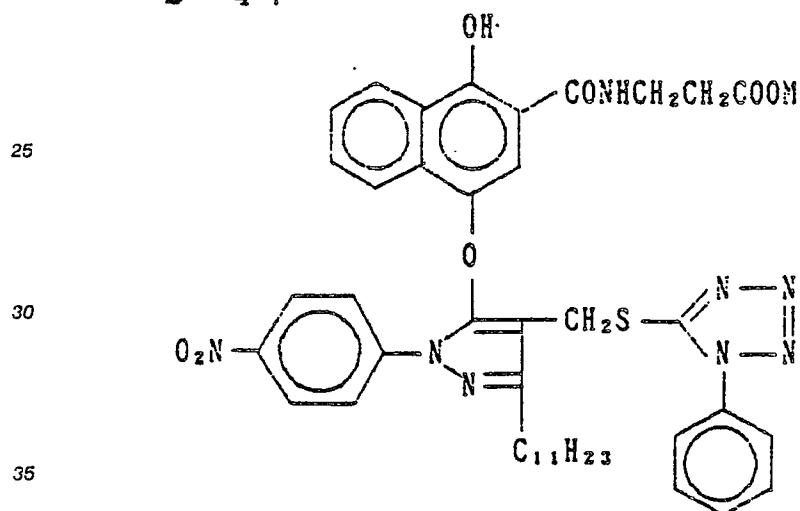


Examples of preferred timing DIR compounds used in this invention are shown below.

D - 4 6



20 D - 4 7



(M: an alkali
metal atom such
as Na and K or
NH₄)

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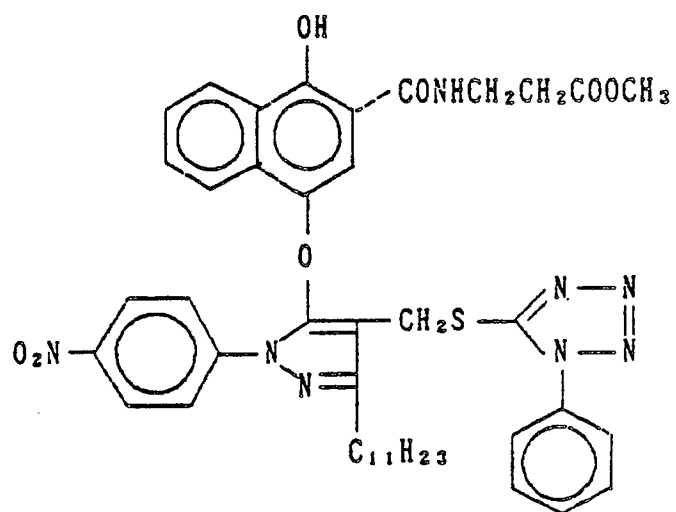
D - 4 8

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D - 4 9

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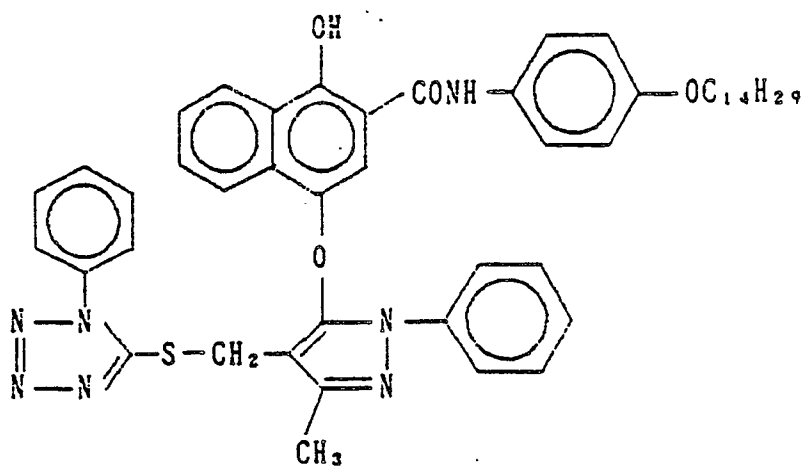
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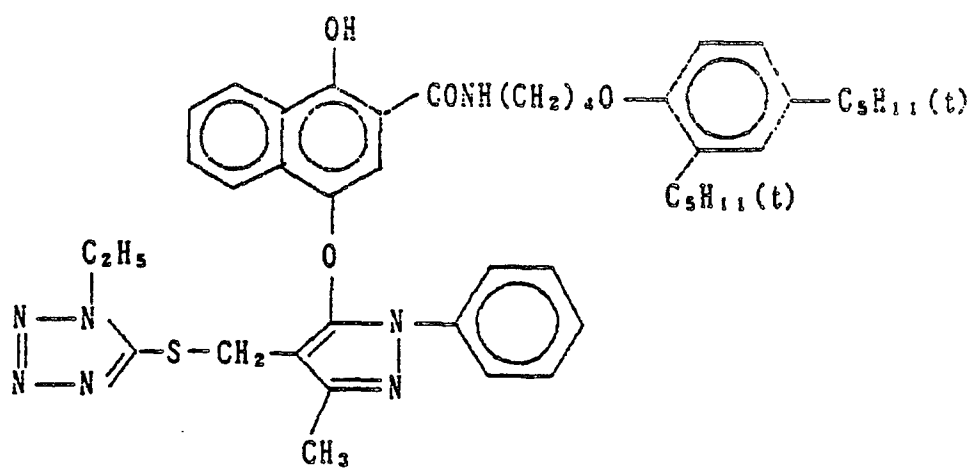
D - 5 0

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D - 5 1

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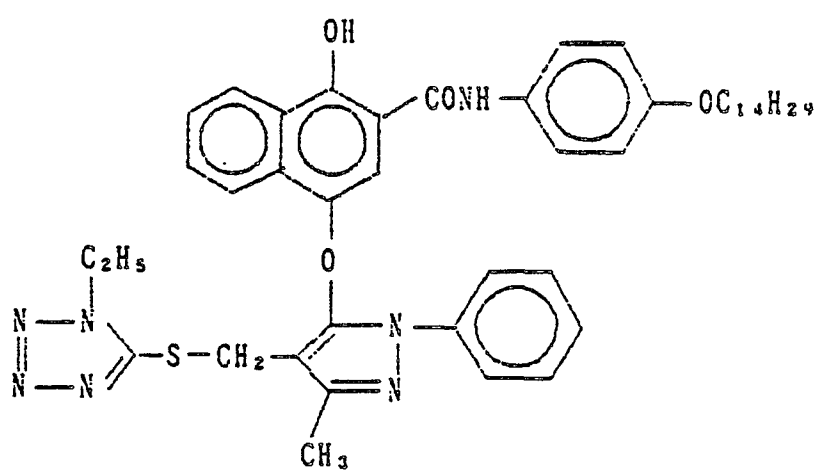
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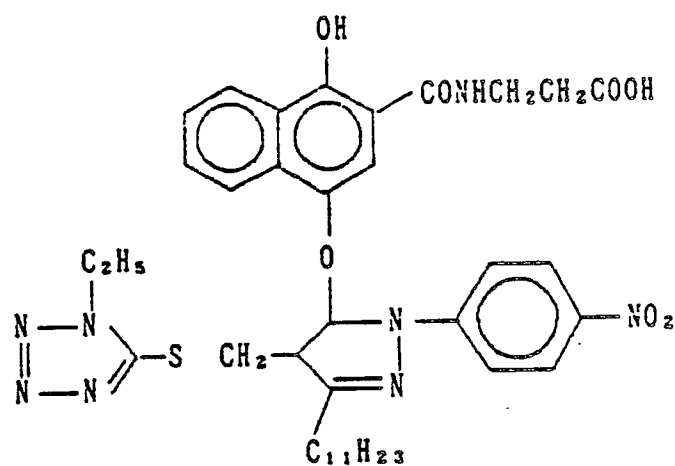
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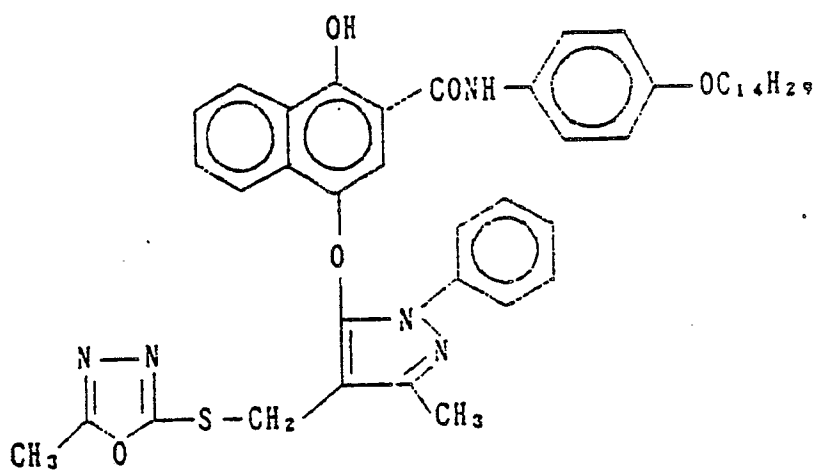
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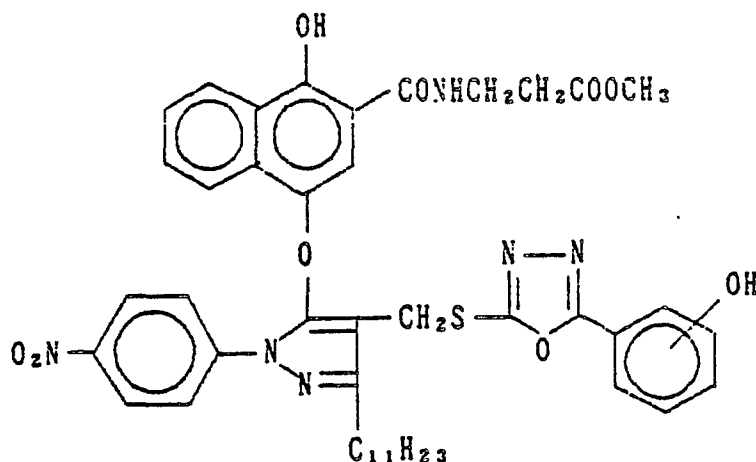


D - 5 2



D - 5 3





The coupler may be introduced into a silver halide emulsion layer by a known method, for example, the method described in U.S. Patent 2,322,027. The coupler is dissolved in, for example, an alkyl phthalate (e.g., dibutyl or dioctyl phthalate), a phosphate (e.g., diphenyl, triphenyl, tricresyl or dioctylbutyl phosphate), a citrate (e.g., tributyl acetyl citrate), a benzoate (e.g., octyl benzoate), an alkylamide (e.g., diethyl-laurylamide), a fatty acid ester (e.g., dibutoxyethyl succinate or dioctyl azelate), a trimesate (e.g., tributyl trimesate), or an organic solvent having a boiling point of about 30 to 150° C such as a lower alkyl acetate (e.g., ethyl or butyl acetate), ethyl propionate, sec-butyl alcohol, methyl isobutyl ketone, β -ethoxyethyl acetate or methyl cellosolve acetate; and then dispersed in a hydrophilic colloid. A mixture of the above-described high-boiling solvent and low-boiling organic solvent may also be used. There can also be used the dispersing methods using polymers as described in JP-B-51-39853 ("JP-B" herein means an "examined Japanese patent publication") and JP-A-51-59943.

The high-boiling organic solvent is described, for example, in U.S. Patents 2,322,027, 2,533,514 and 2,835,579, JP-B-46-23233, U.S. Patent 3,287,134, British Patent 958,414, JP-A 47 1031, British Patent 1,222,753, U.S. Patent 3,936,303, JP A-51-26037 and JP-50-82078, U.S. Patents 2,353,262, 2,852,383, 3,554,755, 3,676,137, 3,676,142, 3,700,454, 3,748,141 and 3,837,863, German OLS 2,538,889, JP-A-51-27921, JP-A-51-27922, JP-A-51-26035, JP-A-26036 and JP-A-50-62632, JP-B-49-29461, U.S. Patents 3,936,303 and 3,748,141, and JP-A-53-1521.

The silver halide grains in the photographic emulsions may be so-called regular grains having regular crystals such as cubic, octahedral and tetradecahedral crystals, or have irregular crystal shapes such as a spherical shape or crystal defects such as a twinning plane, or may be combinations of these various types. As stated hereinabove, they preferably have excellent granularity. It is preferred to use grains of a double or a multiple structure having high quantum sensitivity, or tabular grains having a high color sensitization ratio.

The silver halide photographic emulsions that can be used in this invention can be produced by known methods, for example, the methods disclosed in Research Disclosure (RD), No. 17643 (December 1978), pages 22-23, "I. Emulsion Preparation and Types", and ibid. No. 18716 (November 1979), page 648.

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P. Glafkides, Chimie et Physique Photographique, Paul Montel, 1967, G.F. Duffin, Photographic Emulsion Chemistry (Focal Press, 1966), and V.L. Zelikman et al., Making and Coating Photographic Emulsion, Focal Press, 1964. Namely, any of the acid method, neutral method and ammonia method may be used. The mode of reacting a soluble silver salt with a soluble halogen salt may be a single jet method, a double jet method, or a combination of these. There can also be used a method in which grains are formed in the presence of an excess of a silver ion (the so-called reverse mixing method). As one example of the double jet method, a controlled double jet method may be used in which pAg in the liquid phase where silver halide is formed is maintained constant. This method gives a silver halide emulsion having a regular crystal shape and a nearly uniform grain size.

Two or more silver halide emulsions separately formed may be used as a mixture.

The silver halide emulsion composed of regular grains may be obtained by controlling pAg and pH during grain formation. Details of this method are described, for example, in Photographic Science and Engineering, vol. 6, page 159 to 165 (1962), Journal of Photographic Science, vol. 12, pages 242 to 251 (1964), U.S. Patent 3,655,394, and British Patent 1,413,748.

A typical monodisperse emulsion contains silver halide grains having an average grain diameter of more than about 0.1 micron, and at least about 95% by weight of which have a size within $\pm 40\%$ of the average grain diameter. In the present invention, an emulsion in which the silver halide grains have an average grain diameter of about 0.25 to 2 microns, and at least 95% by weight, or at least 95% by number, of the silver halide grains have a grain size within $\pm 20\%$ of the average grain diameter may be used. The methods of preparing such an emulsion are described in U.S. Patents 3,574,628 and 3,655,394 and British Patent 1,413,748. The monodisperse emulsions described in JP-A-48-8600, JP-A-51-39027, JP-A-51-83097, JP-A-53-137133, JP-A-54-48521, JP-A-54-99419, JP-A-58-37635 and JP-A-58-49938 can be used preferably in the present invention.

Tabular grains having an aspect ratio of at least about 5 may also be used in this invention. The tabular grains can be easily prepared by the methods described in Gutoff, Photographic Science and Engineering, vol. 14, pages 248 to 257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520, and British Patent 2,112,157. U.S. Patent 4,434,226 cited above states in detail that the use of tabular particles has the advantage of increasing the efficiency of color sensitization with sensitizing dyes and enhancing the granularity of the grains and the sharpness of images.

Emulsion grains having a uniform crystal structure but different halogen compositions between the interior and the exterior may also be used. Or emulsions having a layered structure may also be used. These emulsion grains are disclosed, for example, in British Patent 1,027,146, U.S. Patents 3,505,068 and 4,444,877 and JP A-60-143331. Silver halide grains in which silver halides of different compositions are conjugated by epitaxial conjugation may also be used. Or they may be conjugated with compounds other than silver halide, such as silver rhodanate and lead oxide. These emulsion grains are disclosed, for example, in U.S. Patents 4,094,634, 4,142,900 and 4,459,353, British Patent 2,038,792, U.S. Patents 4,349,622, 4,395,478, 4,433,501, 4,463,087, 3,656,962 and 3,852,067, and JP-A-58-162540.

A mixture of grains having various crystal shapes may be used.

The emulsions to be used in this invention usually undergo physical ripening, chemical ripening and spectral sensitization. Additives used in these steps are described in Research Disclosure, Nos. 17643 and 18716, and the pertinent portions are tabulated below.

Known photographic additives that can be used in this invention are also described in the above-cited two Research Disclosure publications and the pertinent portions are tabulated below.

	Additive	RD17643	RD18716
	1. chemical sensitizer	p. 23	p. 638, right column
	2. sensitivity enhancer		ditto
5	3. spectral sensitizer	pp. 23-24	p. 648, right column to
	supersensitizer		p. 649, right column
	4. bleaching agent	p. 24	
	5. antifoggant and	pp. 24-25	p. 649, right column
	stabilizer		
10	6. light absorber, filter	pp. 25-26	p. 649, right column to
	dye, and ultraviolet		p. 650, left column
	absorber		
	7. stain preventing agent	p. 25, right	p. 650, left to right
		column	column
15	8. dye image stabilizer	p. 25	
	9. hardener	p. 26	p. 651, left column
	10. binder	p. 26	ditto
	11. plasticizer and	p.27	p. 650, right column
	lubricant		
20	12. coating aid and	pp. 26-27	ditto
	surface active agent		
	13. antistatic agent	p. 27	ditto

25 Various color couplers can be used in this invention. Specific examples are described in the patents described in the above-cited Research Disclosure, No. 17643, VII-C to G. Important dye-forming couplers give three primary colors of the subtractive process (i.e., yellow, magenta and cyan). Specific examples of nondiffusion 4-equivalent or 2-equivalent couplers are those described in the patents described in the above-cited RD 17643, VII-C and D and the following couplers can also be preferably used in this invention.

30 Typical examples of the yellow coupler that can be used in this invention are hydrophobic acylacetamide- type couplers having a ballast group, specific examples of which are given, for example, in U.S. Patents 2,407,210, 2,875,057 and 3,265,506. The use of 2-equivalent yellow couplers is preferred in this invention. Typical examples are the oxygen atom-releasing type yellow couplers described in U.S. Patents 3,408,194, 3,447,928, 3,933,501 and 4,022,620, and the nitrogen atom-releasing type yellow couplers described in JP-B-58-10739, and U.S. Patents 4,401,752 and 4,326,024, RD 18053 (April 1979),
35 British Patent 1,425,020, and West German OLS Nos. 2,219,917, 2,261,361, 2,329,587 and 2,433,812. α -Pivaloyl acetanilide-type couplers give dyes having excellent fastness characteristics, particularly light fastness. α -Benzoyl acetanilide type couplers can give a high color density.

Examples of the magenta couplers that can be used in this invention are hydrophobic and ballast group-having couplers of the indazolone and cyanoacetyl types, preferably of the 5-pyrazolone and
40 pyrazoloazole types. 5-pyrazolone-type couplers are those in which the 3 position is substituted by an arylamino group or an acylamino group are preferred from the viewpoint of the color hue of the developed dye and its density. Typical examples are described, for example, in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896 and 3,936,015. The nitrogen atom releasing groups described in U.S. Patent 4,310,619 and the arylthio groups described in U.S. Patent 4,351,897 are especially preferred
45 as the releasing groups of 2-equivalent 5-pyrazolone-type couplers. The 5-pyrazolone-type couplers having a ballast group which are described in European Patent 73,636 can give high color development densities. Examples of pyrazoloazole-type couplers include the pyrazolobenzimidazoles described in U.S. Patent 3,061,432, preferably the pyrazolo[5,1-c][1,2,4]triazoles described in U.S. patent 3,725,087, pyrazolotetrazoles described in Research Disclosure, 24220 (June 1984) and JP-A-60-33552, and the
50 pyrazolopyrazoles described in Research Disclosure, 24230 (June 1984) and JP-A-60-43659. In view of the less yellow subsidiary absorptions of formed dyes and lightfastness, the imidazo[1,2-b]pyrazoles described in U.S. Patent 4,500,630 are preferred, and the pyrazolo[1,5-b][1,2,4]triazole described in U.S. Patent 4,540,654 is especially preferred.

55 Hydrophobic nondiffusible naphthol type and phenol type couplers may be used as the cyan couplers in this invention. Typical examples of the naphthol-type cyan couplers are the naphthol-type couplers described in U.S. Patent 2,474,293, preferably the oxygen atom releasing type 2-equivalent naphthol-type couplers described in U.S. Patents 4,052,212, 4,146,396, 4,228,233 and 4,296,200. Specific examples of the phenolic couplers are described, for example, in U.S. Patents 2,369,929, 2,801,171, 2,772,162 and

2,895,826. Couplers capable of forming cyan dye which is fast to humidity and temperature can be preferably used in this invention. Typical examples include the phenolic cyan couplers having an alkyl group with at least 2 carbon atoms at the meta-position of the phenol ring, the 2,5-diacylamino-substituted phenolic couplers described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011 and 4,327,173, West German OLS 3,329,729, and European Patent 121,365, and the phenolic couplers having a phenylureido group at the 2-position and an acylamino group at the 5-position described in U.S. Patents 3,446,622, 4,333,999, 4,451,559 and 4,427,767. Cyan couplers having a sulfonamide group, an amide group, etc. substituted at the 5-position of naphthol, which are described in European Patent 161,626A gives a colored image of excellent fastness, and can be preferably used in this invention.

In order to correct unwanted absorptions of the formed dye, it is preferred to mask the coupler in the color light-sensitive material for photographing by using a colored coupler in combination. The yellow-colored magenta couplers described in U.S. Patent 4,163,670 and JP-B-57-39413 and the magenta-colored cyan couplers described in U.S. Patents 4,004,929 and 4,138,258 and British Patent 1,146,368 may be cited as typical examples of such couplers. Other colored couplers are described in the above-cited RD 17643, VII to G. There can also be cited compounds having a group capable of being coordinated with a metal and forming a color, as a releasing group described in U.S. Patents 4,555,477 and 4,555,478. Unlike the colored couplers, these couplers are colorless before coupling with the oxidation product of a developing agent. But after development, the exposed area assumes the color of the dye formed by coupling as the released metal ligand is washed out. In the unexposed area, the metal ligand fixed to the coupler is coordinated with a metal ion such as Fe (II) in the processing liquor to form a color. As a result, the decrease of sensitivity due to the filter effect of the colored coupler is reduced, and the above couplers can be favorably used in this invention. A photographic material containing the above coupler may be processed in an ordinary development processings, or in a separate processing step in a specific bath containing a metal ion. Examples of the metal ion are Fe (II), Co (II), Cu (I), Cu (II) and Ru (II). Fe (II) is preferably used.

Granularity may be improved by using a coupler which gives a dye having moderate diffusibility in combination with the above-described couplers. Specific examples of such a coupler are described in U.S. Patent 4,366,237 and British Patent 2,125,570 (magenta couplers), and European Patent 96,570 and West German OLS 3,234,533 (yellow, magenta and cyan couplers).

The dye-forming couplers and the special couplers described above may form dimers or higher polymers. Typical examples of polymerized dye-forming couplers are described in U.S. Patents 3,451,820 and 4,080,211. Typical examples of polymerized magenta couplers are described in British Patent 2,102,173 and U.S. Patent 4,367,282. Couplers which release photographically useful residues during coupling may favorably be used in this invention. Useful DIR couplers which release development inhibitors are described in the patents disclosed in the above-cited RD 17643, VII to F.

Examples of preferred couplers used in combination with this invention are the developer solution deactivating type couplers typically described in JP-A- 57-151944, the timing-type couplers typically described in U.S. Patent 4,248,962 and JP-A-57-154234, and the reactive type couplers typically described in JP-A-59-39653. Especially preferred are the developer solution deactivating type DIR couplers described in JP-A-57-151944 and JP-A-58-217932, and JP-A-60-218644, JP-A-60-225156, and JP-A-60-233650, and the reactive-type DIR couplers described in JP-A-60-184248.

In the photographic material, a coupler which releases a nucleating agent or a development accelerator or a precursor thereof imagewise during development may be used. Specific examples of such a compound are described in British Patents 2,097,140 and 2,131,188. Couplers which releases a nucleating agent, etc. having adsorptive action on silver halide are especially preferred, and specific examples thereof are described, for example, in JP-A-59-157638 and JP-A-59-170840.

In the present invention, red sensitive layer, a green-sensitive layer and a blue-sensitive layer may be provided on a support in any order, however, it is preferably provided in this order (i.e., B/G/R/support). When a color sensitive layer is divided in two layers, the slow speed layer is provided prior to providing the fast speed layer (e.g., B/G_f/R_f/G_s/R_s// support: wherein f means fast speed and s means slow speed).

In the present invention the combination of each coupler and color sensitivity of the emulsion layer containing the coupler is also optional, however, from the view point of proper printing characteristics to color paper, it is preferable that a cyan coupler is incorporated into a red-sensitive layer, a magenta coupler is incorporated into a green-sensitive layer and a yellow coupler is incorporated into a blue-sensitive layer.

Supports which can be suitably used in this invention are described, for example, in the above-cited RD No. 17643, page 28, and *ibid.* No. 18716, page 647, right column to page 648, left column.

The color photographic material in accordance with this invention can be developed by ordinary methods described, for example, in the above-cited RD No. 17643, pages 28 to 29 and No. 18716, page 651, left column to right column.

The color photographic material of this invention is subjected to an ordinary rinsing treatment or stabilizing treatment after development, bleach-fixing or fixing.

Generally, the rinsing step is carried out by providing two or more tanks in a countercurrent manner, and thus saving rinsing water. A typical example of the stabilization treatment is a multistage countercurrent stabilization treatment as described in JP-A-57-8543 to be carried out in place of the rinsing step. This step requires 2 to 9 countercurrent baths. Various compounds are added to the stabilizing bath in order to stabilize the image. Typical examples of the additives include various buffers for adjusting the film pH (for example, pH 3 to 8) (e.g., borates, metaborates, borax, phosphates, carbonates, potassium hydroxide, sodium hydroxide, aqueous ammonia, monocarboxylic acids, dicarboxylic acids and polycarboxylic acids used in combination), and formalin. As required, hard water softening agents (e.g., inorganic phosphoric acid, aminopolycarboxylic acids, organic phosphoric acid, aminopolyphosphonic acid and phosphonocarboxylic acid), fungicides (e.g., benzointhiazolinone, isothiazolone, 4-thiazolinebenzimidazole and a halogenated phenol), surface active agents, fluorescent bleaching agents, and hardeners may also be used. Two or more of such additives having the same or different purposes may be used in combination.

It is also preferred to add various ammonium salts such as ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium phosphate, ammonium sulfite and ammonium thiosulfate as a film pH adjusting agent after processing.

The present invention can be applied to various color light-sensitive materials for photographing, typically general or motion-picture color negative films, and slide or television color reversal films.

The following examples clarify the effects of this invention. It should be understood, however, that the scope of the invention are not limited to these examples. It is particularly noted that the same effect can be obtained even in a photographic material of an ordinary layer construction corresponding to the photographic material in the examples which does not have the 11th layer (a toner layer to a red-sensitive layer) and contains large amounts of the DIR compounds in the 6th, 7th and 8th green-sensitive layers.

EXAMPLE

A multilayer color photographic material composed of layers of the following compositions on an undercoated cellulose triacetate film support was prepared as Sample 101.

Composition of the photographic layers

The amounts of silver halide and colloid silver are expressed by g/m² as silver. The amounts of the couplers, additives and gelatin are expressed by g/m². The amount of each sensitizing dye is expressed by moles per mole of silver halide in the same layer. The symbols showing the additives have the following meanings. Where an additive has two more utilities, only one of them is indicated as a representative.

UV: ultraviolet absorber
Solv: high-boiling organic solvent
ExF: dye
ExS: sensitizing dye
ExC: cyan coupler
ExM: magenta coupler
ExY: yellow coupler
Cpd: additive

First layer (antihalation layer)

	Black colloidal silver	0.15
5	Gelatin	2.9
	UV-1	0.03
	UV-2	0.06
10	UV-3	0.07
	Solv-2	0.08
15	ExF-1	0.01
	ExF-2	0.01
20		

Second layer (low-sensitivity red-sensitive emulsion layer)

25	Silver iodobromide emulsion (AgI 4 mol%; uniform type; sphere equivalent diameter 0.4 μ ; variation coefficient of the sphere equivalent diameter 37%; tabular grains; diameter/thickness ratio 3.0)	0.4
	Gelatin	0.8
35	ExS-1	2.3×10^{-4}
	ExS-2	1.4×10^{-4}
40	ExS-5	2.3×10^{-4}
	ExS-7	8.0×10^{-6}
	ExC-1	0.17
45	ExC-2	0.03
	ExC-3	0.13

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Third layer (medium-sensitivity red-sensitive emulsion layer)

5	Silver iodobromide emulsion	0.65
	(AgI 6 mol%; high internal AgI type	
	with a core-shell ratio of 2:1	
	(molar ratio of AgX: the same	
	hereinafter); sphere equivalent	
10	diameter 0.65 μ ; variation	
	coefficient of the sphere	
	equivalent diameter 25%; tabular	
	grains; diameter/thickness ratio 2.0)	
15	Silver iodobromide emulsion	0.1
	(AgI 4 mol%; uniform AgI type;	
	sphere equivalent diameter 0.4 μ ;	
	variation coefficient of the sphere	
	equivalent diameter 37%; tabular	
20	grains; diameter/thickness ratio 3.0)	
	Gelatin	1.0
25	ExS-1	2×10^{-4}
	ExS-2	1.2×10^{-4}
30	ExS-5	2×10^{-4}
	ExS-7	7×10^{-6}
	ExC-1	0.31
35	ExC-2	0.01
	ExC-3	0.06

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Fourth layer (high-sensitivity red-sensitive emulsion layer)

5	Silver iodobromide emulsion	0.9
	(AgI 6 mol%; high internal AgI type with a core-shell ratio of 2:1; sphere equivalent diameter 0.7 μ ; variation coefficient of the sphere equivalent diameter 25%; tabular grains; diameter/thickness ratio 2.5)	
10	Gelatin	0.8
15	ExS-1	1.6×10^{-4}
	ExS-2	1.6×10^{-4}
	ExS-5	1.6×10^{-4}
20	ExS-7	6×10^{-4}
	ExC-1	0.07
25	ExC-4	0.05
	Solv-1	0.07
	Solv-2	0.20
30	Cpd-7	4.6×10^{-4}

35 Fifth layer (interlayer)

	Gelatin	0.6
40	UV-4	0.03
	UV-5	0.04
	Cpd-1	0.1
45	Polyethylacrylate latex	0.08
		(solid content)
	Solv-1	0.05

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Sixth layer (low-sensitivity green-sensitive emulsion layer)

5	Silver iodobromide emulsion (AgI 4 mol%; uniform type; sphere equivalent diameter 0.4 μ ; the variation coefficient of the sphere equivalent diameter 37%; tabular grains; diameter/thickness ratio 2.0)	0.18
10	Gelatin	0.4
	ExS-3	2×10^{-4}
15	ExS-4	7×10^{-4}
	ExS-5	1×10^{-4}
20	ExM-5	0.11
	ExM-7	0.03
	ExY-8	0.01
25	Solv-1	0.09
	Solv-4	0.01

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Seventh layer (medium-sensitivity green-sensitive emulsion layer)

5	Silver iodobromide emulsion (AgI 4 mol%; high surface AgI type with a core-shell ratio of 1:1; sphere equivalent diameter 0.5 μ ; variation coefficient of the sphere equivalent diameter 25%; tabular grains; diameter/thickness ratio 4.0)	0.27
10	Gelatin	0.6
15	ExS-3	2×10^{-4}
	ExS-4	7×10^{-4}
	ExS-5	1×10^{-4}
20	ExM-5	0.17
	ExM-7	0.04
25	ExY-8	0.02
	Solv-1	0.14
	Solv-4	0.02

30

Eighth layer (high-sensitivity green-sensitive emulsion layer)

35	Silver iodobromide emulsion (AgI 8.7 mol%; grains of a multi- layerstructure with a silver amount ratio of 3:4:2 (from the center); AgI content 24, 0 and 3 mol% from the interior; sphere equivalent diameter 0.7 μ ; variation coefficient of the sphere equivalent diameter 25%; tabular grains; diameter/thickness ratio 1.6)	0.7
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	Gelatin	0.8
	ExS-4	5.2×10^{-4}
50	ExS-5	1×10^{-4}

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	ExS-8	0.3×10 ⁻⁴
	ExM-5	0.1
5	ExM-6	0.03
	ExY-8	0.02
	ExC-1	0.02
10	ExC-4	0.01
	Solv-1	0.25
15	Solv-2	0.06
	Solv-4	0.01
20	Cpd-7	1×10 ⁻⁴

Ninth layer (interlayer)

25	Gelatin	0.6
	Cpd-1	0.04
30	Polyethylacrylate latex	0.12 (solid content)
	Solv-1	0.02

Tenth layer (interlayer effect donor layer for the red-sensitive layer)

40	Silver iodobromide emulsion (AgI 6 mol%; high internal AgI type with a core-shell ratio of 2:1; sphere equivalent diameter 0.7 μ; variation coefficient of the sphere equivalent diameter 18%; monodisperse 45 tabular grains; diameter/thickness ratio 2.0)	0.68
50	Silver iodobromide emulsion (AgI 4 mol%; uniform type; sphere equivalent diameter 0.3 μ; variation coefficient of the sphere equivalent diameter 37%; tabular grains; 55 diameter/thickness ratio 3.0)	0.19

	Gelatin	1.0
	ExS-3	6×10^{-4}
5	ExM-10	0.19
	Solv-1	0.20
10	<u>Eleventh layer (yellow filter layer)</u>	
	Yellow colloidal silver	0.06
15	Gelatin	0.8
	Cpd-2	0.13
20	Solv-1	0.13
	Cpd-1	0.07
	Cpd-6	0.002
25	H-1	0.13
30	<u>Twelfth layer (low-sensitivity blue-sensitive layer)</u>	
	Silver iodobromide emulsion (AgI 4.5 mol%; uniform AgI type; sphere equivalent diameter 0.7 μ ; variation coefficient of the sphere equivalent diameter 25%; tabular grains; diameter/thickness ratio 7.0)	0.3
35		
40	Silver iodobromide emulsion (AgI 3 mol%; uniform AgI type; sphere equivalent diameter 0.3 μ ; variation coefficient of the sphere equivalent diameter 30%; tabular grains; diameter/thickness ratio 7.0)	0.15
45		
	Gelatin	1.8
	ExS-6	9×10^{-4}
50	ExC-1	0.06
	ExC-4	0.03
55	ExY-9	0.14

ExY-11	0.89
Solv-1	0.42

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Thirteenth layer (interlayer)

Gelatin	0.7
ExY-12	0.20
Solv-1	0.34

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Fourteenth layer (high-sensitivity blue-sensitive emulsion layer)

Silver iodobromide emulsion (AgI 10 mol%; high internal AgI type; sphere equivalent diameter 1.0 μ ; variation coefficient of the sphere equivalent diameter 25%; multiple twinning tabular crystals; diameter/thickness ratio 2.0)	0.5
Gelatin	0.5
ExS-6	1×10^{-4}
ExY-9	0.01
ExY-11	0.20
ExC-1	0.02
Solv-1	0.10

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Fifteenth layer (first protective layer)

Fine grain silver iodobromide emulsion (AgI 2 mol%; uniform AgI type; sphere equivalent diameter 0.07 μ)	0.12
Gelatin	0.9
UV-4	0.11
UV-5	0.16
Solv-5	0.02

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	H-1	0.13
	Cpd-5	0.10
5	Polyethylacrylate latex	0.09
		(solid content)

10 Sixteenth layer (second protective layer)

	Fine grain silver iodobromide emulsion (AgI 2 mol%; uniform AgI type; sphere equivalent diameter 0.7 μ)	0.36
15	Gelatin	0.55
	Polymethylmethacrylate particles (diameter 1.5 μ)	0.2
20	H-1	0.17

25 In addition to the above components, a stabilizer for the emulsion, Cpd-3 (0.07 g/m²), and a surface active agent, Cpd-4 (0.03 g/m²), were added to each of the layers as coating aids.

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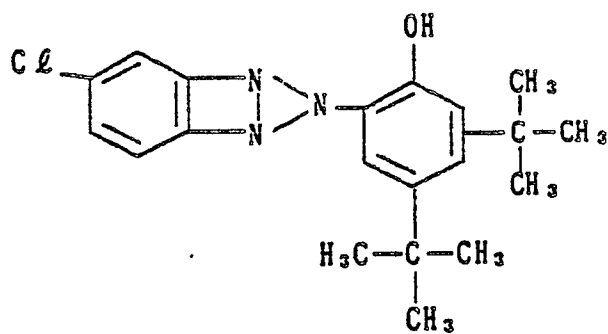
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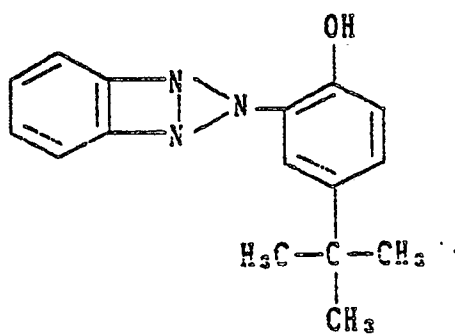
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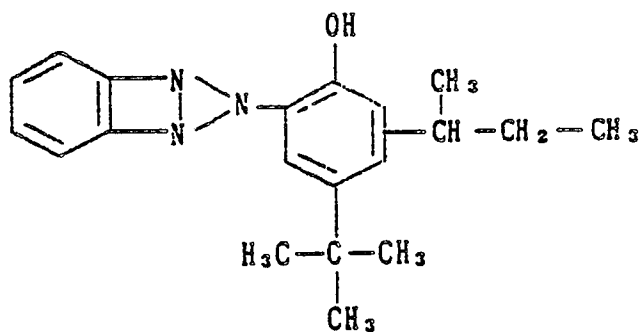
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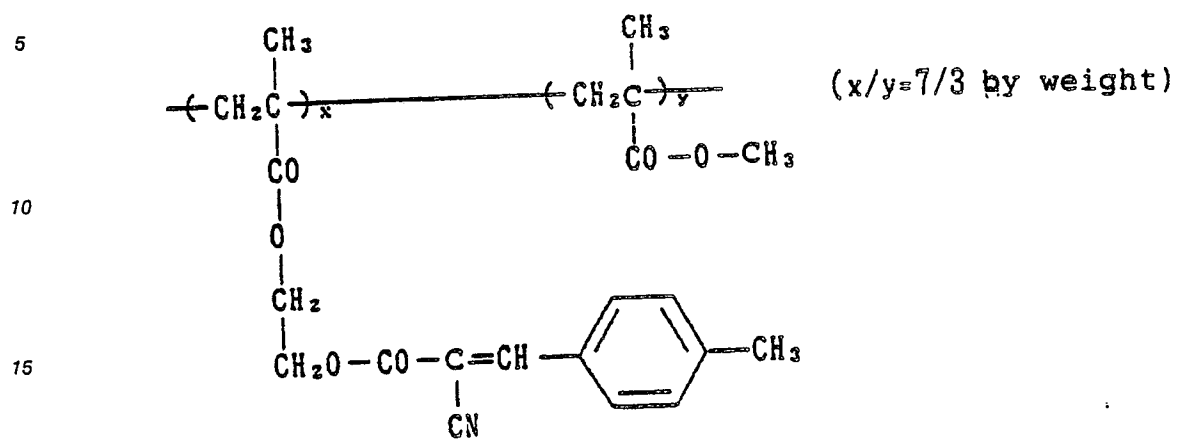
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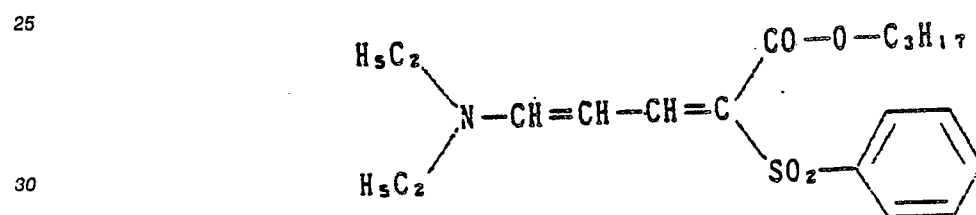
UV - 3



UV - 4



UV - 5



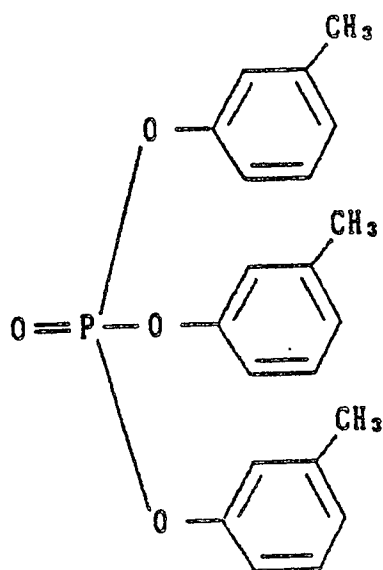
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S o l v - 2

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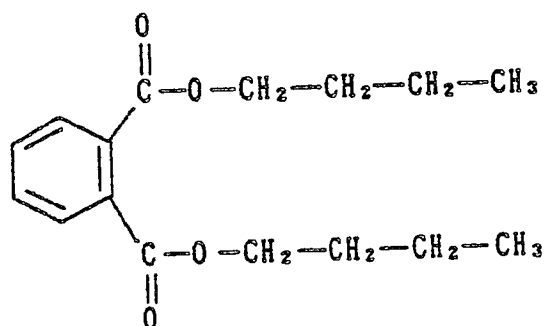
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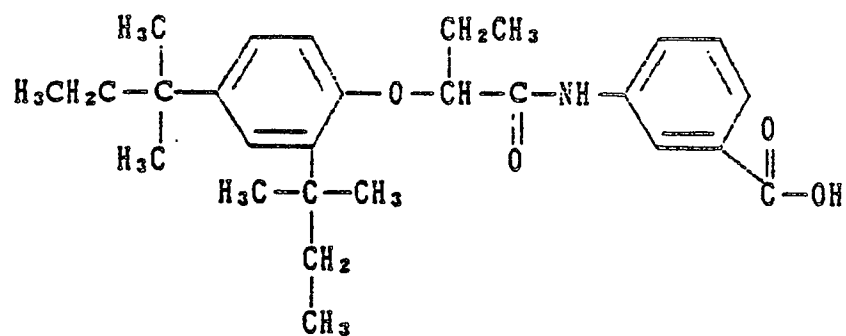
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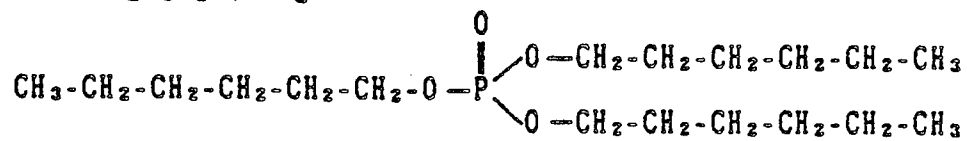
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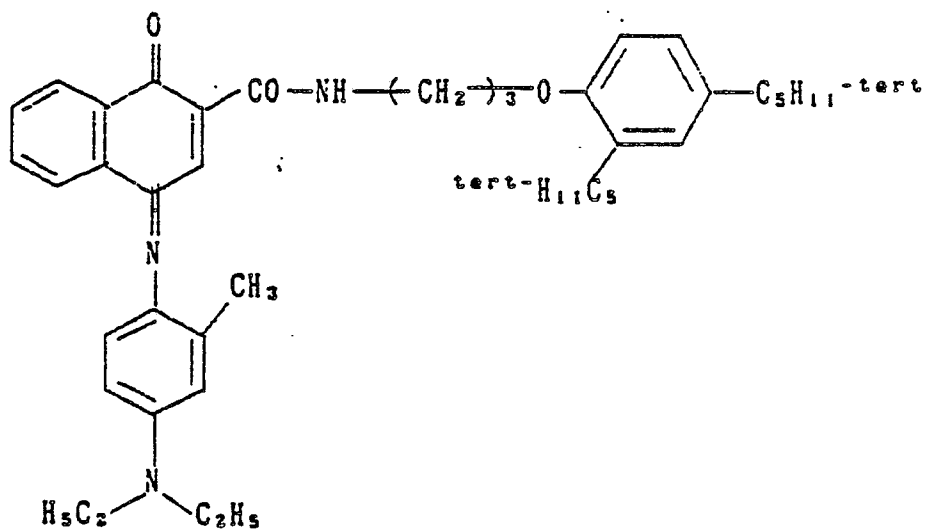
S o l v - 4



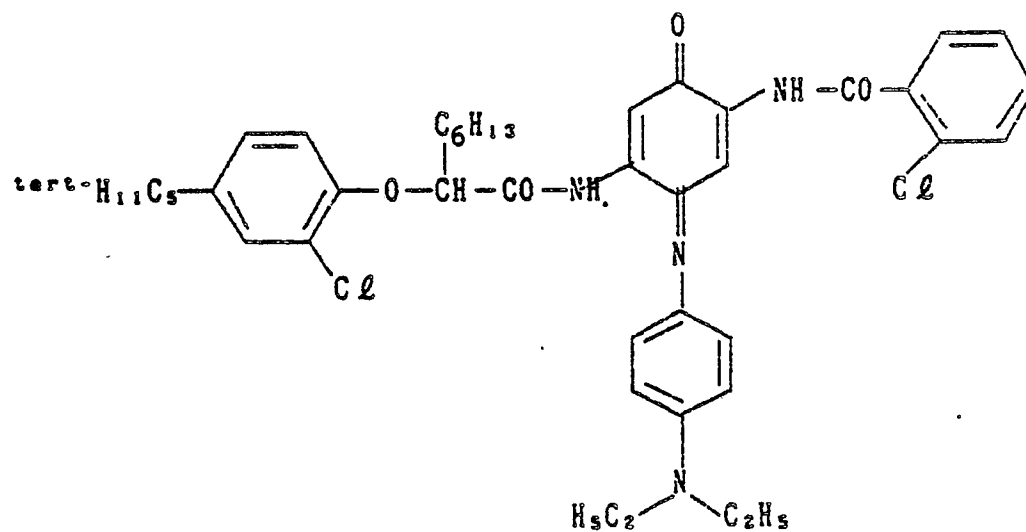
S o l v - 5



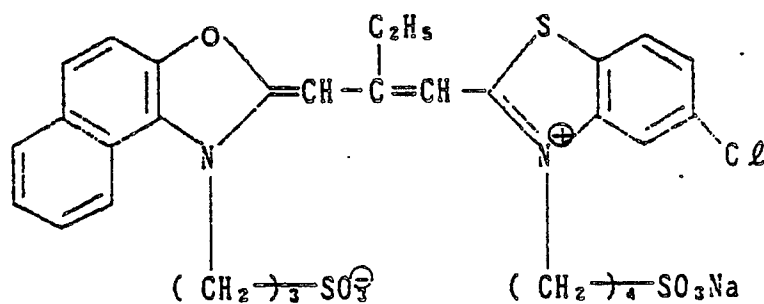
E x F - 1



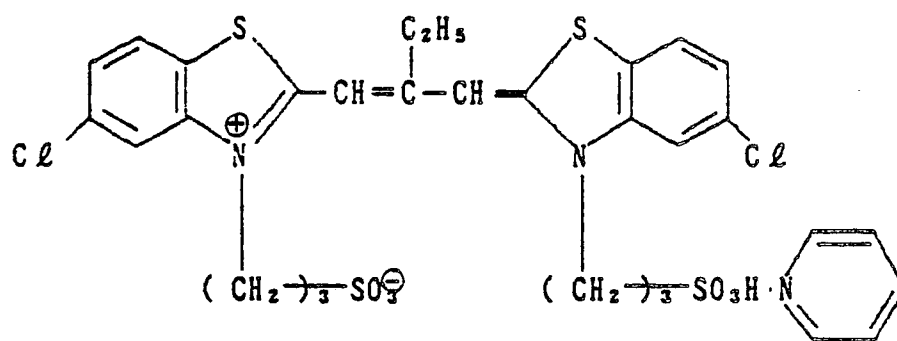
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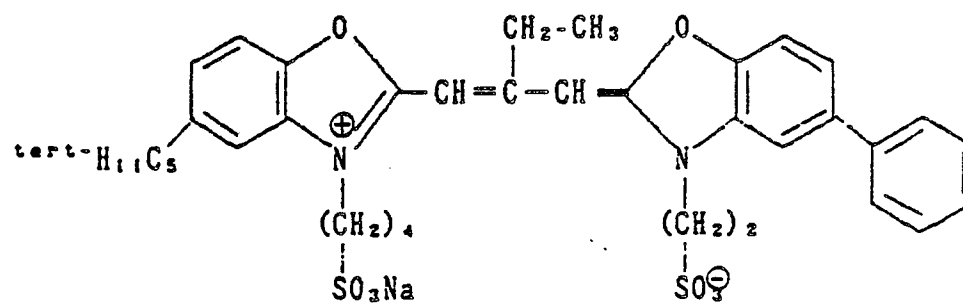
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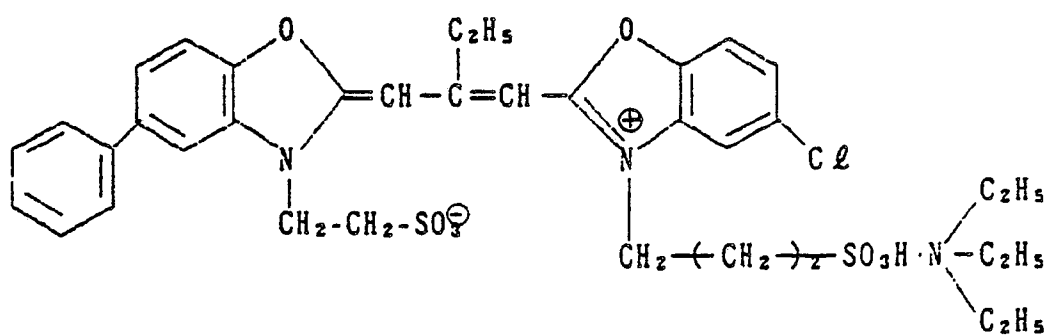
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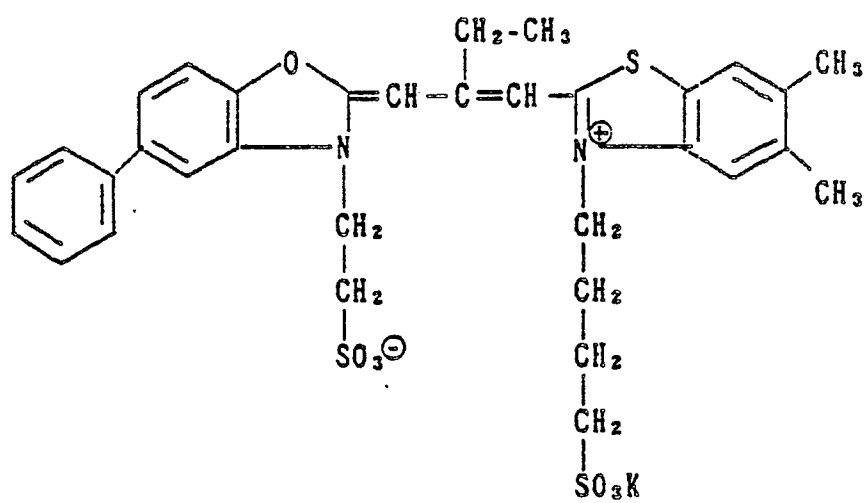
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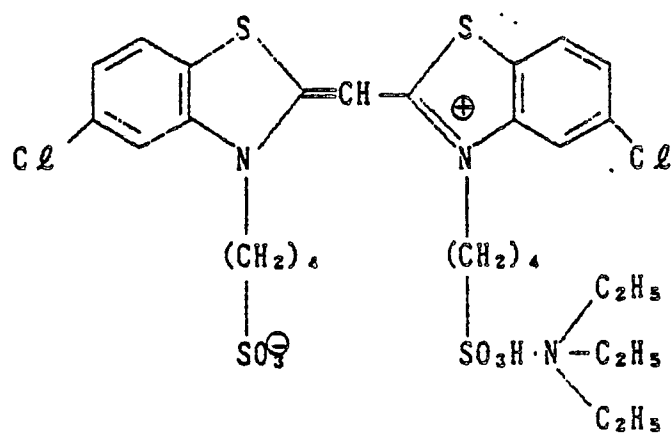
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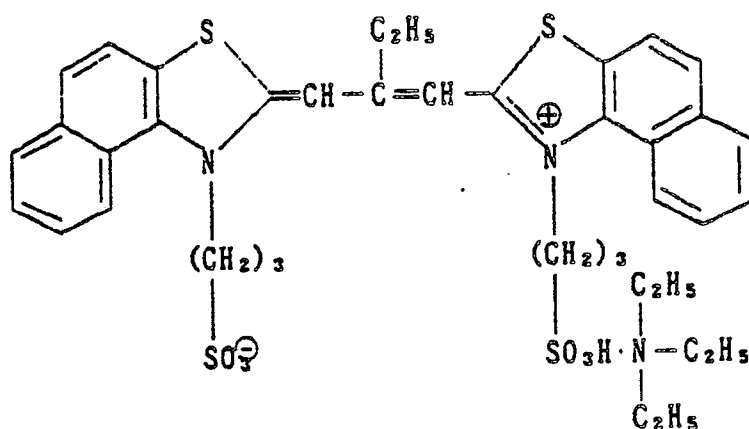
E x S - 5



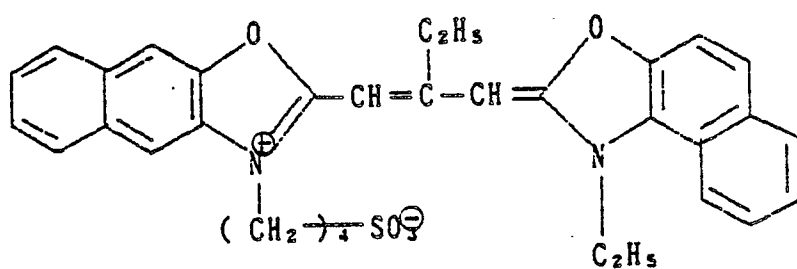
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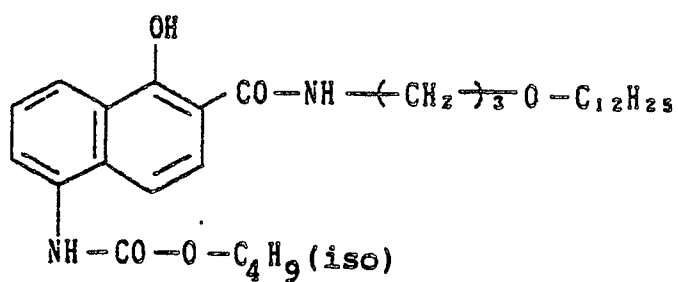
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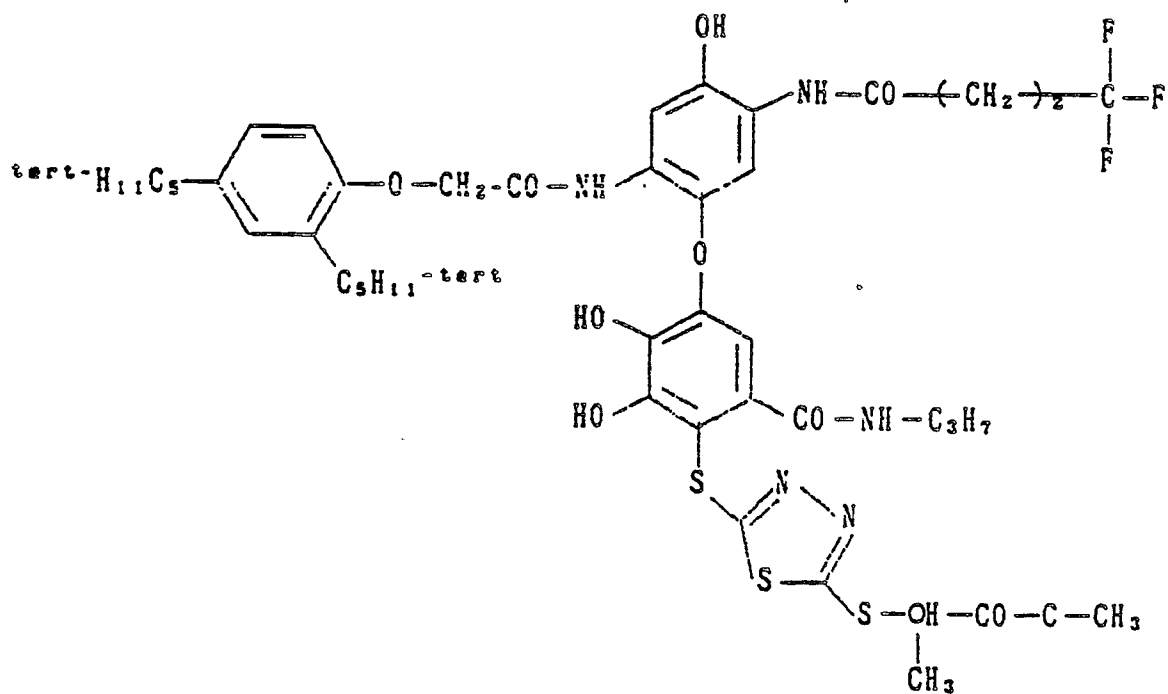
E x S - 8



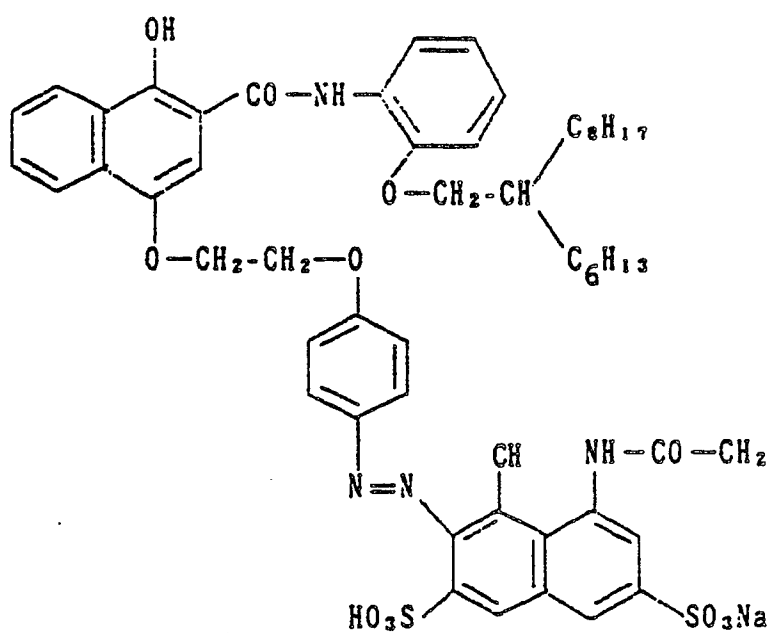
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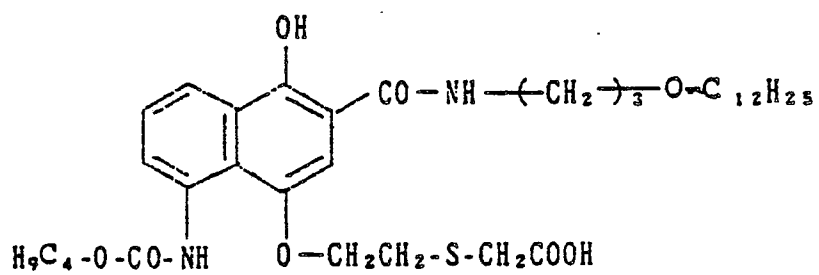
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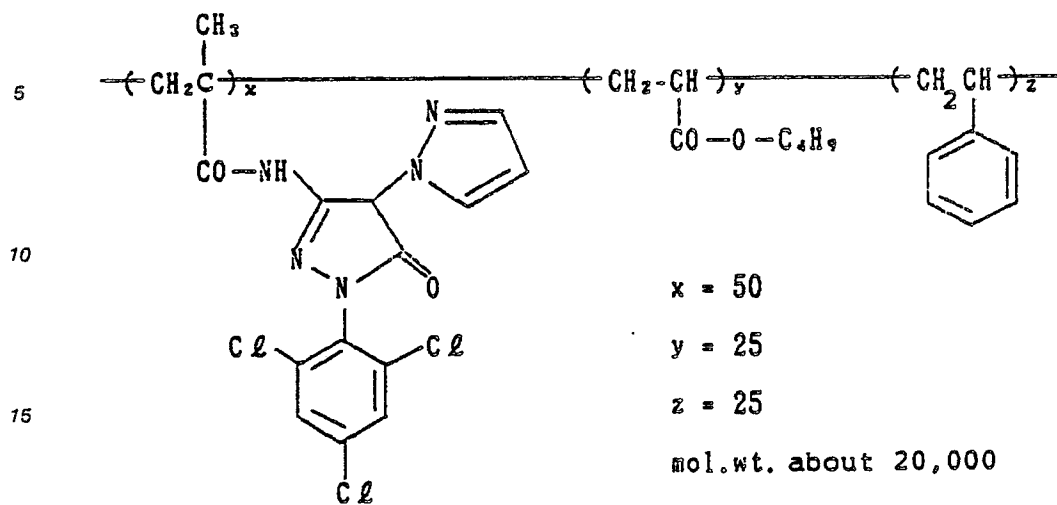
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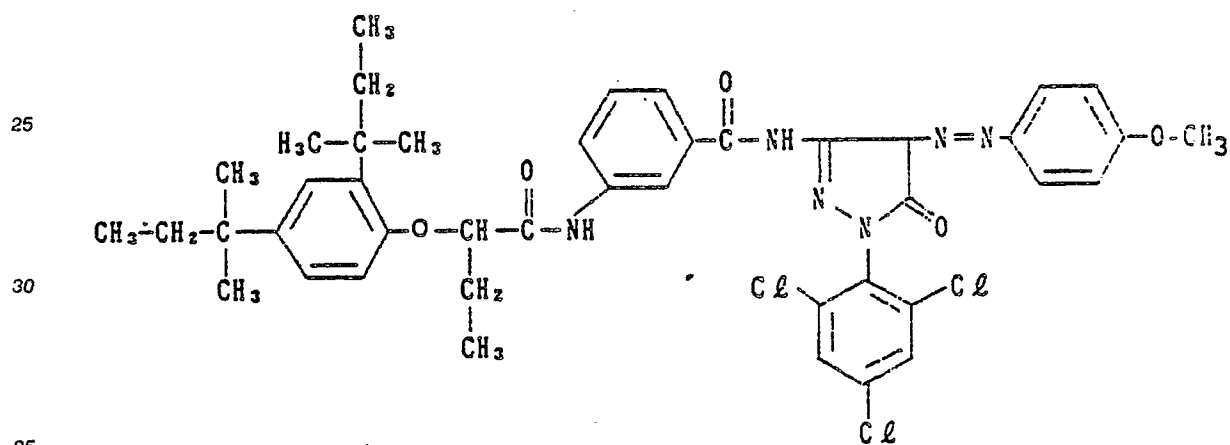
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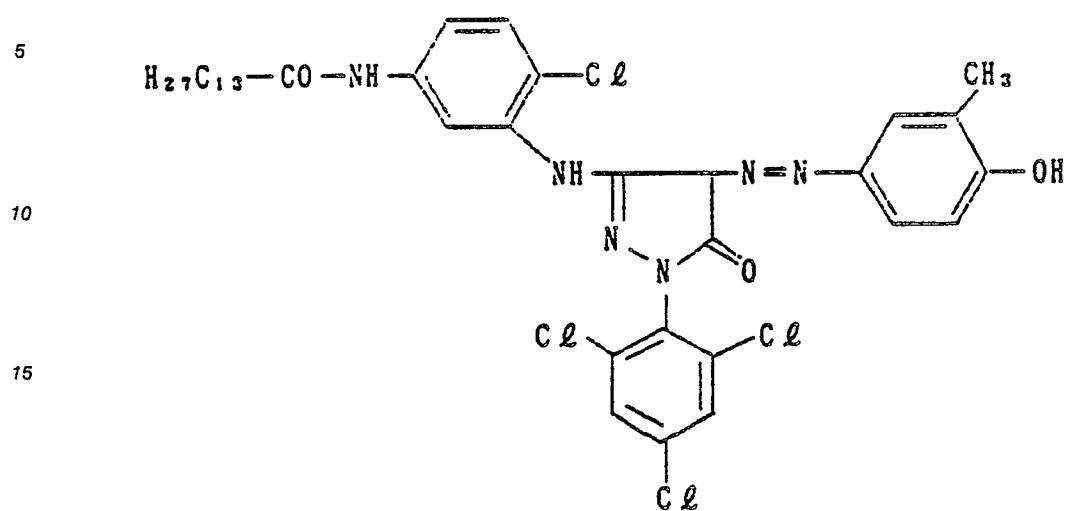
Ex M - 5



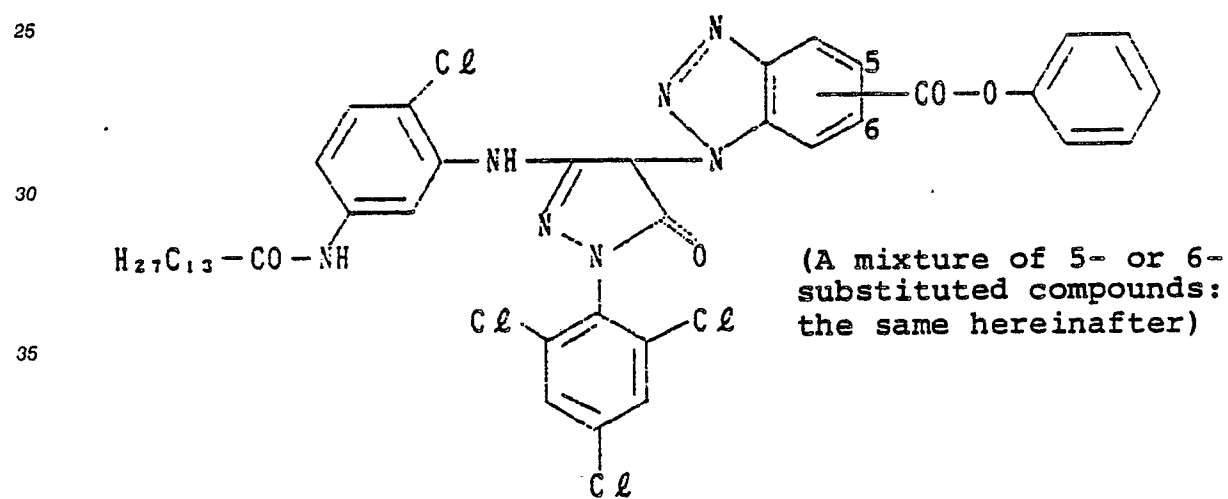
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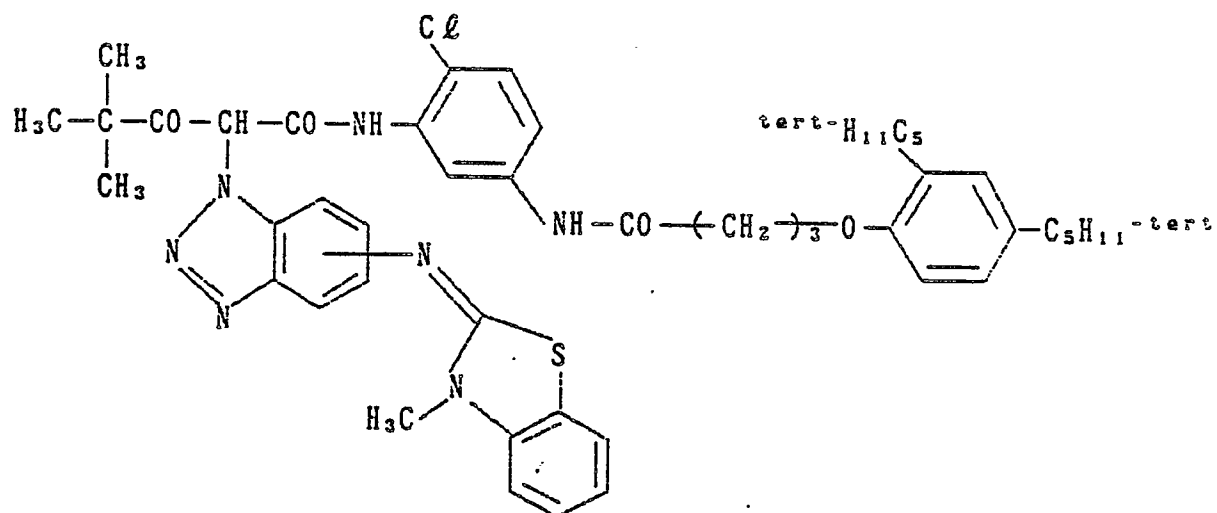
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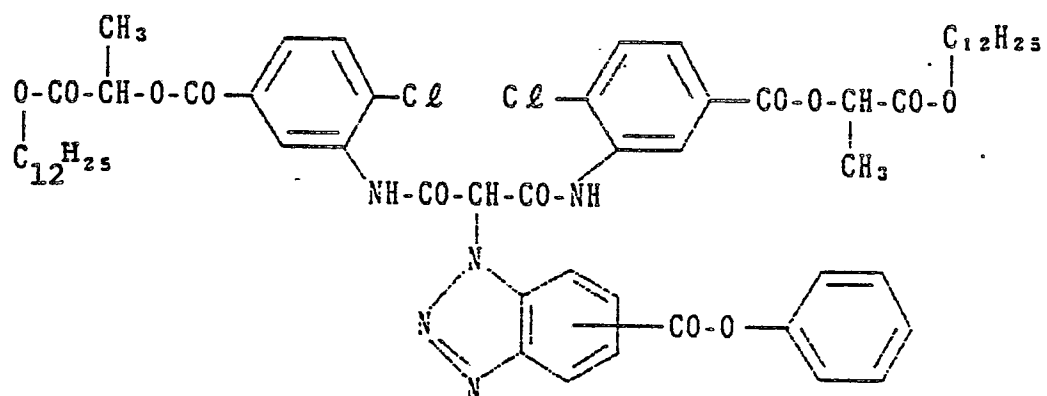
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E x Y - 8



E x Y - 9



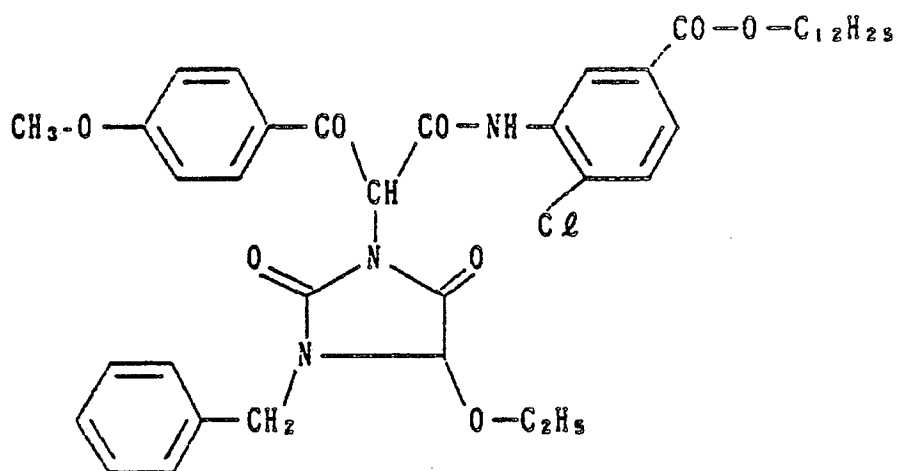
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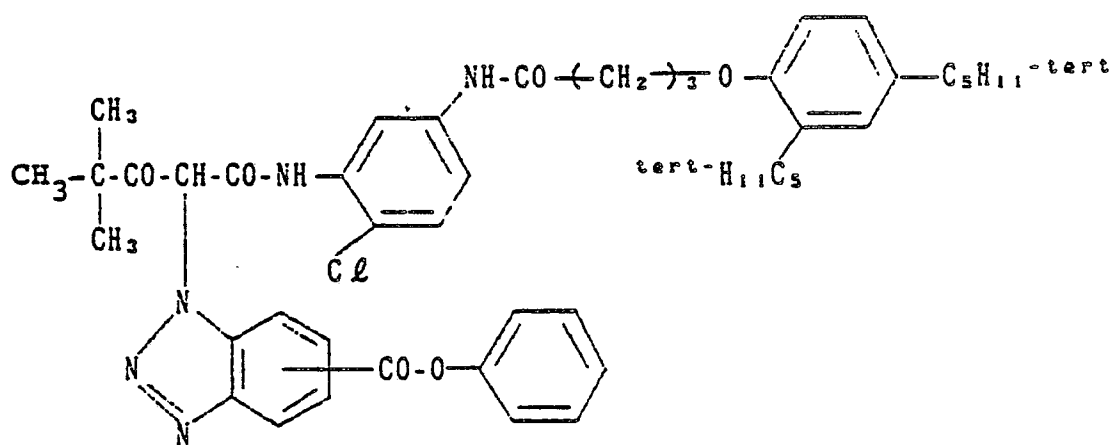
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Ex Y - 1 1



Ex Y - 1 2

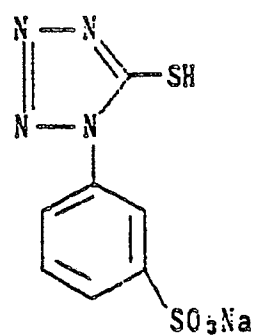


C p d - 7

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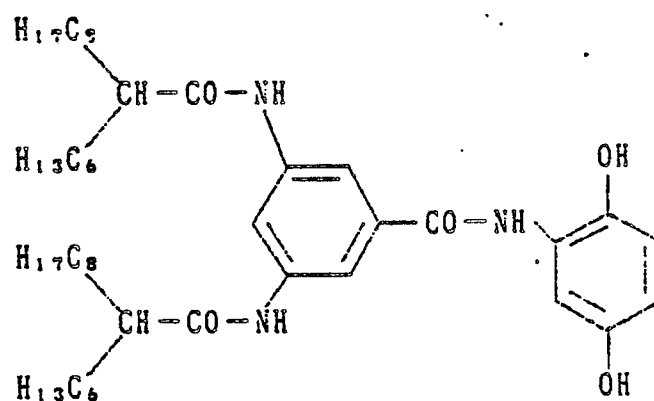
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C p d - 1

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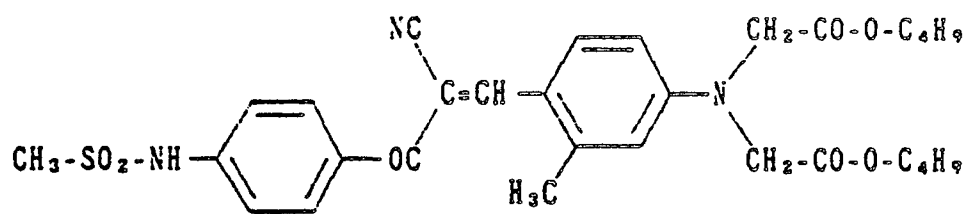
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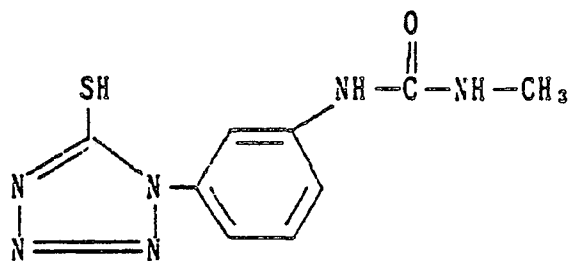
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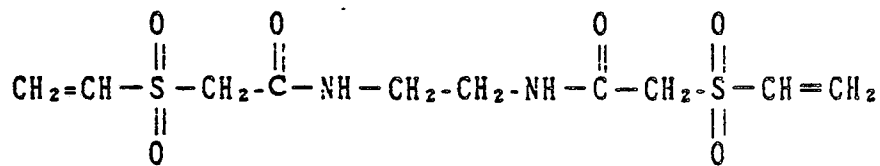
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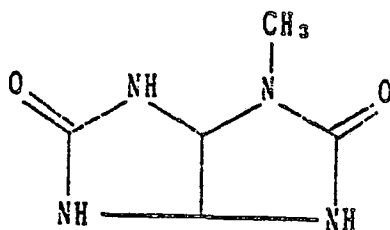
C p d - 6



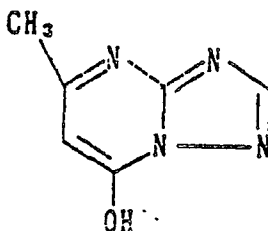
H - 1



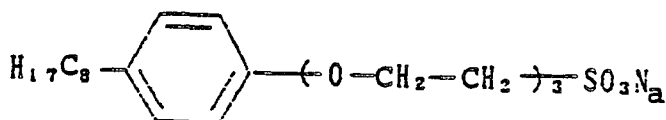
C p d - 5



C p d - 3



C p d - 4



In the above Example, the following material, emulsion, etc. are used. They are, however, not essential for obtaining the effects of the invention, i.e. excellent color reproduction and tone reproduction, and may be replaced by other materials and emulsions to obtain similar color reproduction and tone reproduction so long as the photographic material falls within the scope of the invention.

For example, the fine grain silver iodobromide emulsions in the 15th and 16th layers may be omitted, and Cpd-5 in the 15th layer may be omitted.

Preparation of a Sample 102 (comparison)

Sample 102 was prepared by making the following changes to Sample 101.

The iodine content in the silver iodobromide emulsions in the third layer was changed from 6 mol% to 3 mol%, and from 4 mol% to 2 mol%, respectively.

The iodine content of the silver iodobromide emulsion in the seventh layer was changed from 4 mol% to 2 mol%.

The iodine content of the silver iodobromide emulsion in the twelfth layer was changed from 4.5 mol% to 2.5 mol%, and from 3 mol% to 1.5 mol%, respectively.

Preparation of a Sample 103 (comparison)

Sample 103 was prepared by making the following changes to Sample 101.

The amounts of silver iodobromide emulsions in the third layer coated were decreased from 0.65 to 0.46 and from 0.1 to 0.07, respectively.

The amounts of cyan couplers ExC-1 and ExC-4 in the twelfth layer were increased from 0.06 to 0.12 and from 0.03 to 0.06, respectively. The amount of yellow coupler ExY-11 was increased from 0.89 to 0.93.

5

Preparation of a Sample 104 (comparison)

Sample 104 was prepared by making the following changes to Sample 101.

10 The amounts of cyan couplers ExC-1 and ExC-4 in the twelfth layer were increased from 0.06 to 0.12 and from 0.03 to 0.06, respectively.

The amount of yellow coupler ExY-11 was increased from 0.89 to 0.93.

15 Preparation of a Sample 105 (comparison)

Sample 105 was prepared by making the following changes to Sample 101.

The amounts of silver iodobromide emulsions coated in the third layer were decreased from 0.65 to 0.46 and from 0.1 to 0.07, respectively.

20 The amount of magenta coupler ExM-5 in the seventh layer was increased from 0.17 to 0.25.

The amount of DIR coupler ExM-10 in the tenth layer was decreased from 0.19 to 0.095.

The amount of yellow coupler ExY-11 in the twelfth layer was decreased from 0.89 to 0.80.

25 Preparation of a Sample 106 (comparison)

Sample 106 was prepared by making the following changes to Sample 101.

The amount of DIR coupler ExM-10 was decreased from 0.19 to 0.095.

The amount of yellow coupler ExYU-11 in the twelfth layer was decreased from 0.89 to 0.80.

30 The amount of magenta coupler ExM-5 in the seventh layer was increased from 0.17 to 0.25.

Preparation of a Sample 107 (comparison)

35 Sample 107 was prepared by making the following changes to Sample 101.

Coupler ExC-2 in the third layer was excluded, and the amounts of the silver iodobromide emulsions were decreased from 0.65 to 0.52 and from 0.1 to 0.08, respectively.

The amount of silver iodobromide coated in the seventh layer was decreased from 0.27 to 0.22.

Yellow coupler ExY-11 in the twelfth layer was decreased from 0.89 to 0.85.

40

Preparation of a Sample 108 (comparison)

Sample 108 was prepared by making the following changes to Sample 101.

45 Coupler ExC-2 in the third layer was excluded, and the amounts of silver iodobromide emulsions were decreased from 0.65 to 0.52 and from 0.1 to 0.08, respectively.

The amount of yellow coupler ExY-11 in the twelfth layer was decreased from 0.89 to 0.85.

50 Preparation of a Sample 109 (comparison)

Sample 109 was prepared by making the following changes to Sample 101.

The amount of the silver iodobromide emulsion coated in the seventh layer was decreased from 0.27 to 0.22.

55 DIR coupler ExY-9 in the twelfth layer was excluded. Cyan couplers ExC-1 and ExC-4 were also excluded. The amount of yellow coupler ExY-11 was decreased from 0.89 to 0.62.

Preparation of a Sample 110 (comparison)

Sample 110 was prepared by making the following changes to Sample 101.

DIR coupler ExY-9 in the twelfth layer was excluded. Cyan couplers ExC-1 and ExC-4 were also
5 excluded. The amount of yellow coupler ExY-11 was decreased from 0.89 to 0.62.

Preparation of a Sample 111 (comparison)

10 Sample 111 was prepared by making the following changes to Sample 101.

Colored coupler ExM-7 in the seventh layer was excluded.

The amounts of silver iodobromide emulsions in the twelfth layer were decreased from 0.3 to 0.24 and
from 0.15 to 0.12, respectively.

15

Preparation of a Sample 112 (comparison)

Sample 112 was prepared by making the following changes to Sample 101.

Colored coupler ExM-7 in the seventh layer was excluded.

20

Preparation of a Sample 113 (comparison)

Sample 113 was prepared by making the following changes to Sample 101.

25 Yellow coupler ExY-11 was added to the third layer in an amount of 0.10.

The amounts of the silver iodobromide emulsions in the twelfth layer were decreased from 0.3 to 0.24
and from 0.15 to 0.12, respectively.

30 Preparation of a Sample 114 (invention)

Sample 114 was prepared by making the following changes to Sample 101.

Yellow coupler ExY-11 was added to the third layer in an amount of 0.10.

35

Preparation of a Sample 115 (invention)

Sample 115 was prepared by making the following changes to Sample 101.

40 The amounts of the silver iodobromide emulsions coated in the third layer were increased from 0.65 to
0.78 and from 0.1 to 0.12, respectively.

Cyan couplers ExC-1 and ExC-4 were removed from the twelfth layer. The amount of yellow coupler
ExY-11 was decreased from 0.89 to 0.85.

45 Preparation of a Sample 116 (invention)

Sample 116 was prepared by making the following changes to Sample 101.

The amounts of the silver iodobromide emulsions coated in the third layer were increased from 0.65 to
0.78 and from 0.1 to 0.12, respectively.

50 The amount of magenta coupler ExM-5 in the seventh layer was decreased from 0.17 to 0.01.

The amount of DIR coupler ExM-10 in the tenth layer was increased from 0.19 to 0.27, and the amounts
of the silver iodobromide emulsions coated were decreased from 0.68 to 0.54 and from 0.19 to 0.15,
respectively.

55

Preparation of a Sample 117 (invention)

Sample 117 was prepared by making the following changes to Sample 101.

The amount of coupler ExC-2 in the third layer was increased from 0.01 to 0.15. The amounts of the silver iodobromide emulsions coated were increased from 0.65 to 0.78 and from 0.10 to 0.12, respectively.

The amount of the silver iodobromide emulsion coated in the seventh layer was increased from 0.27 to 0.32.

5

Preparation of a Sample 118 (invention)

Sample 118 was prepared by making the following changes to Sample 101.

10 The amount of the silver iodobromide emulsion coated in the seventh layer was increased from 0.27 to 0.32.

The amounts of the silver iodobromide emulsions coated in the twelfth layer were increased from 0.3 to 0.36 and from 0.15 to 0.18, respectively. The amount of DIR coupler ExY-9 was increased from 0.14 to 0.20. The amounts of cyan couplers ExC-1 and ExC-4 were increased from 0.06 to 0.07 and from 0.03 to 0.04.

15

Preparation of a Sample 119 (invention)

20 Sample 119 was prepared by making the following changes to Sample 101.

The amount of magenta coupler ExM-5 in the seventh layer was increased from 0.17 to 0.25.

The amount of DIR coupler ExM-10 in the 10th layer was decreased from 0.19 to 0.095.

Cyan couplers ExC-1 and ExC-4 in the twelfth layer were excluded, and the amount of yellow coupler ExY-11 was decreased from 0.89 to 0.80.

25

Preparation of a Sample 120 (invention)

Sample 120 was prepared by making the following changes to Sample 101.

30 Coupler ExC-2 in the third layer was excluded. The amounts of the silver iodobromide emulsions were decreased from 0.65 to 0.52 and from 0.1 to 0.08, respectively.

The amounts of the silver iodobromide emulsions coated in the twelfth layer were increased from 0.3 to 0.36 and from 0.15 to 0.18, respectively. The amount of DIR coupler ExY-9 was increased from 0.14 to 0.20. The amounts of cyan couplers ExC-1 and ExC-4 were increased from 0.06 to 0.07 and from 0.03 to 0.04, respectively.

35

Preparation of a Sample 121 (invention)

40 Sample 121 was prepared by making the following changes to Sample 101.

The amount of coupler ExC-2 in the third layer was increased from 0.01 to 0.015. The amounts of the silver iodobromide emulsions coated were increased from 0.65 to 0.78 and from 0.10 to 0.12, respectively.

DIR coupler ExY-9 in the twelfth layer was excluded. Cyan couplers ExC-1 and ExC-4 were also excluded. The amount of yellow coupler ExY-11 was decreased from 0.89 to 0.62.

45

Test

50 Samples 101 to 121 were processed into formats and skins and hairs of black, white and yellow human species and the color rendition chart of MacBeth Company were photographed on these formats under various illuminations. The photographic materials were then subjected to the color processing shown below, and printed properly on Fuji color papers. The photographs were evaluated by a panel of 20 persons. Significant results obtained by the organoleptic evaluation of the panelists were gathered, and are summarized in Table 1.

55 The results show that Samples 115 to 118 which satisfy the conditions of the invention, γ_R^P , γ_G^P , γ_B^P , γ_R , γ_G and γ_B , showed generally good color reproduction. Samples 119-121 which satisfy the preferred conditions of the above-described γ_R^P to γ_B showed more preferred results, and above all, ideal color reproduction was obtained with Sample 101 which also satisfied the IE(X/Y) conditions. These results clearly

substantiate the effects of the present invention.

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Table 1

Sample		Gradient						Magnitude of the Interlayer effect				Other characteristics	
		Y _P			Y _B			IE (R/G)	IE (G/R)	IE (R/B)	IE (G/B)		
		Y _R	Y _G	Y _B	Y _P	Y _G	Y _B						
101	Invention	0.95 ○	0.95 ○	0.80 ○	0.61 ○	0.70 ○	0.22 ○	0.30 ○	0.20 ○	0.75 ○	faithful	faithful	Perfect with excellent reproduction of objects of all colors and brightnesses
102	Comparison	1.04 ○	1.10 ○	0.92 ○	0.67 x	0.70 x	0.84 x				too dark	too bright	Poor ability to depict highlights and shadows
103	"	0.76 x	0.95 ○	0.80 ○	0.60 ○	0.63 ○	0.70 ○				with a cyan tint	cyan at the shadow	The root portion of fair hair blackish and tends to be taken for dyed hair
104	"	0.95 ○	0.95 ○	0.78 ○	0.79 x	0.63 ○	0.68 ○				with a saturation tint of cyan	cyan at the shadow	
105	"	0.76 x	0.93 ○	0.75 ○	0.62 ○	0.60 ○	0.71 ○				faithful saturation low, the facial color of a sick person	slightly yellowish	Yellow green was reproduced as yellow
106	"	0.95 ○	0.93 ○	0.75 ○	0.75 x	0.60 ○	0.70 ○				with a tint of cyan	too red	cyan at the shadow

Table 1 (cont'd)

Sample		Gradient				Magnitude of the Interlayer effect				Skin of the black	Skin of the white	Skin of the yellow	Other character-istics	
		γ_R^P	γ_G^P	γ_B^P	γ_R	γ_G	γ_B	IE (R/G)	IE (G/R)					IE (R/B)/IE (G/B)
107	Compri-son	0.97 O	0.78 x	0.80 O	0.60 O	0.62 O	0.69 O	.	with a tint of cyan	too yellow	too yellow	red into vermillion, and orange into lemon		
108	"	0.97 O	0.95 O	0.80 O	0.60 O	0.72 x	0.69 O		faithful	greenish	too yellow	saturation of green decreased		
109	"	0.95 O	0.78 x	0.85 O	0.63 O	0.60 O	0.72 O		faithful	too red	reddish	blue into a tint of cyan and orange into lemon		
110	"	0.95 O	0.95 O	0.80 O	0.63 O	0.70 x	0.71 O		too red	too red	reddish			
111	"	0.95 O	0.92 O	0.64 x	0.61 O	0.60 O	0.67 O		faithful	faithful	yellow too much removed	the green of leaves had a tint of cyan; sky blue became hazy		
112	"	0.95 O	0.92 O	0.80 O	0.61 O	0.59 O	0.81 x		yellowish	bluish	faithful			
113	"	0.93 O	0.92 O	0.63 x	0.60 O	0.62 O	0.70 O		faithful	too red	reddish	red into magenta		
114	"	0.93 O	0.92 O	0.80 O	0.59 O	0.58 O	0.80 x		faithful	too red	faithful			

Table 1 (cont'd)

Sample		Gradient						Magnitude of the Interlayer effect					Other characteristics
		P			P			IE (R/G)	IE (G/B)	IE (R/B)	IE (G/B)		
		Y _R	Y _G	Y _B	Y _R	Y _G	Y _B						
115	Invention	1.16	0.95	0.80	0.63	0.60	0.70			slightly reddish	slightly reddish	slightly reddish at the shadow	Crimson became slightly reddish
116	"	1.16	0.90	0.80	0.60	0.61	0.67			faithful	faithful	slightly reddish	The green of leaves showed a slight tint of cyan
117	"	0.90	1.12	0.80	0.60	0.62	0.70			slightly reddish	slightly reddish	red	the shadow of the green of leaves was slightly bright
118	"	0.92	1.13	0.78	0.59	0.60	0.71			faithful	slightly yellowish	slightly yellowish	orange slightly into lemon
119	"	0.95	0.94	0.78	0.62	0.60	0.70	0.14	0.33	0.22	1.05	faithful	faithful
120	"	0.95	0.95	0.79	0.60	0.62	0.70	0.27	0.14	0.35	0.60	faithful	faithful
121	"	0.92	0.95	0.82	0.61	0.60	0.70	0.20	0.40	0.13	1.10	slightly reddish	faithful

Notes:

○: The value is within the scope of the
present invention

×: The value is outside the scope of the
present invention

△: The value is within the scope of the
present invention but is not within the
preferred range of the present invention

Effects of the Invention

(1) When $\gamma_R^p < 0.80$, various defects occur. Specifically, the skin of the black is reproduced in a darker color than the actual model. Reproduction of the root of fair hair is excessively dark. The saturation of the skin of the white is low, and the face looks that of a sick person. Yellow green is reproduced as yellow.

(2) When $\gamma_G^p < 0.80$, various defects occur. For example, the skin of the black is reproduced in a color with a tint of cyan. The skins of the white and the yellow are reproduced in a yellowish color. Or the skins of the white and the yellow are reproduced in a reddish color.

(3) When $\gamma_B^p < 0.65$, yellow color is excessively removed from the skin color of the yellow or the skin of the white is reproduced in an excessively reddish color.

(4) When $\gamma_R, \gamma_G > 0.65$ and $\gamma_B > 0.75$, the skin of the black is excessively dark, and the skin of the white is excessively bright. Furthermore, the ability to depict the highlight and shadow portions of various objects is inferior. Furthermore, if any of γ_R, γ_G and γ_B falls outside the scope of this invention, the image of a gray object forms color shift in addition to the defects in color reproduction shown in Table 1 above.

The samples of this invention show excellent reproduction of the color of the skin which is most important, and can perform reproduction with a sufficient three-dimensional feel without a color change in the highlight to shadow portions of various objects.

Foreign patents corresponding to Japanese Patent Publications cited in this application are shown below.

JP-A-50-2537: U.S. Patent 3,990,899,
West German OLS 2,421,544,
British Patent 1,460,991

JP-A-61-34541 U.S. Patent 4,705,744,
EP 167,173

JP-A-57-151944: U.S. Patent 4,477,563,
DE 3,209,486,
British Patent 2,099,167

JP-A-54-145135: U.S. Patent 4,248,962,
DE 2,855,697,
British Patent 2,010,818

JP-A-62-54255: EP 2,00,502,

WO 83/234

JP-58-100847: U.S. Patent 4,511,648,
EP 70,182

JP-A-61-153460: EP 161,626

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A silver halide color photographic material comprising a support and formed thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one blue-sensitive silver halide emulsion layer, wherein gradients γ_R^P , γ_G^P and γ_B^P in monochromatic exposure of each wavelength giving peak sensitivities are

$$0.80 < \gamma_R^P$$

$$0.80 < \gamma_G^P$$

$$0.65 < \gamma_B^P$$

and gradients γ_R , γ_G and γ_B in standard white light source exposure are

$$\gamma_R < 0.65$$

$$\gamma_G < 0.65$$

$$\gamma_B < 0.75.$$

2. The photographic material of claim 1, wherein the magnitude $IE(X/Y)$ of the interlayer effect defined in the specification is

$$0.15 < IE(R/G)$$

$$0.15 < IE(G/R)$$

$$0.15 < IE(G/B)$$

$$IE(R/B)/IE(G/B) < 1.0.$$

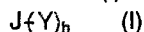
3. The photographic material of claim 1, wherein said gradients γ_R^P , γ_G^P and γ_B^P are
- 5 $\gamma_R^P < 1.15$
 $\gamma_G^P < 1.10$
 $\gamma_B^P < 1.2.$

4. The photographic material of claim 1, wherein said gradients γ_R , γ_G and γ_B are
- 10 $0.4 < \gamma_R$
 $0.4 < \gamma_G$
 $0.4 < \gamma_B.$

5. The photographic material of claim 1, wherein at least one of the silver halide emulsion layer contains silver halide grains containing silver iodide in an average amount of not more than 15 mol%.

6. The photographic material of claim 1, wherein at least one of the silver halide emulsion layer contains
- 15 at least one nondiffusible coupler which releases a diffusible development inhibitor or its precursor.

7. The photographic material of claim 6, wherein said nondiffusible coupler is represented by the formula (I)



- wherein J represents a coupler component, h represents 1 or 2, and Y is a group which is bonded to the
- 20 coupling site of the coupler component J and split off upon reaction with an oxidation product of a color developing agent, to produce a development inhibitor.

8. The photographic material of claim 7, wherein said development inhibitor has a diffusibility of at least 0.4.

9. The photographic material of claim 1, wherein said photographic material is a light-sensitive material
- 25 for photographing.

10. The photographic material of claim 1, wherein said light-sensitive material is a material selected from the group consisting of color negative film, motion-picture color negative film, slide color reversal film, and television color reversal film.

11. A method for producing a color image, which comprises exposing a silver halide color photographic
- 30 material comprising a support and formed thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one blue-sensitive silver halide emulsion layer, wherein gradients γ_R^P , γ_G^P and γ_B^P in monochromatic exposure of each wavelength giving peak sensitivities are

$$0.80 < \gamma_R^P$$

$$35 \quad 0.80 < \gamma_G^P$$

$$0.65 < \gamma_B^P$$

and gradients γ_R , γ_G and γ_B in standard white light source exposure are

$$\gamma_R < 0.65$$

$$\gamma_G < 0.65$$

$$40 \quad \gamma_B < 0.75,$$

developing the photographic material and subjecting the photographic material to printing using a color paper having a gradient of 2.7 ± 0.1 in terms of colorimetric density.

12. A method for producing a color image, which comprises exposing a silver halide color photographic
- 45 material comprising a support and formed thereon at least one red-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one blue-sensitive silver halide emulsion layer, wherein gradients γ_R^P , γ_G^P and γ_B^P in monochromatic exposure of each wavelength giving peak sensitivities are

$$50 \quad \frac{0.80}{\alpha} < \gamma_R^P$$

$$\frac{0.80}{\alpha} < \gamma_G^P$$

$$55 \quad \frac{0.65}{\alpha} < \gamma_B^P$$

and gradients γ_R , γ_G and γ_B in standard white light source exposure are

$$\gamma_R < \frac{0.65}{\alpha}$$

$$\gamma_G < \frac{0.65}{\alpha}$$

$$\gamma_B < \frac{0.75}{\alpha} ,$$

developing the photographic material and subjecting the photographic material to printing using a color paper having a gradient of α time a gradient of 2.7 ± 0.1 in terms of colorimetric density.

Fig. 1A

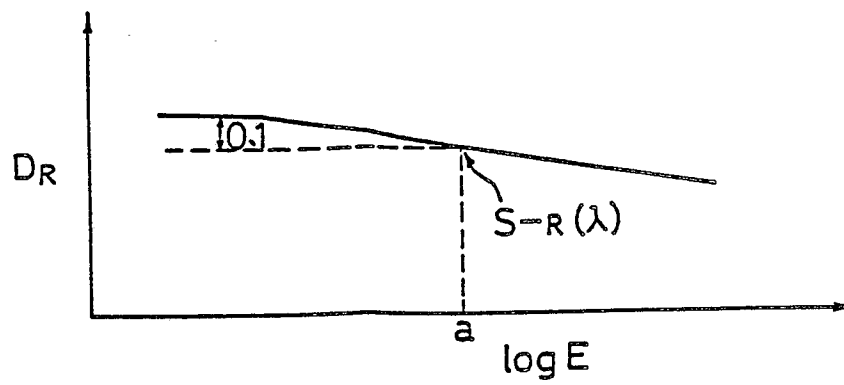


Fig. 1B

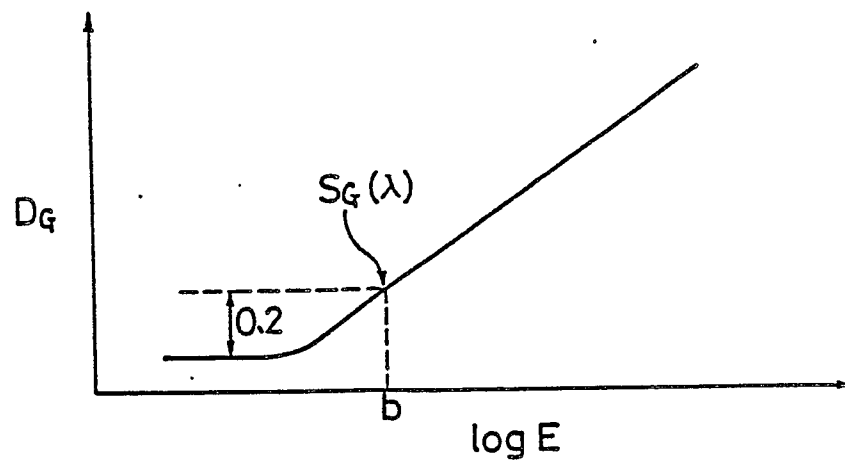


Fig. 1C

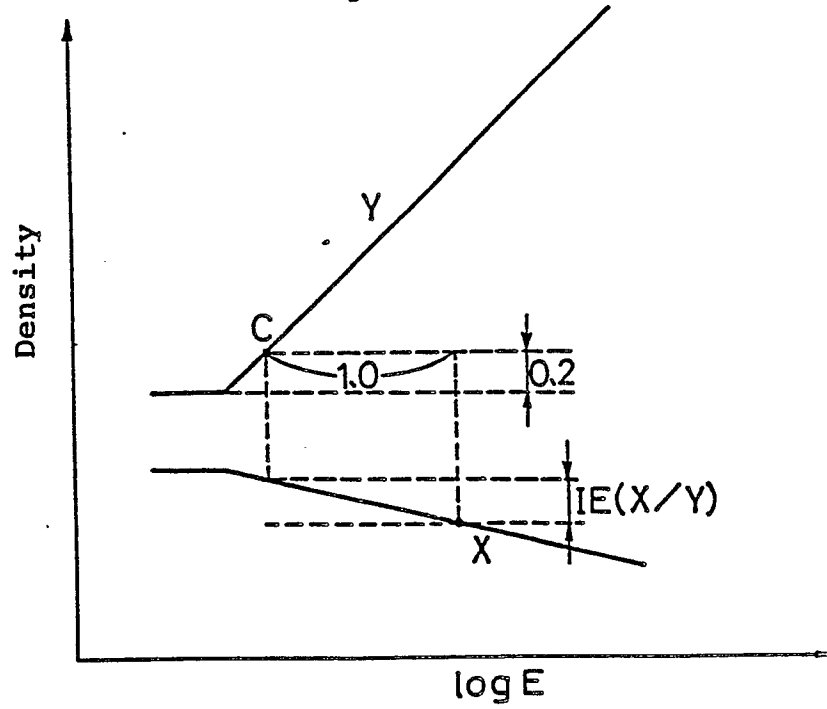
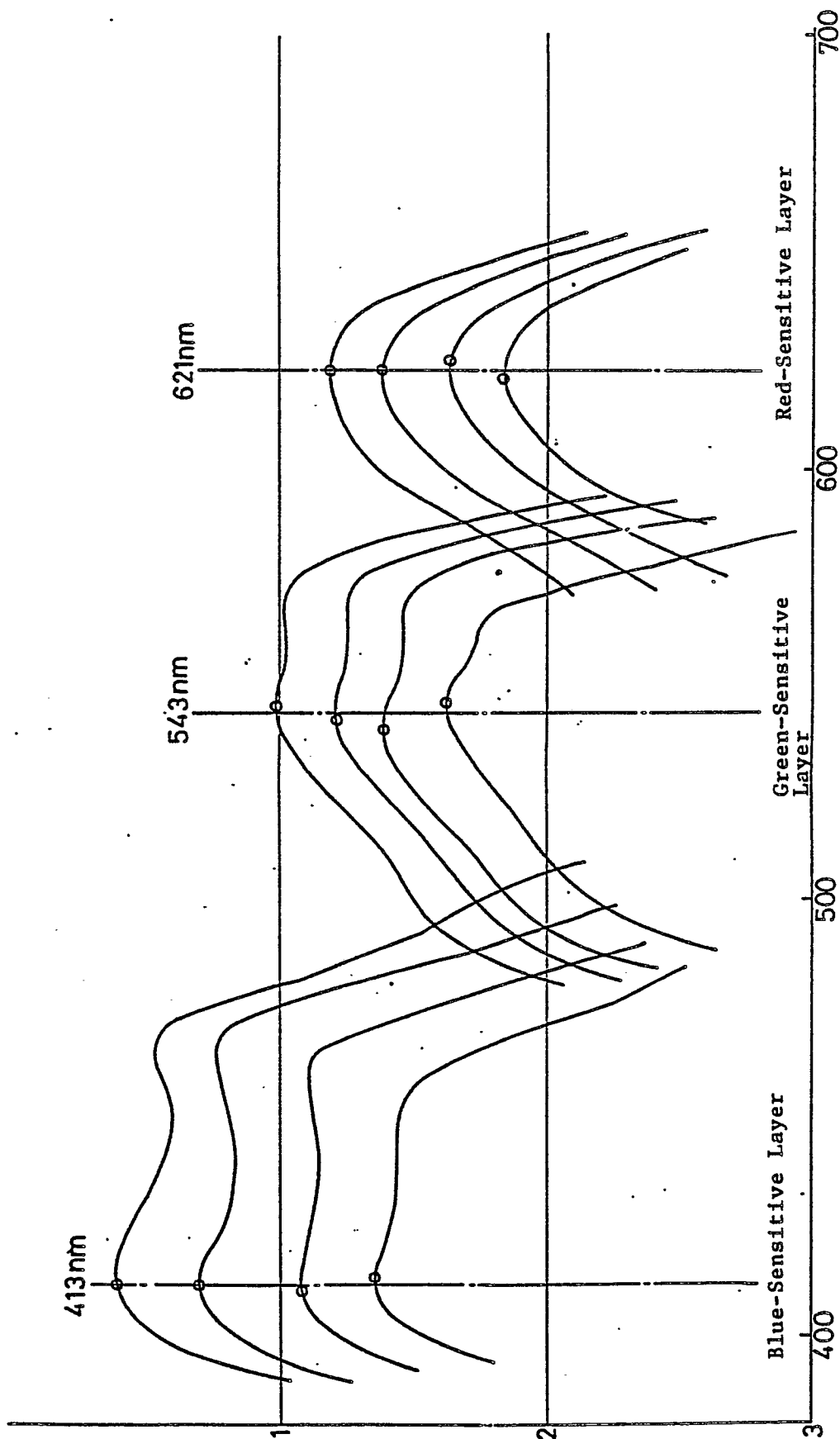


Fig. 2



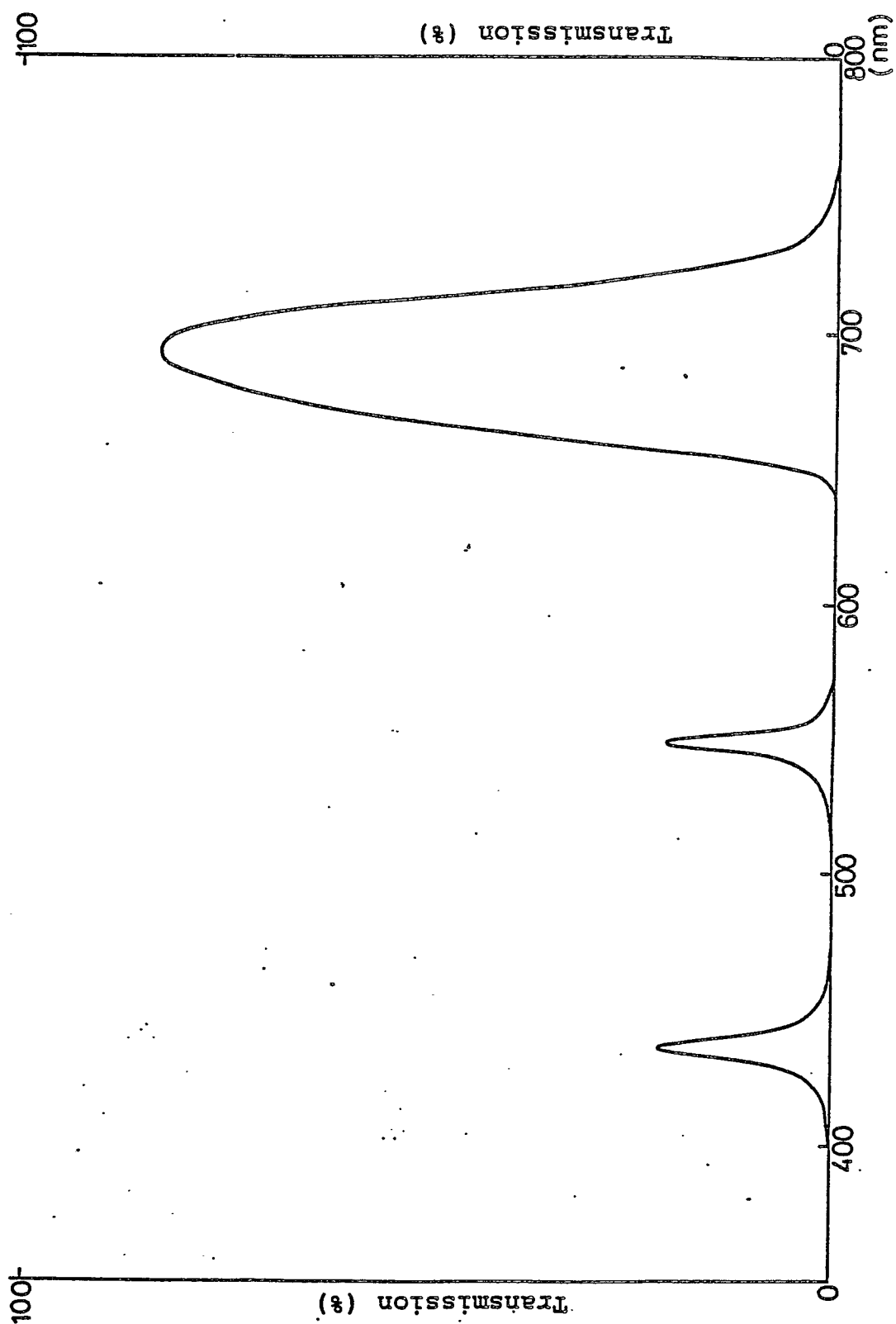


Fig. 3