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(54) Silver halide photographic material.

(57) A silver halide photographic material, which is excellent in sharpness and drying property and enables rapid processing within 45 seconds or less, having on a support at least one hydrophilic colloid layer containing a solid dye dispersed therein and at least one silver halide emulsion layer provided thereon, wherein the amount of all the hydrophilic colloids present on each side of the photographic material is 2.5 g/m^2 or less, and all the hydrophilic colloid layers present are hardened to a degree sufficient to attain a swelling rate of less than 200%.

EP 0 457 153 A1

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic material, and more particularly to a silver halide photographic material which can be rapidly processed and has a dye layer. The present invention also relates to a method for processing the same.

BACKGROUND OF THE INVENTION

In recent years, black-and-white photographic materials generally used, for example, for X-ray photography, plate making and microphotography have been processed by automatic processors within a time of 1 to 5 minutes. It is, however, desired to complete the processing as rapidly as possible to deal with the increased photographs to be processed.

Photographic materials used for quick feedback of results, such as medical X-ray photographic materials, are required to be processed within the shortest possible time. In these circumstances, the processing time of photographic materials is reduced from 1 minute or more to less than 1 minute, and is being reduced to shorter time.

It is desired to improve the image quality of medical X-ray photographic materials for improving diagnostic accuracy. The photographic materials for plate making pass through a dot to dot work stage repeatedly. Hence, when the photographic materials do not have sufficient resolution, images are blurred every time the photographic materials pass through the dot to dot work stage, which leads to poor image quality. Therefore, it is desired to improve the image quality. In recent years, photographic materials for plate making are frequently exposed to lasers, so the photographic materials must be capable of maintaining high image quality even when exposed to high intensity light. As to the photographic materials for microphotography, photographic images are observed not directly, but through an enlarging device such as used in police investigations. Therefore, it is necessary to have clear images for admissibility of photographic evidence. For these reasons, it is required to improve the image quality.

As described above, black-and-white photographic materials are required to be rapidly processed within a time of less than 45 seconds and to have high image quality.

For the purpose of improving the image quality of photographic materials, photographic emulsion layers or other layers are colored to absorb light having a particular wavelength. The light scattered when the incident light passes through the photographic emulsion layer or after passing through the emulsion layer is reflected from the interface of the emulsion layer and a support or from the surface of the photographic material opposite to the emulsion layer and reenters the photographic emulsion layer.

In order to prevent blurred images due to the above described phenomenon known as halation, a colored layer is provided between the photographic emulsion layer and the support, or on the surface of the support opposite to the photographic emulsion layer. Such a colored layer is called an antihalation layer (hereinafter referred to as an AH layer). Further, the X-ray photographic materials are sometimes provided with colored layers as crossover cut layers for decreasing crossover light to improve sharpness.

In many cases, these colored layers are formed of hydrophilic colloids. Further, dyes are usually contained in the layers for coloring. The dyes must meet the following requirements.

(1) They have proper spectral absorption depending on desired applications.

(2) They are photochemically inactive. Specifically, they do not exert chemical adverse effects, for example, a reduction in sensitivity, latent image fading and fog, on the silver halide photographic layers.

(3) They are decolorized or removed by dissolution during processing and do not leave harmful residual color on the photographic materials after processing.

Methods for forming the dye layers include the method of dissolving a soluble dye in a hydrophilic colloid layer, as disclosed in British Patents 1,414,456, 1,477,638 and 1,477,639. This method has the disadvantage that an improvement in residual color by enhancing the water solubility of the dye weakens the fixation of the dye. Thus, the dye is diffused into adjacent layers, which causes desensitizing and transfer of the dye to other light-sensitive materials. Furthermore, U.S. Patents 2,548,564, 4,124,386 and 3,625,694 disclose the method of adding a hydrophilic polymer having a charge opposite to that of a dissociated anionic dye to a layer as a mordant and localizing the dye in the particular layer by the interaction of the dye molecule and the polymer mordant. According to this method, however, if an anionic substance other than the dye is present in the same layer, the dye is not well localized, or coagulation is induced in the coating solution, which exerts an unfavorable effect on the manufacturing process.

As a method for improving these defects, the method of adding a dye dispersed in a microcrystalline state between a support and an emulsion layer is disclosed in U.S. Patent 4,803,150 and PCT International Publication No. WO 88/04794. This method is not accompanied by desensitization and is an excellent technique for improving image quality.

However, this technique is not suitable for rapid processing within a time of less than 45 seconds which has recently been required, as described above.

When an additional or separate layer is provided as the AH layer, the total amount of hydrophilic colloids is increased because the AH layer is usually formed of a hydrophilic colloid. If the amount of hydrophilic colloids is increased, water is absorbed in large amounts by the light-sensitive material in the processing stage, which results in a deterioration in the drying property. This is a major problem when using rapid processing within a time of less than 45 seconds.

Further, medical X-ray photographic materials and photographic materials for microphotography are ordinarily stored for a long period of time. It is, therefore, necessary to reduce the amount of hypo (sodium thiosulfate) remaining in the photographic materials after processing. If the hydrophilic colloids are used in large amounts, the amount of hypo absorbed in the fixing solution increases. Accordingly, the washing time must be prolonged to wash out the hypo. This is a further obstacle to rapid processing.

In order to impart rapid processing characteristics to silver halide photographic materials, the coated amount of hydrophilic colloids has been reduced, or a hardening agent has been added in sufficient amounts to decrease the swelling degree on processing. However, when the swelling degree is decreased, residual color after processing tends to increase. Because of this problem, an AH layer is provided to improve sharpness.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a silver halide photographic material which has reduced residual color, high image quality and can be rapidly processed.

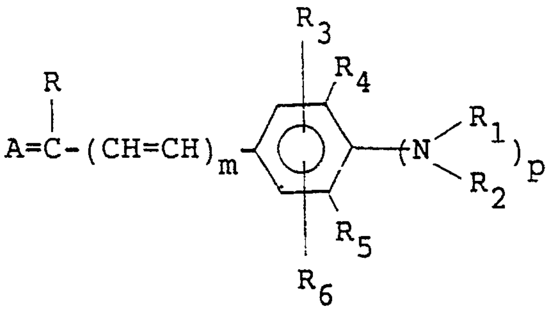
Another object of the present invention is to provide a method for processing the above photographic material.

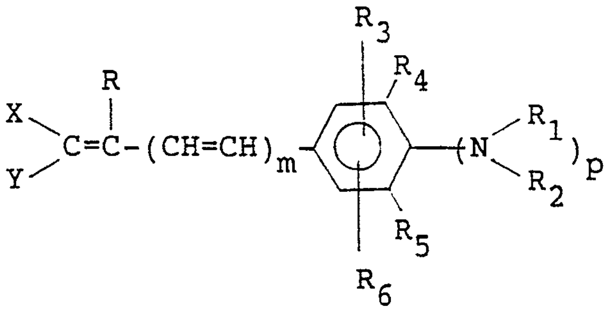
The above described objects are achieved by a silver halide photographic material having on a support at least one hydrophilic colloid layer containing a solid disperse dye and at least one silver halide emulsion layer provided thereon, in which the amount of all the hydrophilic colloids present on each side of the photographic material is 2.5 g/m^2 or less, and all the hydrophilic colloid layers are hardened to a sufficient degree to attain a swelling rate of less than 200%, wherein the swelling rate is determined by (a) incubating the photographic material at a temperature of 38° C at a relative humidity of 50% for 3 days, (b) measuring the thickness of the layers, (c) immersing the photographic material in distilled water at a temperature of 21° C for 3 minutes, and (d) measuring the thickness of the layers thus treated to obtain the percent changes in thickness compared to the thickness measured in step (b).

Preferably, the photographic material is processed within a time of 45 seconds or less, and more preferably within a time of 30 seconds.

DETAILED DESCRIPTION OF THE INVENTION

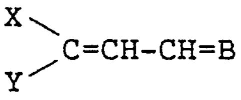
The dyes used in the present invention include the dyes shown in Tables I to X of PCT International Publication No. WO 88/04794, and the dyes represented by general formulae (I) to (VII) shown below:


(I)

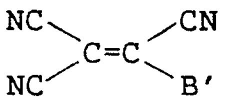

(II)

$$A=L_1-(L_2=L_3)_n-A' \qquad \text{(III)}$$

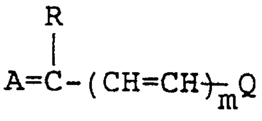
$$A=(L_1-L_2)_{2-q}=B \qquad \text{(IV)}$$


(V)

$$\begin{matrix}X\\Y\end{matrix}\!>C=CH-CH=B$$


(VI)

$$\begin{matrix}NC\\NC\end{matrix}\!>C=C<\!\begin{matrix}CN\\B'\end{matrix}$$


(VII)

$$A=\overset{R}{\overset{|}{C}}-(CH=CH)_m Q$$

wherein A and A', which may be the same or different, each represents an acidic nucleus; B represents a basic nucleus; X and Y, which may be the same or different, each represents an electron attractive group;

R represents a hydrogen atom or an alkyl group; each of R_1 and R_2 represents an alkyl group, an aryl group, an acyl group or a sulfonyl group, and R_1 and R_2 may combine together to form a 5-membered or 6-membered ring; each of R_3 and R_6 represents a hydrogen atom, a hydroxyl group, a carboxyl group, an alkyl group, an alkoxy group or a halogen atom; each of R_4 and R_5 represents a hydrogen atom or a nonmetallic atom; R_1 can combine with R_4 to form a 5-membered or 6-membered ring wherein R_4 is a nonmetallic atom necessary to form such a ring; or R_2 can combine with R_5 to form a 5-membered or 6-membered ring wherein R_5 is a nonmetallic atom necessary to form such a ring;

each of L_1, L_2 and L_3 represents a methine group; m represents 0 or 1; each of n and q represents 0, 1 or 2; p represents 0 or 1; when p is 0, R_3 represents a hydroxyl group or a carboxyl group and each of R_4 and R_5 represents a hydrogen atom;

B' represents a heterocyclic group having a carboxyl group, a sulfamoyl group or a sulfonamido group;

Q represents a heterocyclic group; and compounds represented by general formulae (I) to (VII) contain at least one dissociative group per molecule which has a pKa of from 4 to 11 in a mixed solution of water and methanol in a volume ratio of 1:1.

First, compounds represented by formulae (I) to (VII) are described in detail.

The acidic nucleus represented by A or A' is preferably 2-pyrazoline-5-one, rhodanine, hydantoin, thiohydantoin, 2,4-oxazolidinedione, isooxazolidinone, barbituric acid, thiobarbituric acid, indandione, pyrazolopyridine or hydroxypyridine.

The basic nucleus represented by B is preferably pyridine, quinoline, indolenine, oxazole, benzoxazole, naphthoxazole or pyrrole.

Examples of the heterocyclic rings represented by B' include pyrrole, indole, thiophene, furan, imidazole, pyrazole, indolizine, quinoline, carbazole, phenothiazine, phenoxazine, indoline, thiazole, pyridine, pyridazine, thiadiazine, pyran, thiopyran, oxadiazole, benzoquinolizine, thiadiazole, pyrrolothiazole, pyrrolopyridazine and tetrazole.

The heterocyclic ring represented by Q is preferably a 5-membered heterocyclic ring which may be formed by benzo condensed ring, and more preferably a 5-membered nitrogen-containing heterocyclic ring which may be formed by benzo condensed ring. Examples of the heterocyclic rings represented by Q include pyrrole, indole, pyrazole, pyrazolopyrimidone and benzoindole.

For the dissociative proton-containing group having a pKa (acid dissociation constant) of from 4 to 11 in the mixed solution of water and methanol in a volume ratio of 1:1, the kind and substituting position on the dye molecule are not particularly limited as long as it substantially insolubilizes the dye molecule in water at a pH of 6 or less and substantially solubilizes the dye molecule in water at a pH of 8 or more. However, such a group is preferably a carboxyl group, a sulfamoyl group, a sulfonamido group and a hydroxyl group, and more preferably a carboxyl group. The dissociative group may be substituted not only directly on the dye molecule, but also through a divalent connecting group such as an alkylene group or a phenylene group. Examples of the groups that can be substituted through the divalent connecting groups include 4-carboxyphenyl, 2-methyl-3-carboxyphenyl, 2,4-carboxyphenyl, 3,5-dicarboxyphenyl, 3-carboxyphenyl, 2,5-dicarboxyphenyl, 3-ethylsulfamoylphenyl, 4-phenylsulfamoylphenyl, 2-carboxyphenyl, 2,4,6-trihydroxyphenyl, 3-benzenesulfonamidophenyl, 4-(p-diaminobenzenesulfonamido)phenyl, 3-hydroxyphenyl, 2-hydroxyphenyl, 4-hydroxyphenyl, 2-hydroxy-4-carboxyphenyl, 3-methoxy-4-carboxyphenyl, 2-methyl-4-phenylsulfamoylphenyl, 4-carboxybenzyl, 2-carboxybenzyl, 3-sulfamoylphenyl, 4-sulfamoylphenyl, 2,5-disulfamoylphenyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl and 8-carboxyoctyl.

The alkyl group represented by R, R_3 or R_6 is preferably an alkyl group having 1 to 10 carbon atoms. Examples of such alkyl groups include methyl, ethyl, n-propyl, isoamyl and n-octyl groups.

The alkyl group represented by R_1 or R_2 is preferably a substituted or unsubstituted alkyl group having an alkyl back bone of 1 to 20 carbon atoms (for example, methyl, ethyl, n-propyl, n-butyl, n-octyl, n-octadecyl, isobutyl or isopropyl). Examples of substituent groups include halogen atoms such as chlorine and bromine, nitro, cyano, hydroxyl, carboxyl, alkoxy (for example, methoxy and ethoxy), alkoxycarbonyl (for example, methoxycarbonyl and i-propoxycarbonyl), aryloxy (for example, phenoxy), phenyl, amido (for example, acetylamino and methanesulfonamido), carbamoyl (for example, methylcarbamoyl and ethylcarbamoyl) and sulfamoyl (for example, methylsulfamoyl and phenylsulfamoyl) groups.

The aryl group represented by R_1 or R_2 is preferably a phenyl group or a naphthyl group, and may have at least one substituent group. Such substituent groups include the above described substituent groups for the alkyl groups represented by R_1 or R_2 and alkyl groups (for example, methyl and ethyl).

The acyl group represented by R_1 or R_2 is preferably an acyl group having 2 to 10 carbon atoms. Examples thereof include acetyl, propionyl, n-octanoyl, n-decanoyl, isobutanoyl and benzoyl groups. The alkylsulfonyl groups or the arylsulfonyl groups represented by R_1 or R_2 include methanesulfonyl, ethanesulfonyl, n-butanesulfonyl, n-octanesulfonyl, benzenesulfonyl, p-toluenesulfonyl, and o-carboxybenzenesulfonyl groups.

The alkoxy group represented by R_3 or R_6 is preferably an alkoxy group having 1 to 10 carbon atoms. Examples thereof include methoxy, ethoxy, n-butoxy, n-octoxy, 2-ethylhexyloxy, isobutoxy and isopropoxy groups. The halogen atoms represented by R_3 or R_6 include chlorine, bromine and fluorine.

The rings formed by the connection of R_1 and R_4 or R_2 and R_5 include, for example, a julolidine ring.

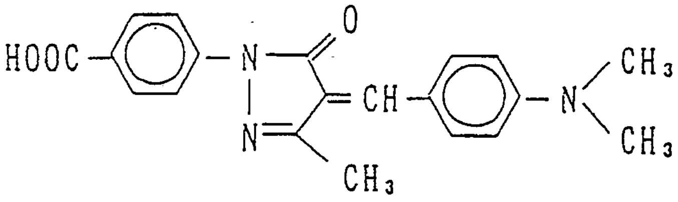
Examples of the 5-membered or 6-membered rings formed by the connection of R_1 and R_2 include piperidine, morpholine and pyrrolidine rings.

The methine group represented by L_1, L_2 or L_3 may have a substituent group (for example, methyl, ethyl, cyano, phenyl, chlorine or hydroxypropyl).

The electron attractive groups represented by X and Y may be the same or different, and each is a cyano group, a carboxyl group or an alkylcarbonyl group (alkylcarbonyl group may be substituted, for example, acetyl, propionyl, heptanoyl, dodecanoyl, hexadecanoyl, 1-oxo-7-chloroheptyl), arylcarbonyl (which may be substituted, for example, benzoyl, 4-ethoxycarbonylbenzoyl or 3-chlorobenzoyl), alkoxycarbonyl (which may be substituted, for example, methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, t-amyloxycarbonyl, hexyloxycarbonyl, 2-ethylhexyloxycarbonyl, octyloxycarbonyl, decyloxycarbonyl, dodecyloxycarbonyl, hexadecyloxycarbonyl, octadecyloxycarbonyl, 2-butoxyethoxycarbonyl, 2-methylsulfonylethoxycarbonyl, 2-cyanoethoxycarbonyl, 2-(2-choroethoxy)ethoxycarbonyl or 2-[2-(2-chloroethoxy)ethoxy]-ethoxycarbonyl), aryloxycarbonyl (which may be substituted, for example, phenoxycarbonyl, 3-ethylphenoxycarbonyl, 4-ethylphenoxycarbonyl, 4-fluorophenoxycarbonyl, 4-nitrophenoxycarbonyl, 4-methoxyphenoxycarbonyl or 2,4-di(t-amyl)phenoxycarbonyl), carbamoyl (which may be substituted, for example, ethylcarbamoyl, dodecylcarbamoyl, phenylcarbamoyl, 4-methoxyphenylcarbamoyl, 2-bromophenylcarbamoyl, 4-chlorophenylcarbamoyl, 4-ethoxydicarbonylphenylcarbamoyl, 4-propylsulfonylphenylcarbamoyl, 4-cyanophenylcarbamoyl, 3-methylphenylcarbamoyl, 4-hexyloxyphenylcarbamoyl, 2,4-di(t-amyl)-phenylcarbamoyl, 2-chloro-3-(dodecyloxycarbamoyl)phenylcarbamoyl or 3-(hexyloxycarbonyl)-phenylcarbamoyl) and sulfamoyl (which may be substituted, for example, sulfamoyl or methylsulfamoyl) groups.

Specific examples of the dyes used in the present invention are illustrated below:

I − 1



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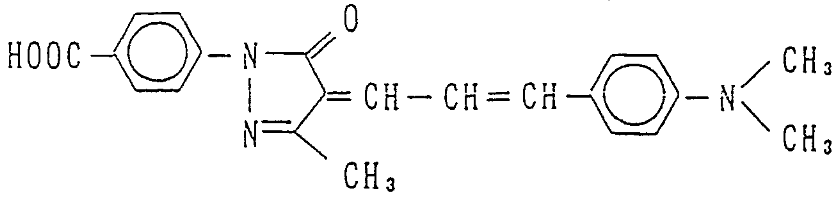
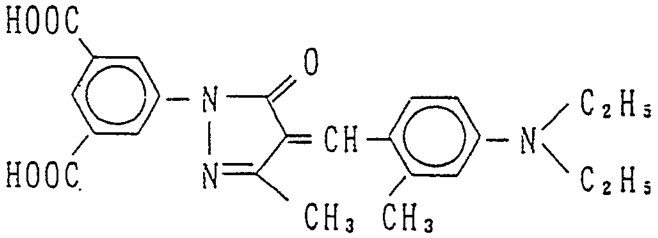
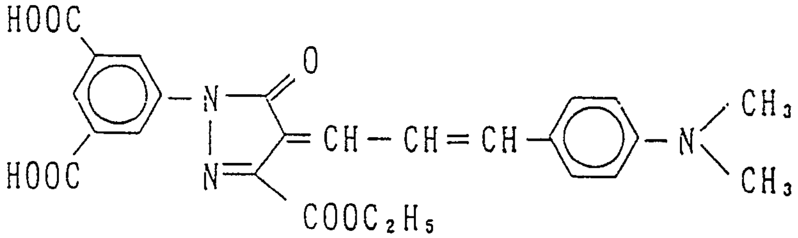


I − 3



I − 4



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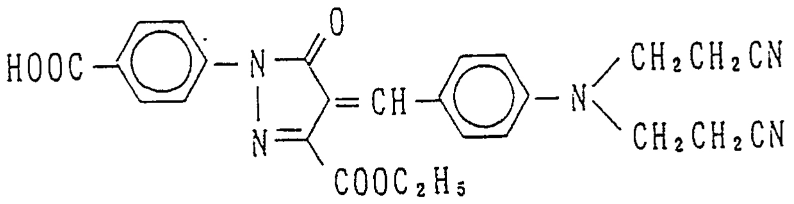

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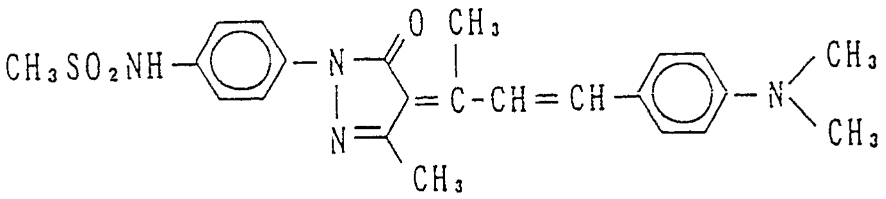

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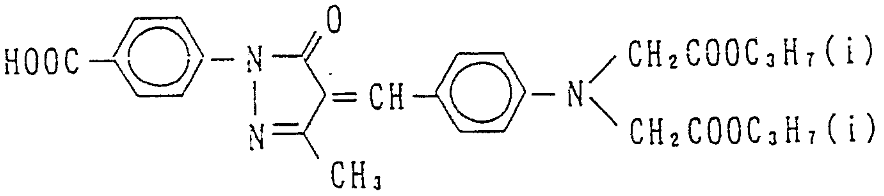

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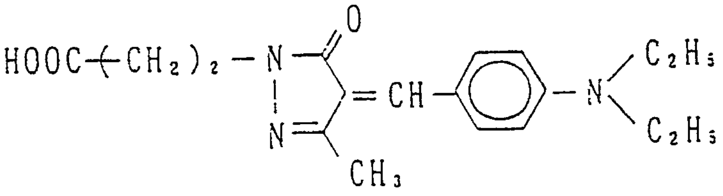

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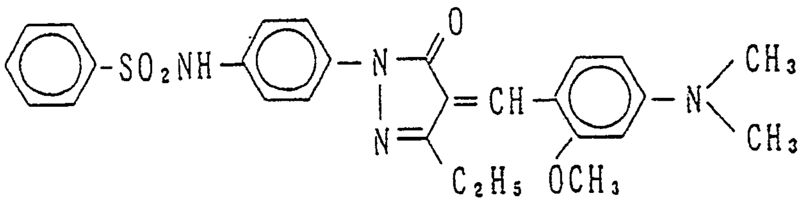
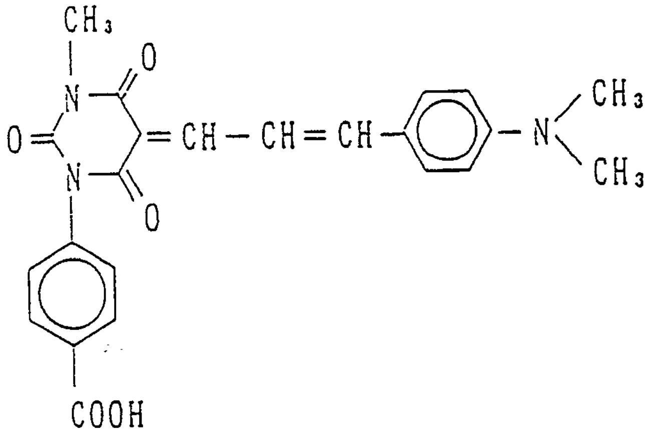
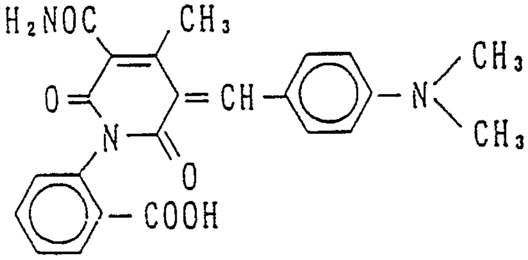


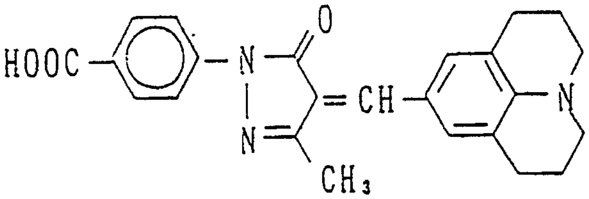
I − 1 0



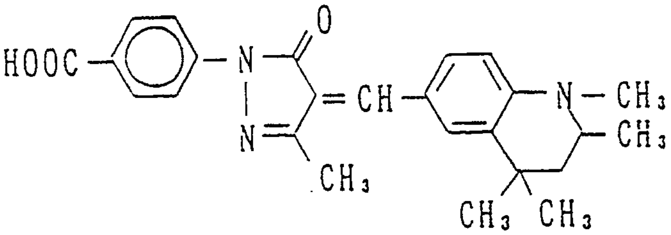
I − 1 1



I－１２



I－１３



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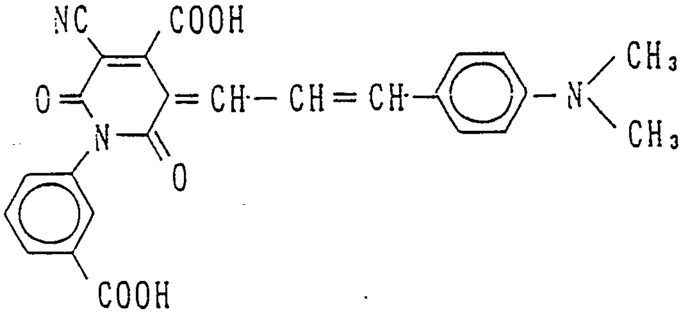

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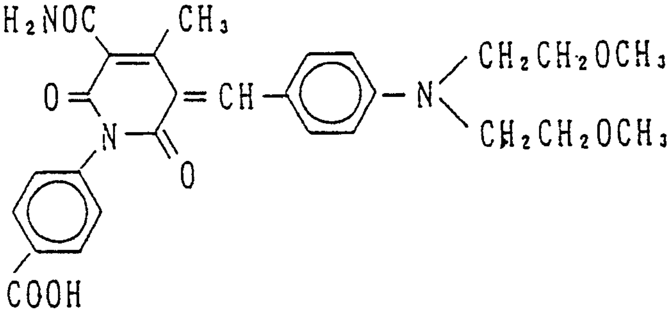

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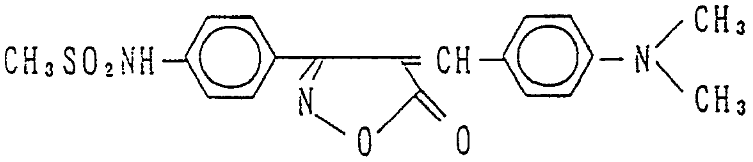

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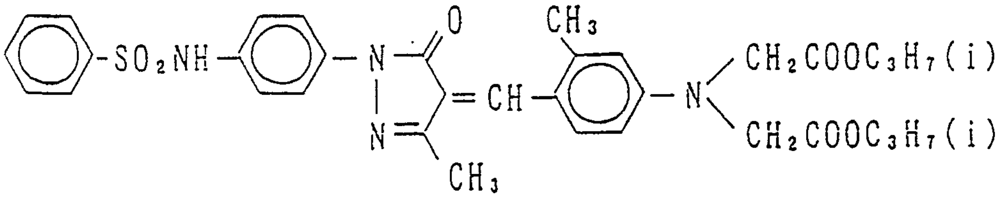

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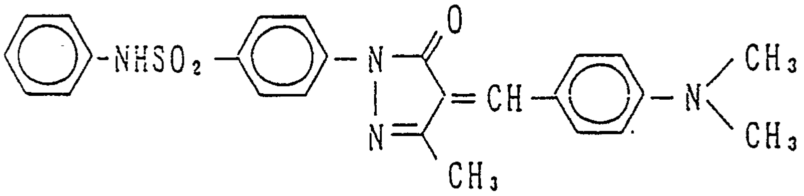
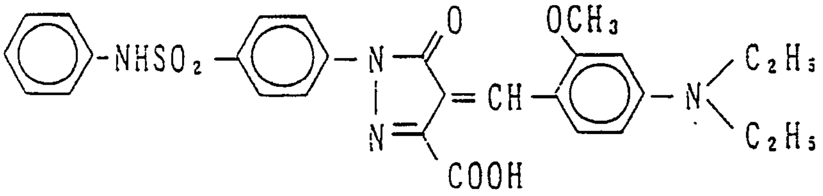
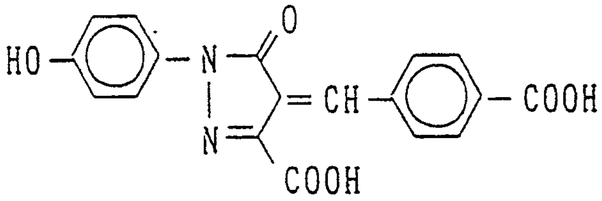


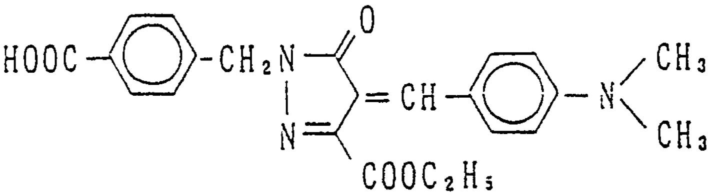
I－１９



I－２０



I－２１



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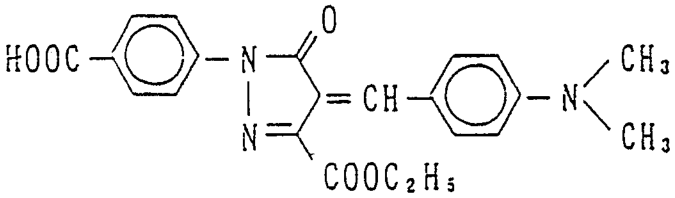

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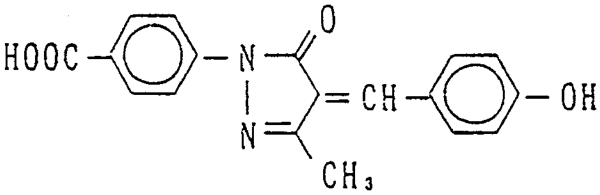

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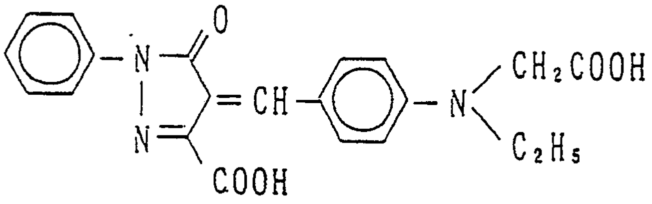

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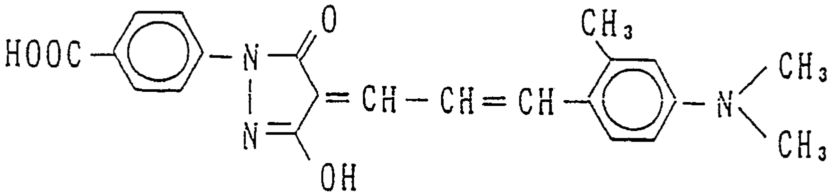

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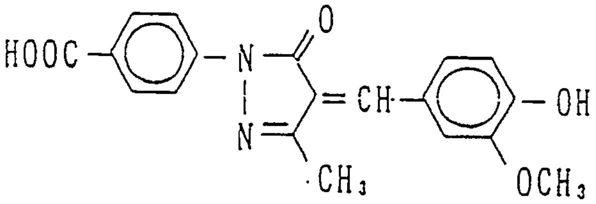
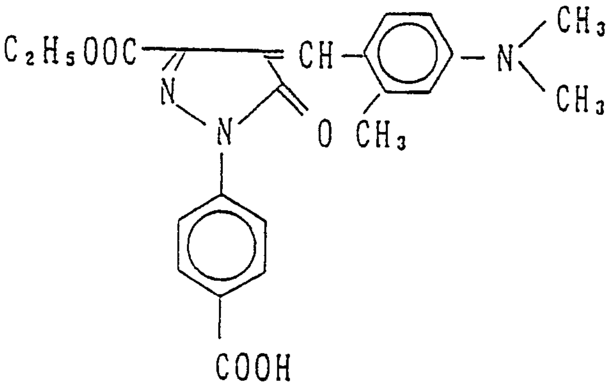
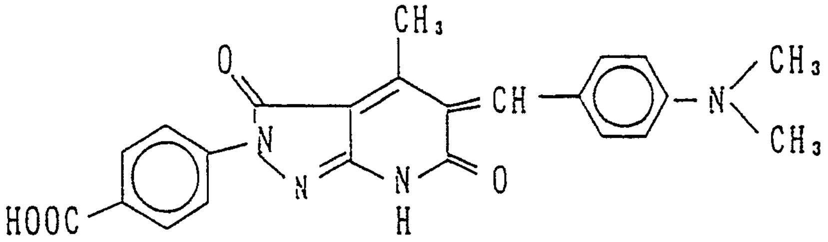


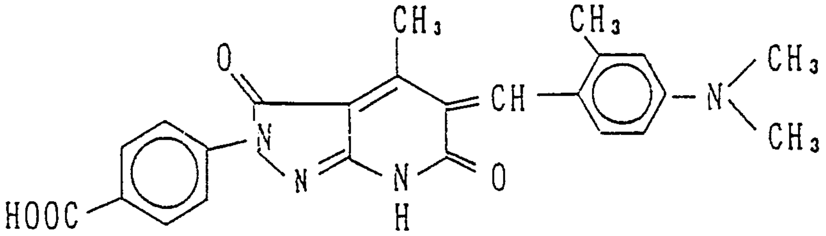
I－29



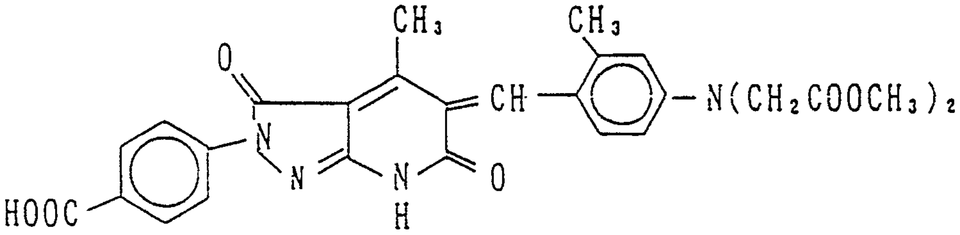
I－３０



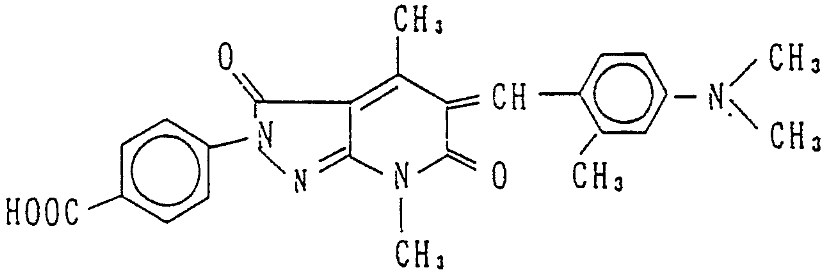
I－３１



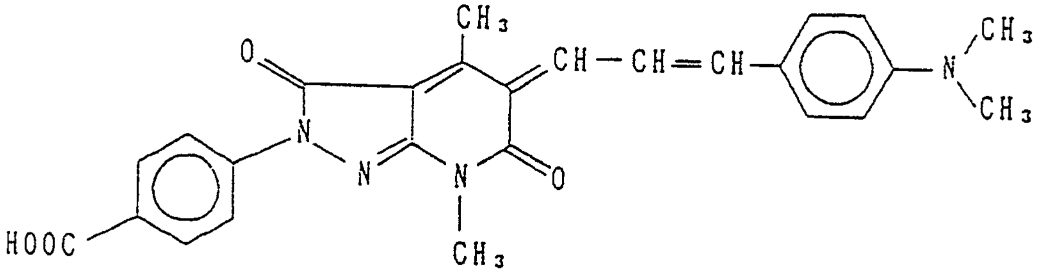
I－３２



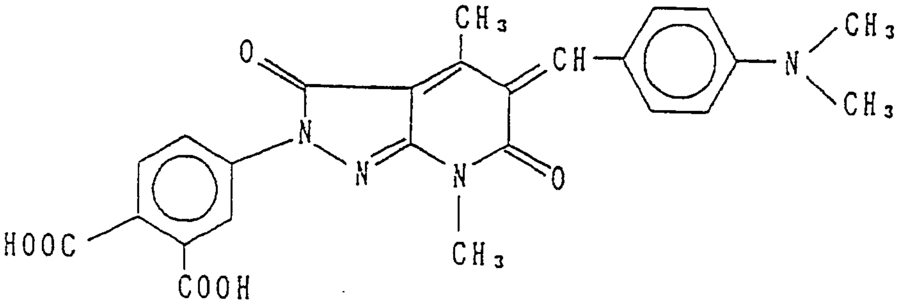
I－３３



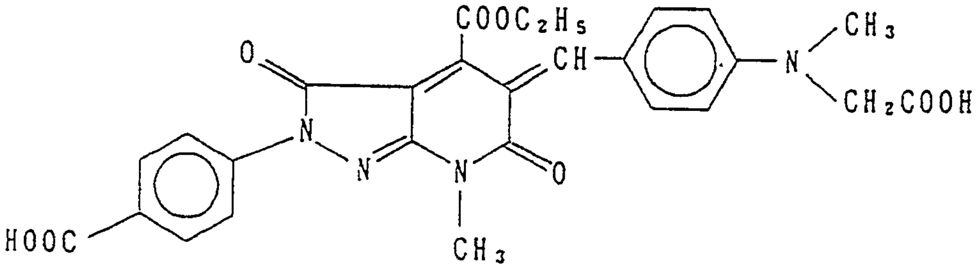
I－３４


CH₃
O
CH－CH═CH
N
CH₃
CH₃
N
N
N
O
HOOC
CH₃

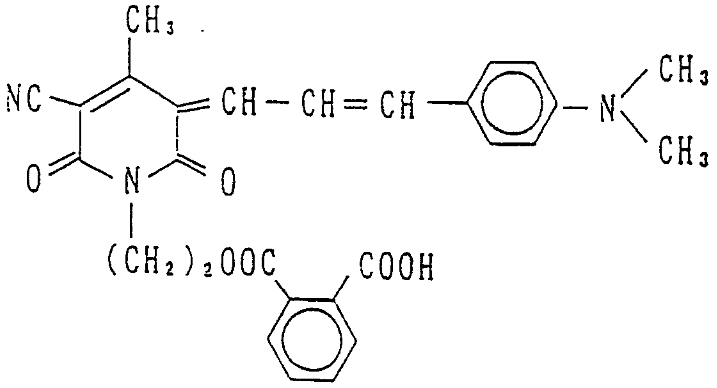
I－３５


CH₃
O
CH
N
CH₃
CH₃
N
N
N
O
HOOC
COOH
CH₃

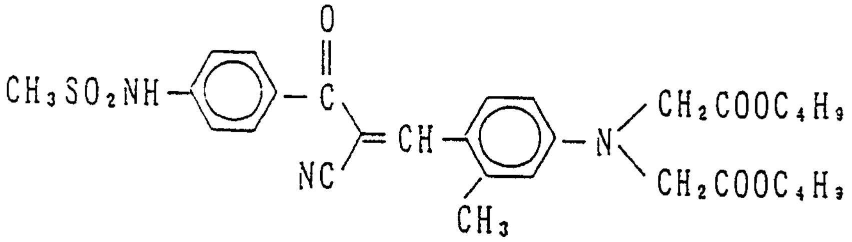
I－３６


COOC₂H₅
O
CH
N
CH₃
CH₂COOH
N
N
N
O
HOOC
CH₃

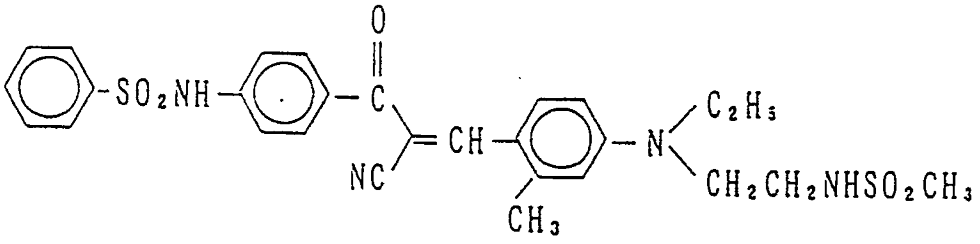
I - 37



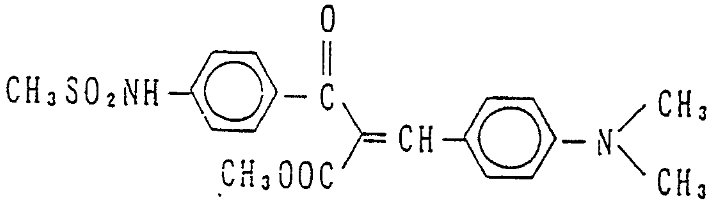
II - 1



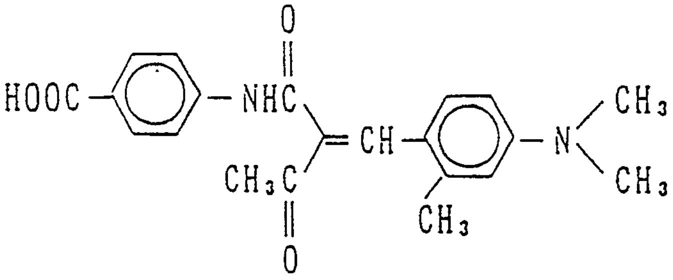
II - 2



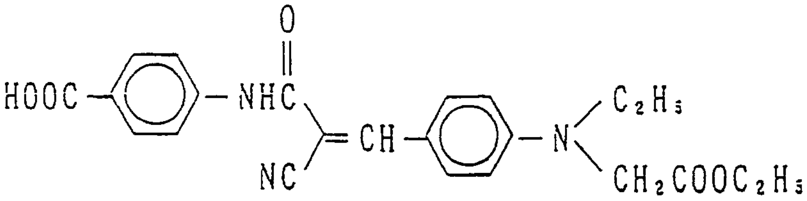
II - 3



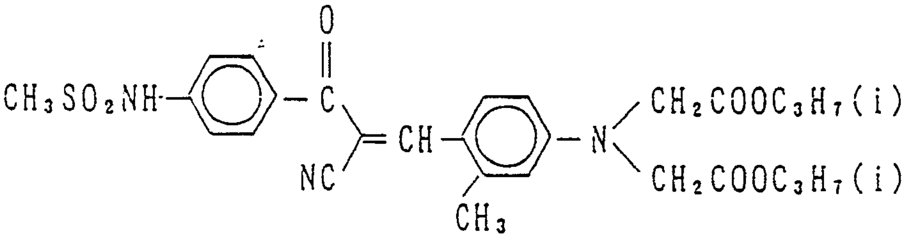
II - 4



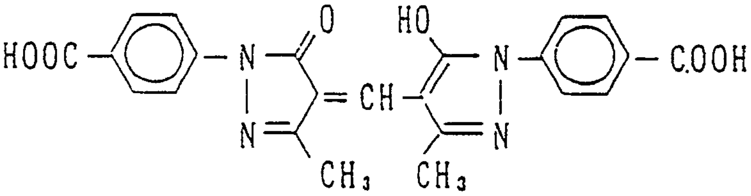
II - 5



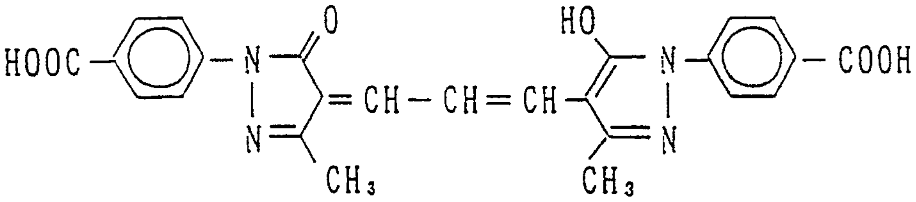
II - 6



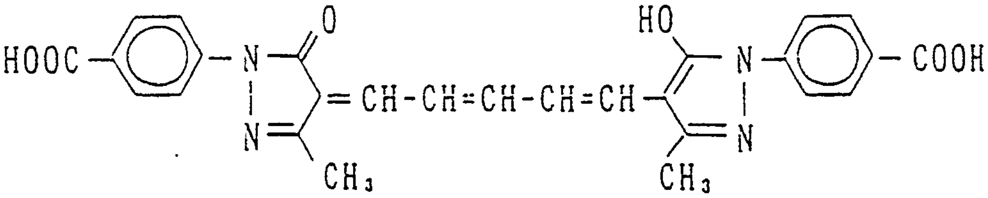
III - 1



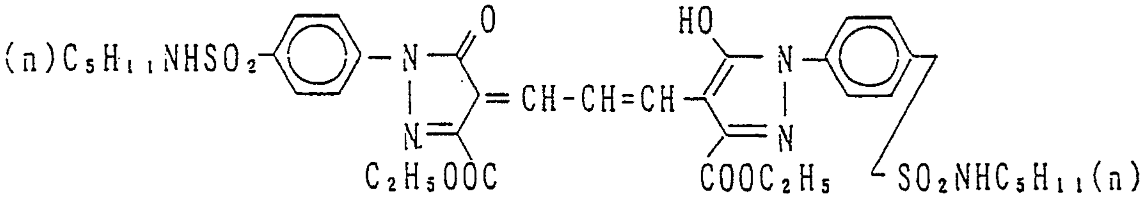
Ⅲ－2



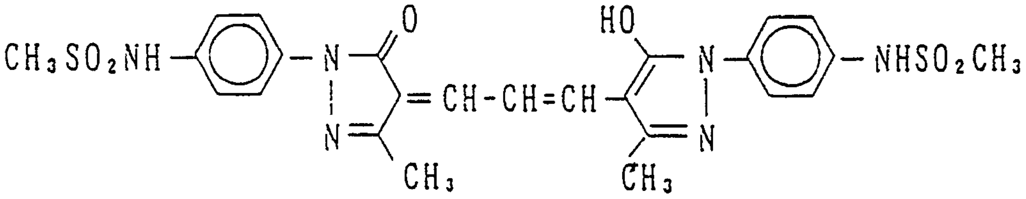
Ⅲ－3



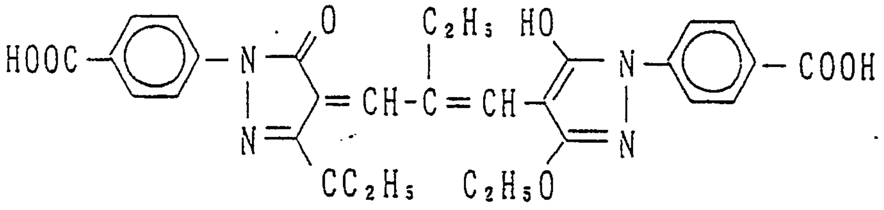
Ⅲ－4



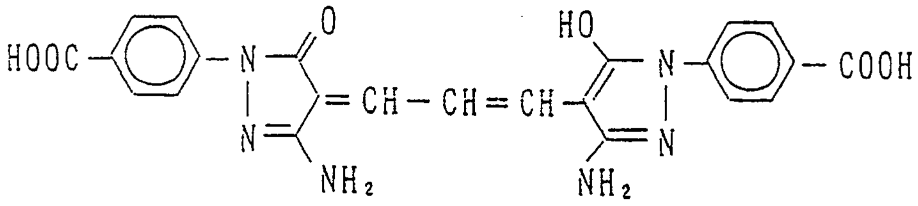
Ⅲ－5



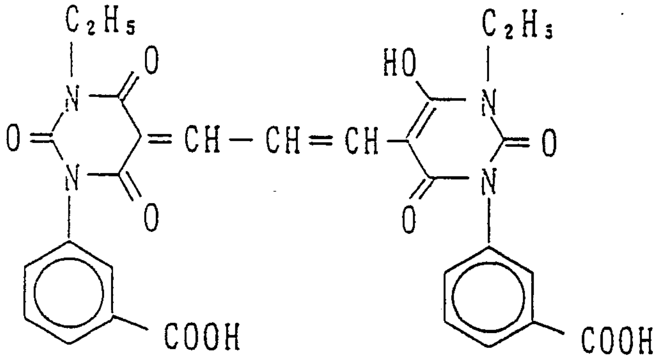
Ⅲ－6



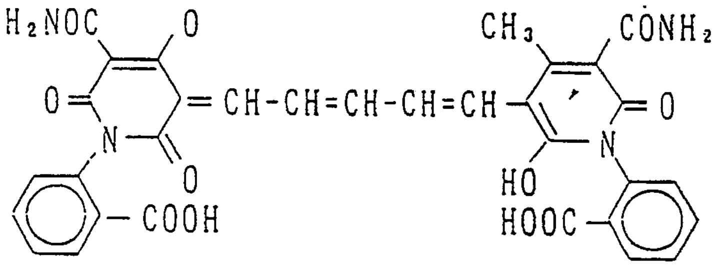
Ⅲ－7



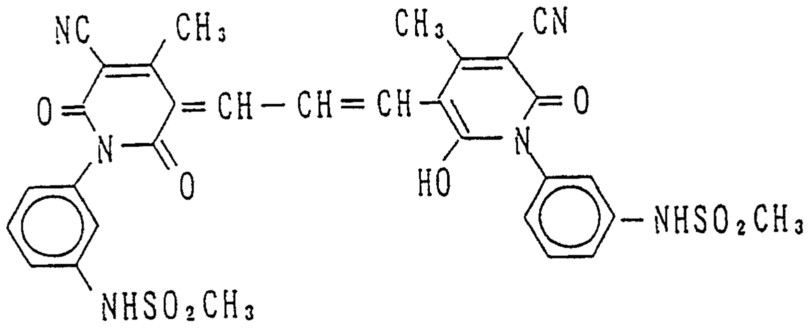
Ⅲ－8



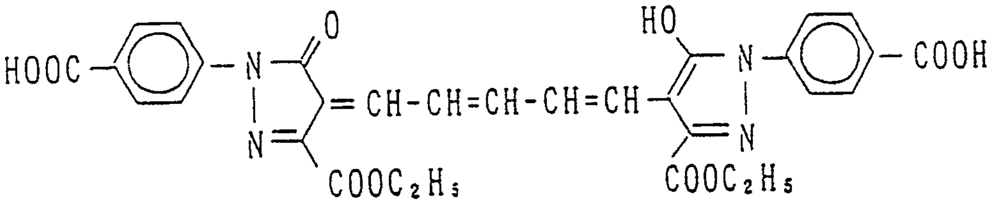
Ⅲ－9



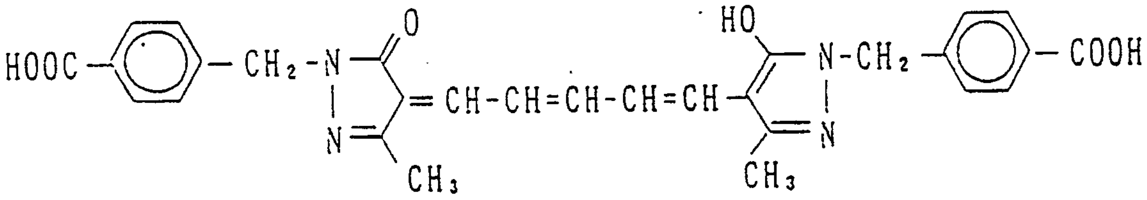
Ⅲ－１０



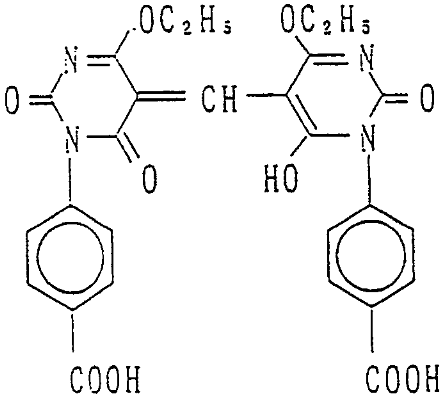
Ⅲ－１１



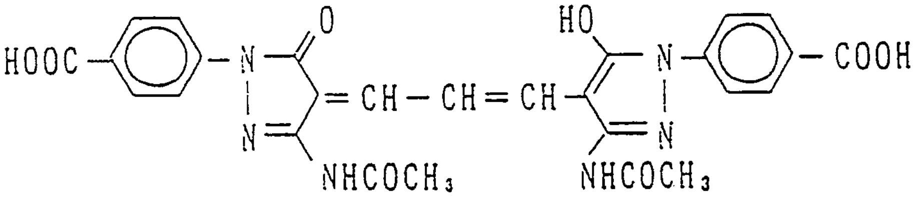
Ⅲ－１２



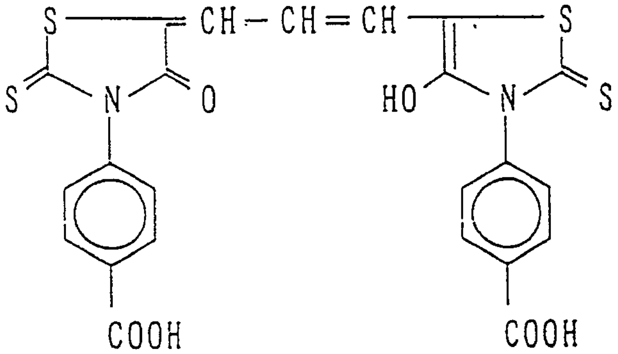
Ⅲ－１３


OC₂H₅
OC₂H₅
N
N
O
O
N
N
CH
O
HO
COOH
COOH

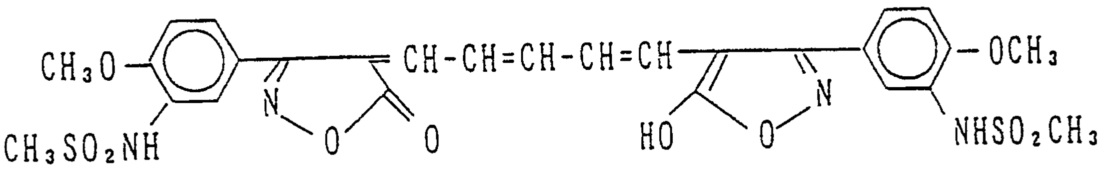
Ⅲ－１４


HOOC
O
HO
N
N
COOH
N
N
CH－CH＝CH
NHCOCH₃
NHCOCH₃

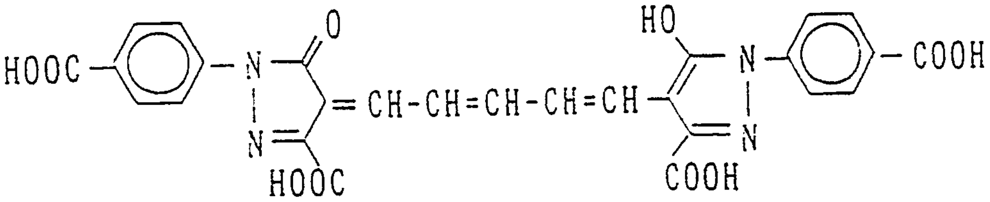
Ⅲ－１５


S
CH－CH＝CH
S
S
N
O
HO
N
S
COOH
COOH

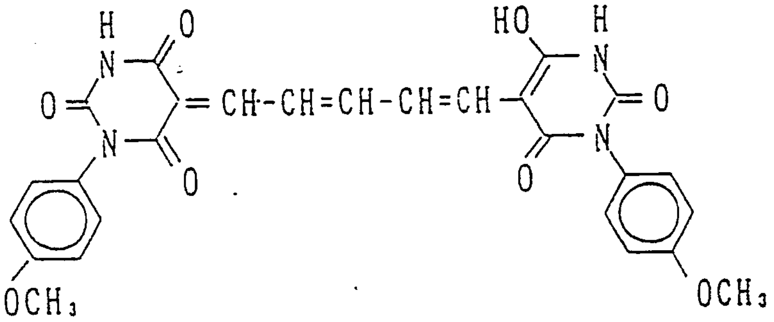
III－16



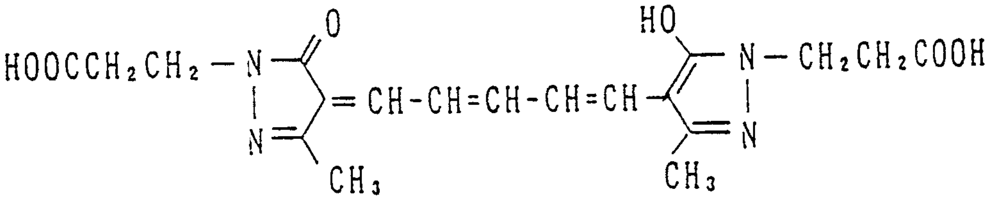
III－17



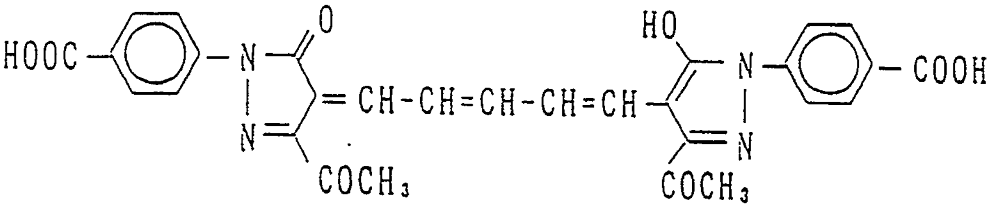
III－18



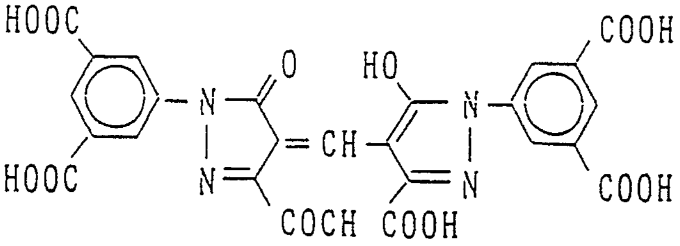
III－19



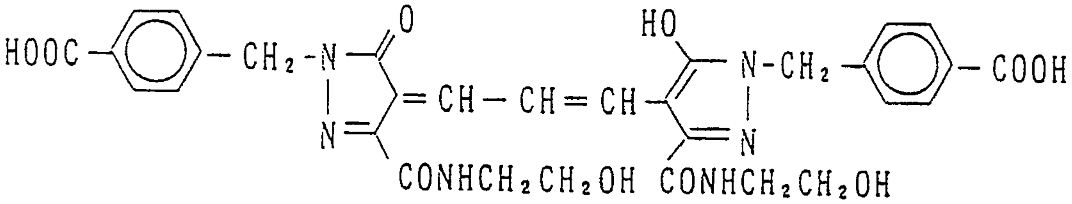
Ⅲ－２０



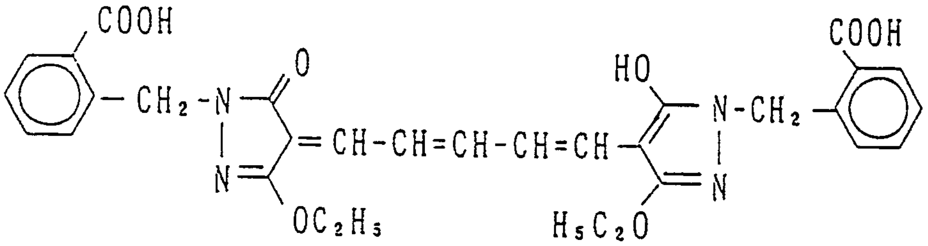
Ⅲ－２１



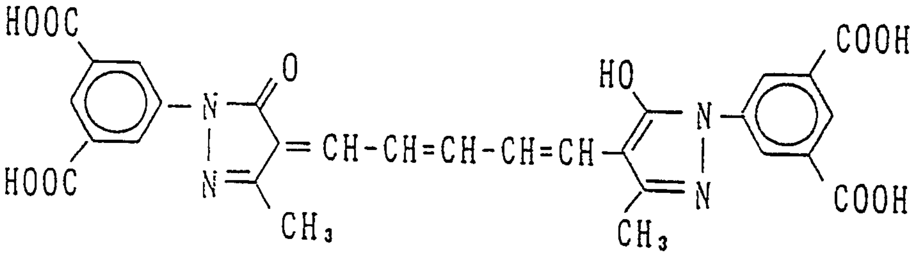
Ⅲ－２２



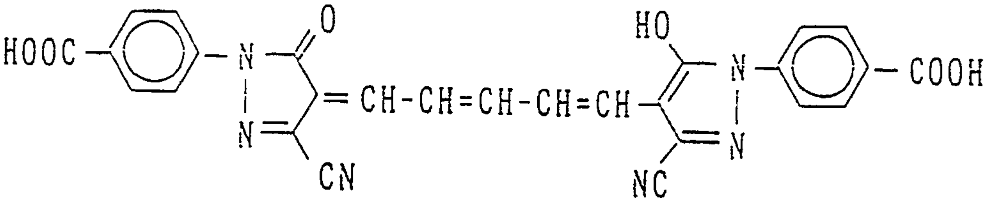
Ⅲ－２３



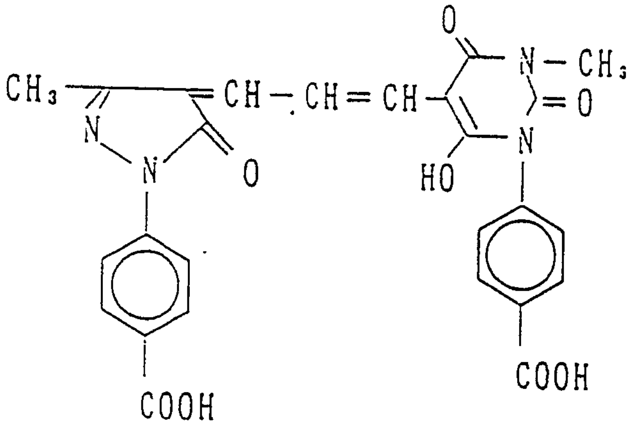
Ⅲ－２４



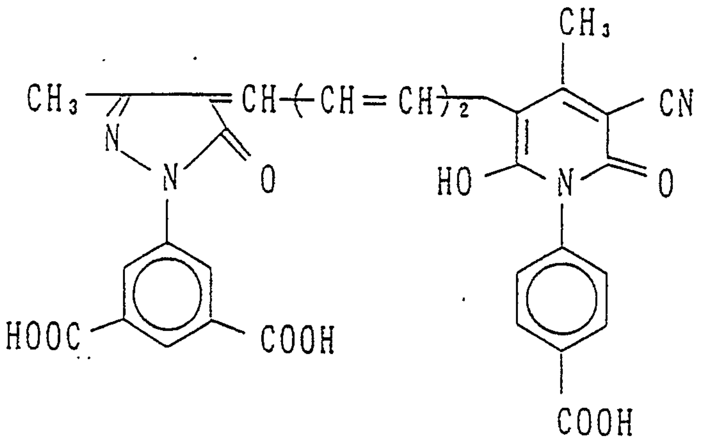
Ⅲ－２５



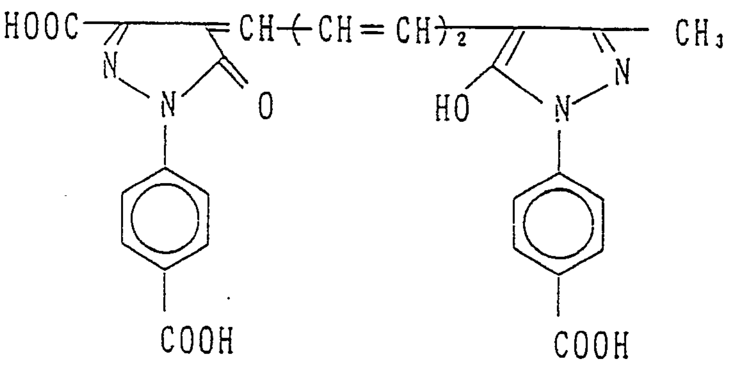
Ⅲ－２６



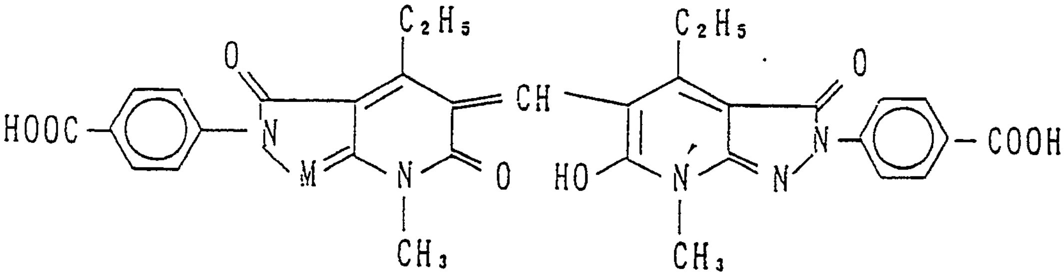
Ⅲ－２７


CH₃
CH₃
CH(CH=CH)₂
CN
N
N
O
HO
N
O
HOOC
COOH
COOH

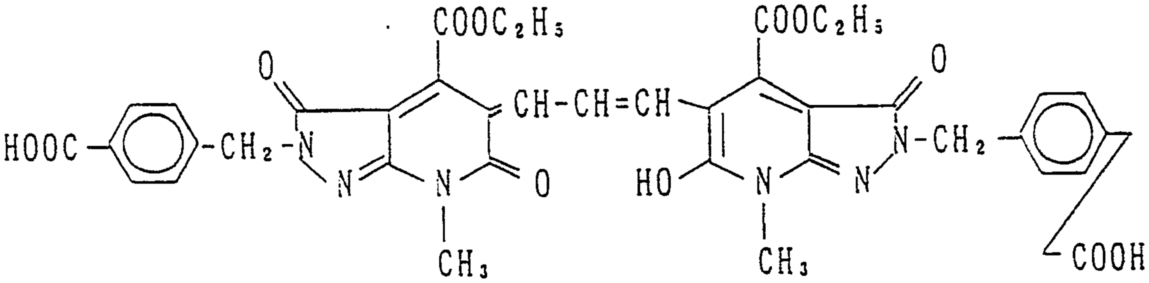
Ⅲ－２８


HOOC
CH(CH=CH)₂
CH₃
N
N
O
HO
N
N
COOH
COOH

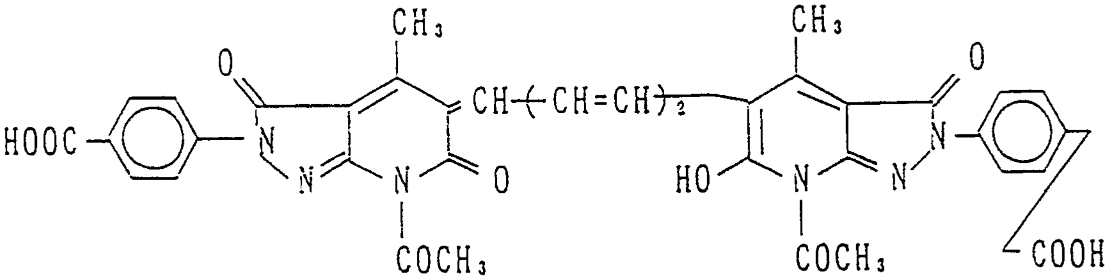
Ⅲ－２９


C₂H₅
C₂H₅
O
O
CH
HOOC
N
COOH
M
N
O
HO
N
N
N
CH₃
CH₃

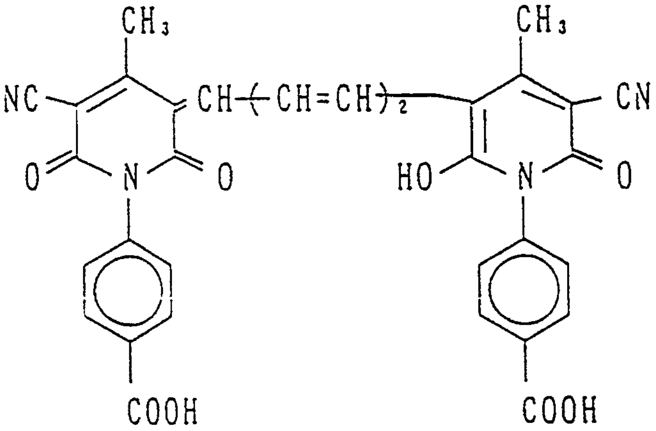
Ⅲ－３０



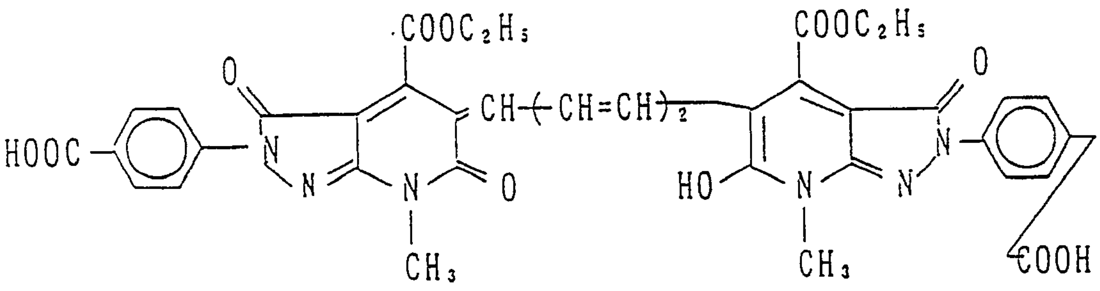
Ⅲ－３１



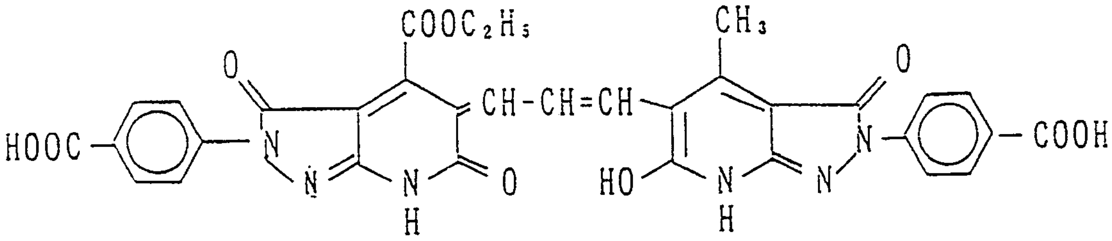
Ⅲ－３２



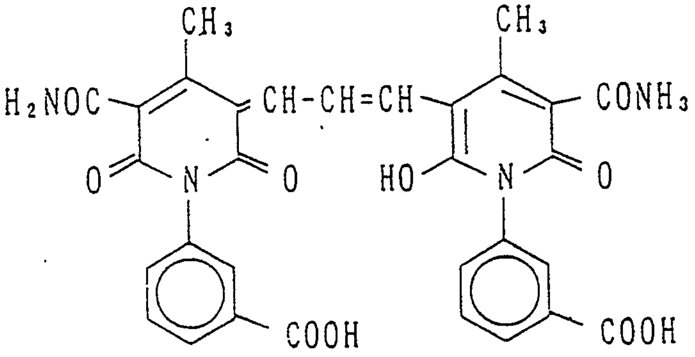
Ⅲ－３３



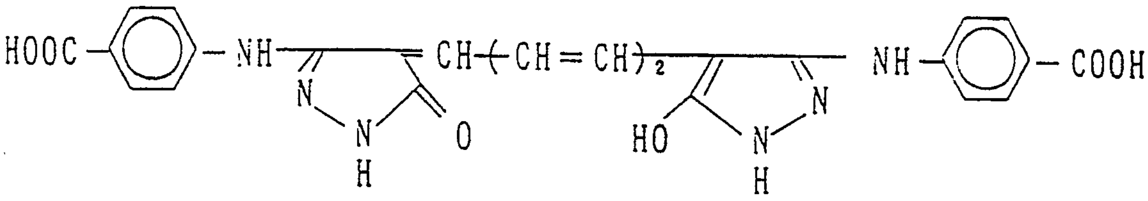
Ⅲ－３４



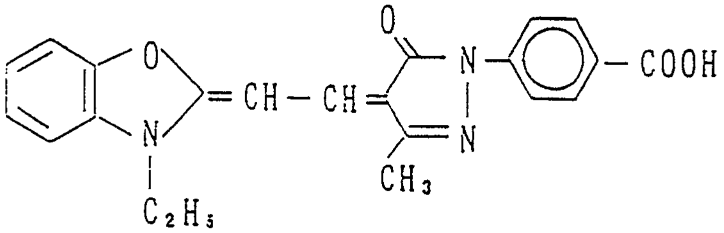
Ⅲ－３５



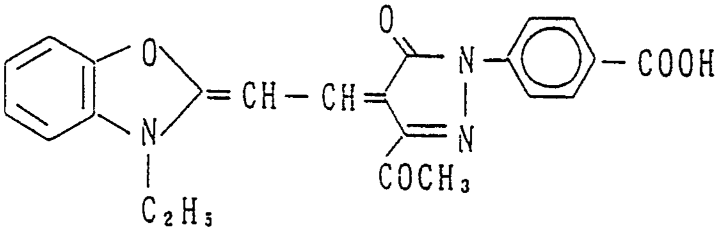
Ⅲ－３６


HOOC
NH
CH
CH=CH
2
N
N
H
O
HO
N
N
H
NH
COOH

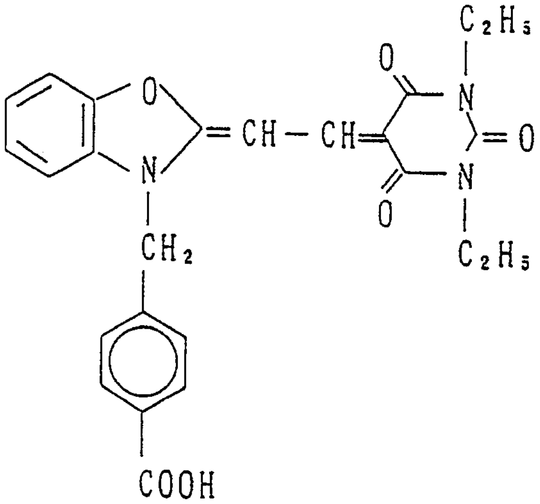
Ⅳ－１


O
N
C2H5
CH－CH
O
N
N
CH3
COOH

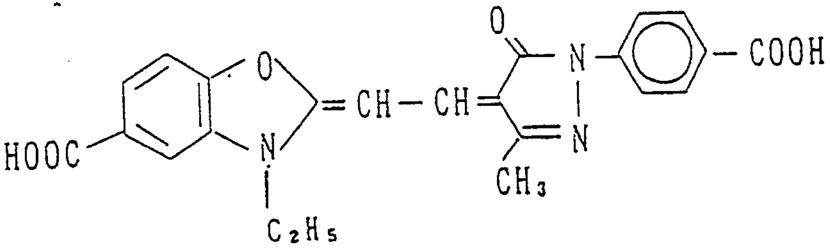
Ⅳ－２


O
N
C2H5
CH－CH
O
N
N
COCH3
COOH

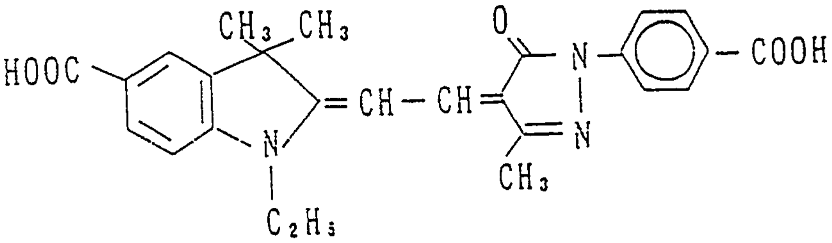
Ⅳ－３


O
N
CH2
COOH
CH－CH
O
O
N
N
O
C2H5
C2H5

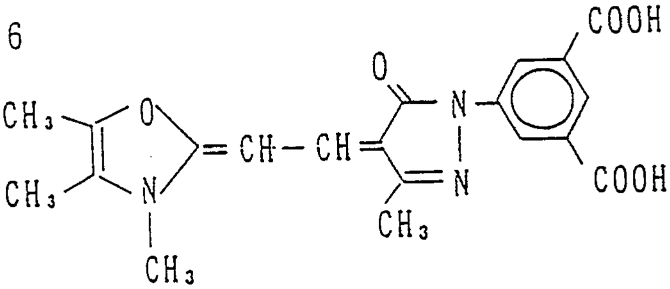
IV − 4



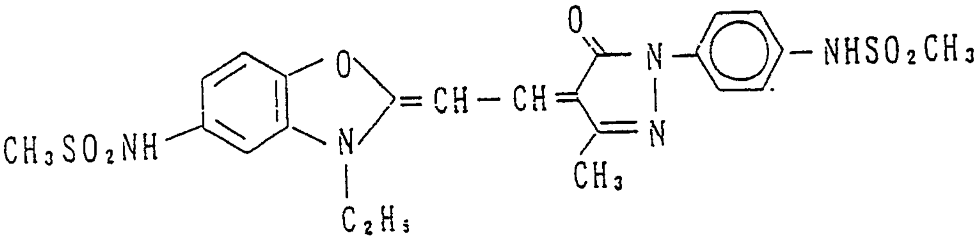
IV − 5



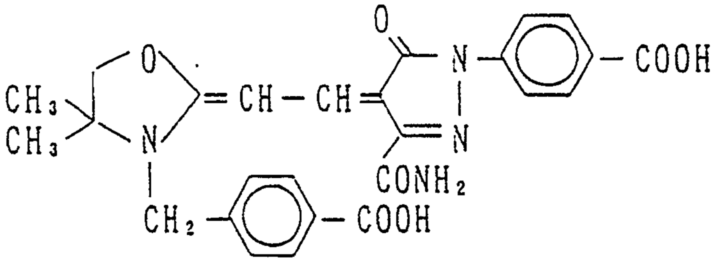
IV − 6



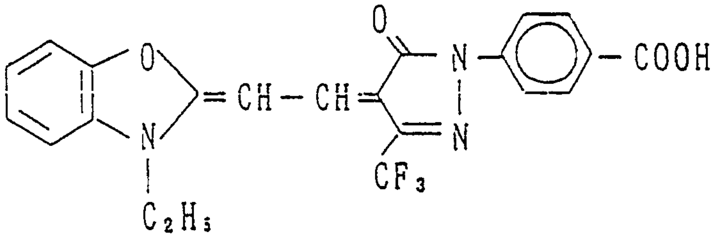
IV − 7



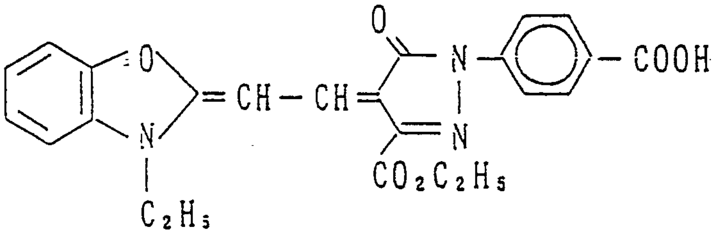
IV－8



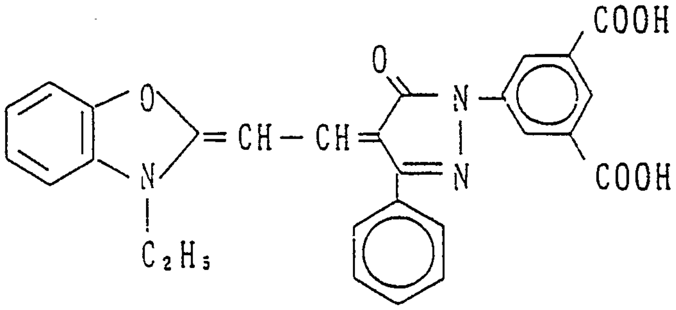
IV－9



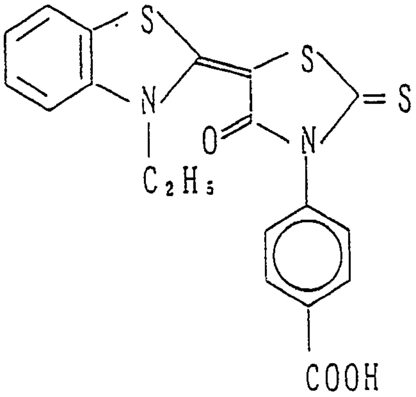
IV－10



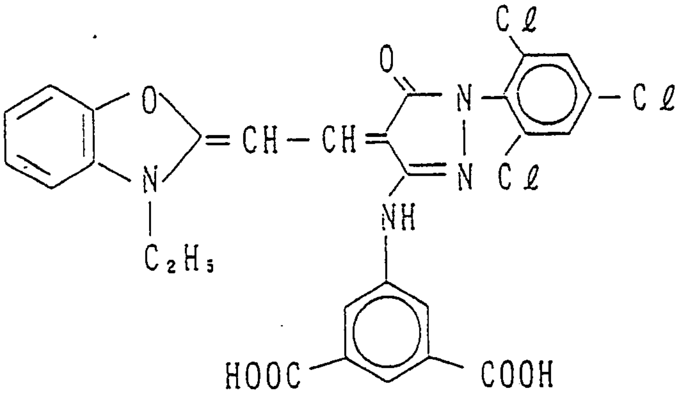
IV－11



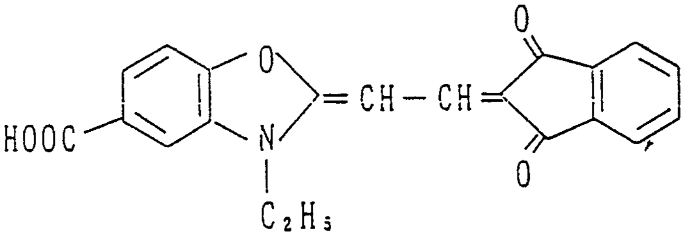
IV − 1 2



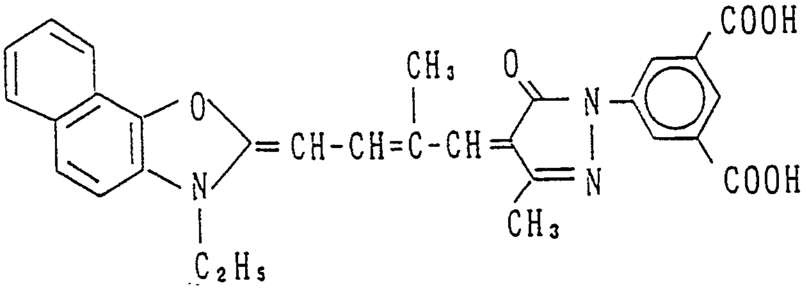
IV − 1 3



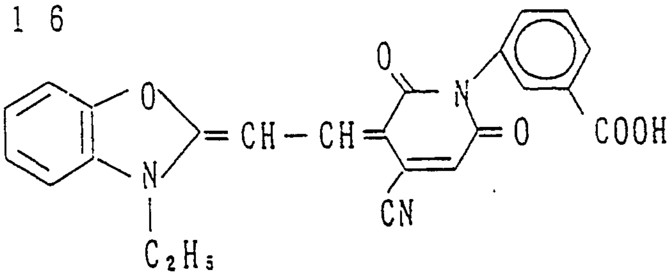
IV − 1 4



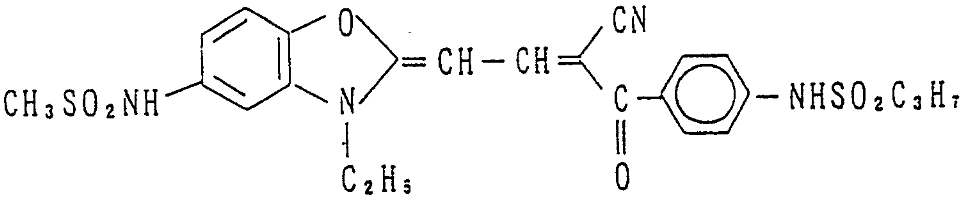
IV－１５



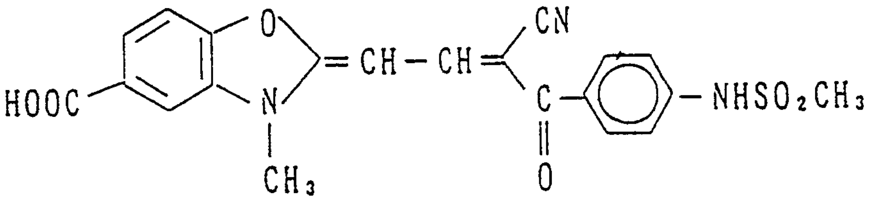
IV－１６



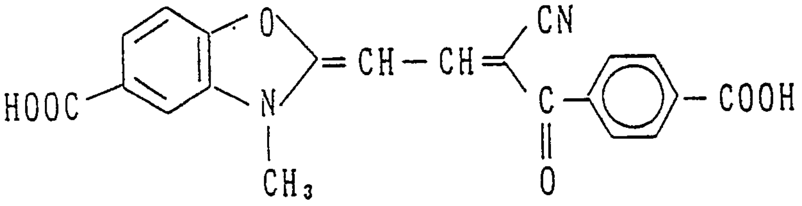
V－１



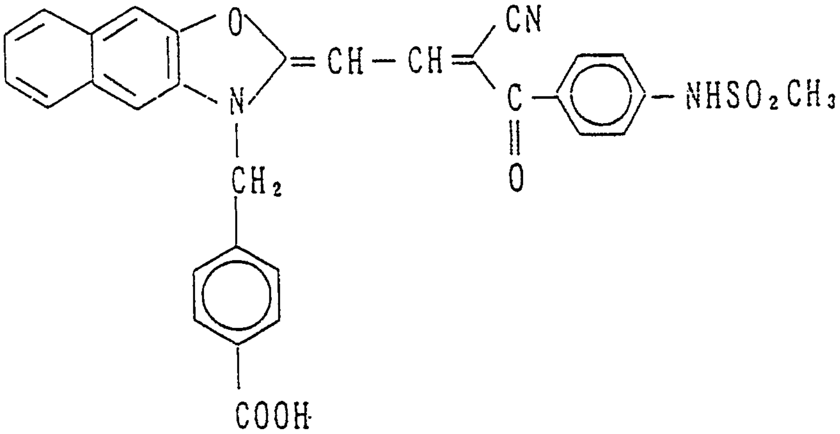
V－２



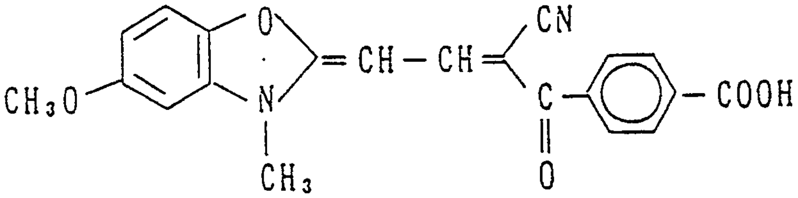
V − 3


O
N
CH₃
HOOC
CH − CH
CN
C
O
COOH

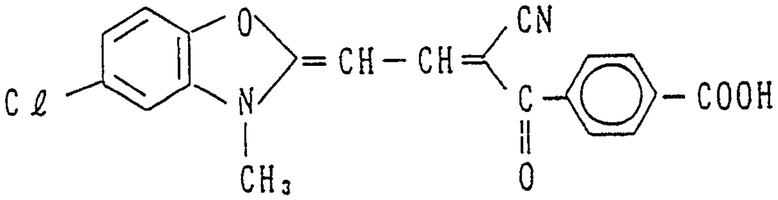
V − 4


O
N
CH₂
COOH
CH − CH
CN
C
O
NHSO₂CH₃

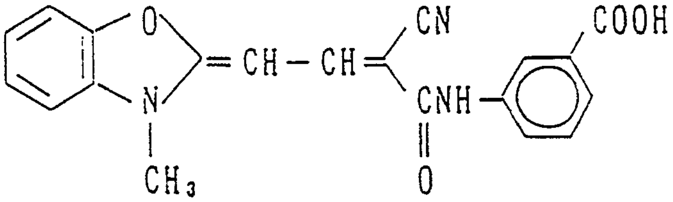
V − 5


O
N
CH₃
CH₃O
CH − CH
CN
C
O
COOH

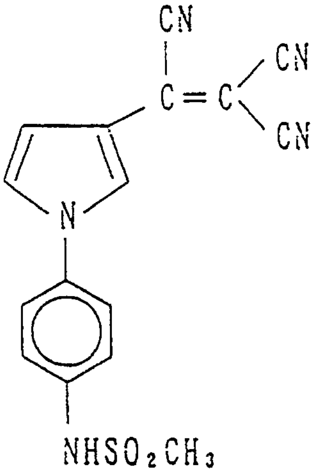
V − 6


O
N
CH₃
Cℓ
CH − CH
CN
C
O
COOH

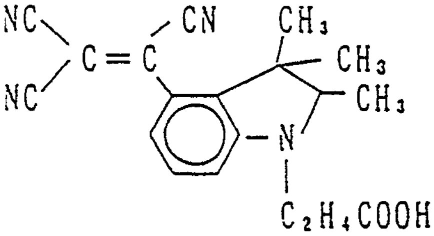
V − 7



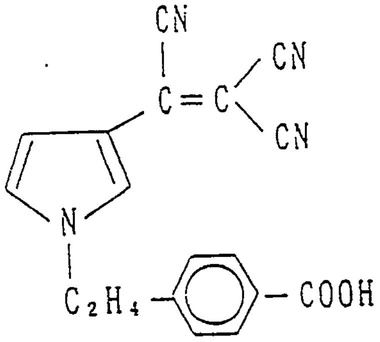
Ⅵ − 1



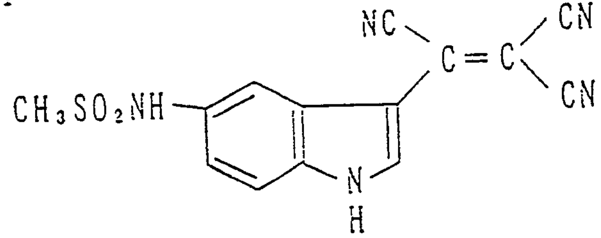
Ⅵ − 2



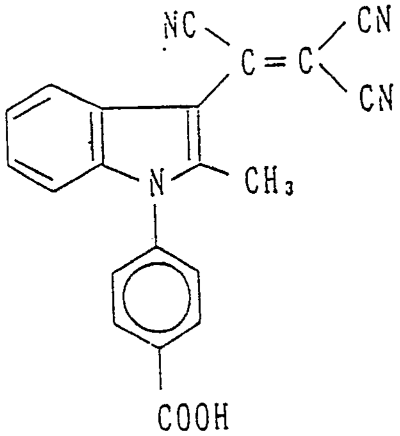
VI－3



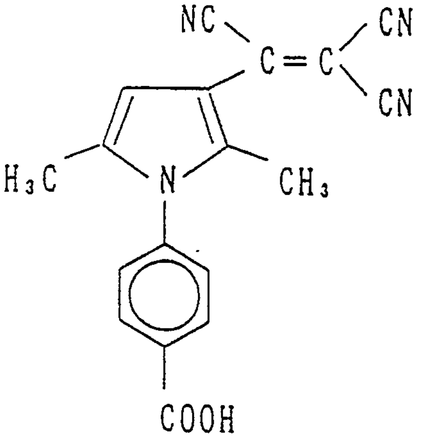
VI－4



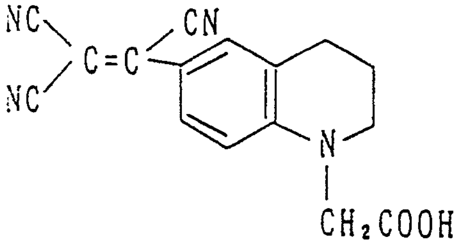
VI－5



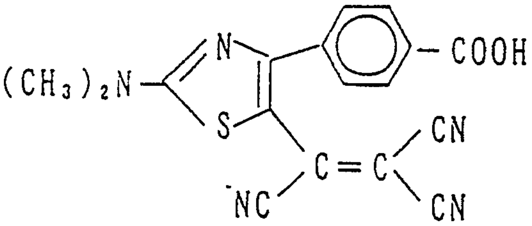
VI − 6


NC
CN
CN
C=C
H₃C
N
CH₃
COOH

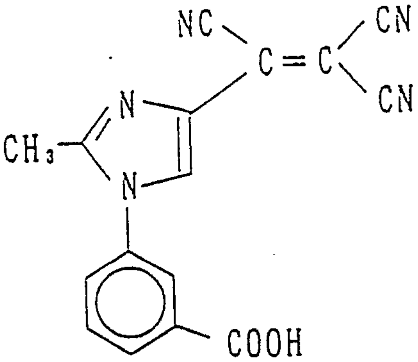
VI − 7


NC
CN
NC
C=C
N
CH₂COOH

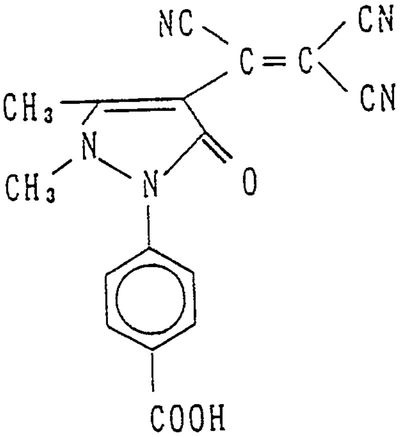
VI − 8


(CH₃)₂N
N
S
COOH
CN
C=C
NC
CN

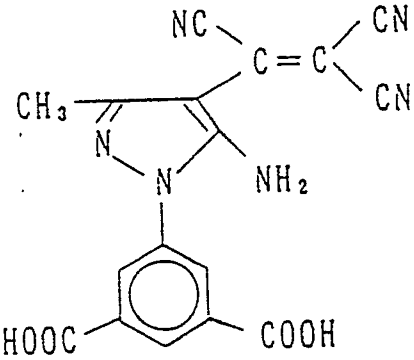
VI－9



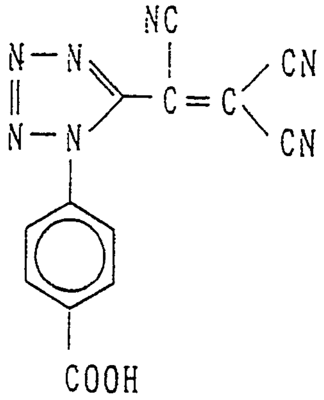
VI－10



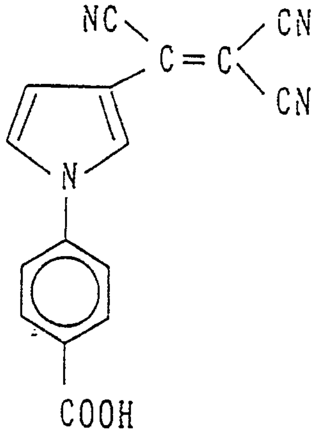
VI－11



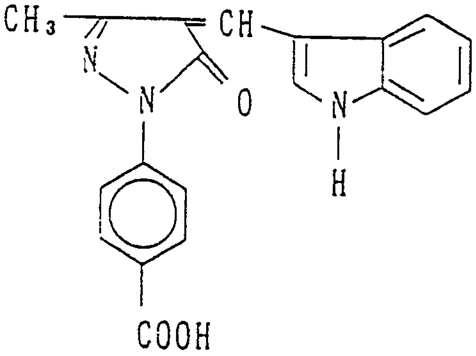
VI－12



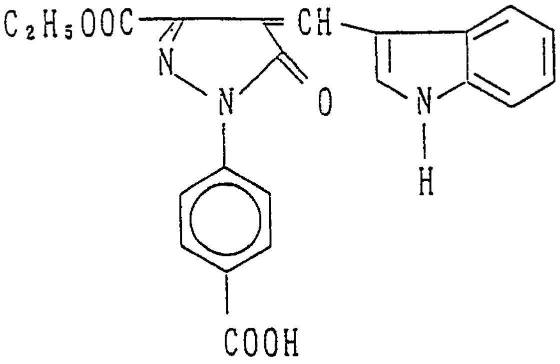
VI－13



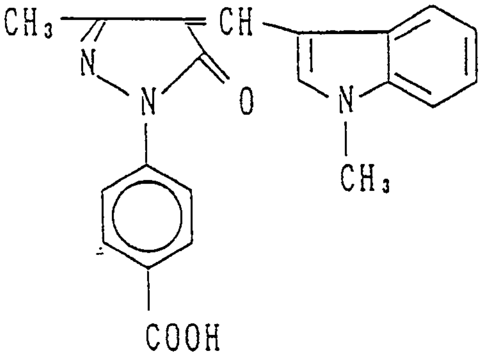
VII－1



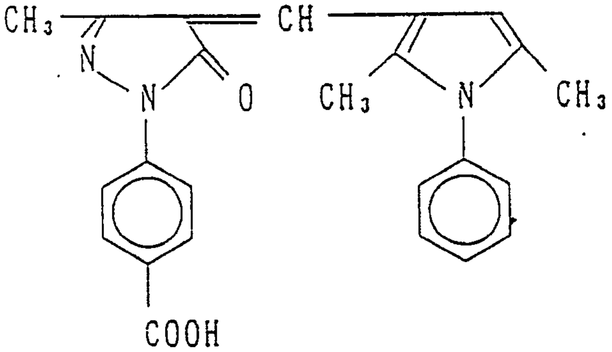
VII－2



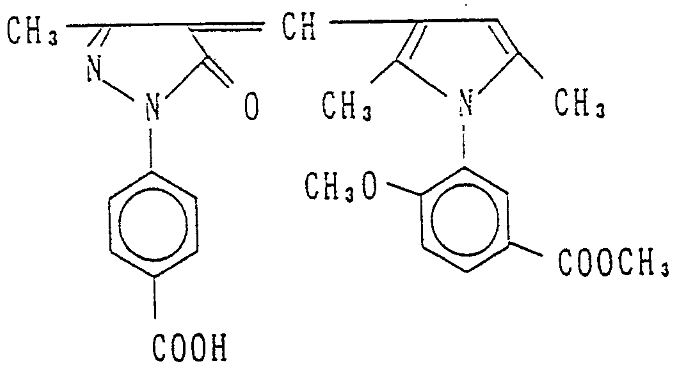
VII－3



VII－4



VII - 5



The dyes used in the present invention can be easily synthesized by or in accordance with the methods described in PCT International Publication No. WO 88/04794, European Patents 0274723A1, 276,566 and 299,435, JP-A-52-92716, JP-A-55-155350, JP-A-55-155351, JP-A-61-205934, JP-A-48-68623, JP-A-2-282244 (the term "JP-A" as used herein refers to a "published unexamined Japanese patent application"), U.S. Patents 2,527,583, 3,486,897, 3,746,539, 3,933,798, 4,130,429 and 4,040,841, and Japanese Patent Application Nos. 1-50874 and 1-307363.

The scope of the present invention is not limited to the dyes described above.

In the present invention, the solid disperse dye means a dye which cannot exist in the form of molecule in the desired colored layer because of the insufficient solubility of the dye. Therefore, it exists as a solid having such a size that it is not substantially diffusible in the layer.

The methods of preparation are described in PCT International Publication WO 88/04794, European Patent 0276566A1 and JP-A-63-197943. The method of grinding the dye with a mill and stabilizing it with a surface active agent and gelatin and the method of dissolving the dye in an alkaline solution and then precipitating it by reducing the pH are preferably used. However, the methods used in the present invention are not limited to these methods of preparation.

When the dye is added to an underlayer in the present invention, the size of grains which can be incorporated in the layer is limited, because the amount of gelatin coated in the underlayer is preferably 0.5 g/m^2 or less. If grains as large as 3 μm or more are added, the dye grains drop out of the dye layer. The grain size is therefore preferably less than 3 μm, more preferably 1 μm or less, and most preferably 0.5 μm or less.

Methods for removing large-sized grains from the dye include, but are not limited to, filtration and centrifugation.

The dye is preferably used in an amount of 5 to 400 mg/m^2, and more preferably in an amount of 10 to 250 mg/m^2.

In the present invention, the gelatin coating layer contained in the colored layer prepared as described above is used in an amount of 1 g/m^2 or less, preferably in an amount of 0.7 g/m^2 or less, and more preferably in an amount of 0.5 g/m^2 or less.

The amount of gelatin used in the above preparation can be appropriately adjusted so as to obtain the amount of gelatin used in the present invention, namely, 1 g/m^2 or less.

If the amount of all the hydrophilic colloids is increased, the amount of water contained in the film layers is increased in the processing solution, which results in unfavorable deterioration of the drying property. The amount of the hydrophilic colloids present on each side is therefore 2.5 g/m^2 or less, and preferably 2 g/m^2 or less.

In the photographic materials, hydrophilic colloids can be used in emulsion layers, surface protective layers, underlayers and back layers. The amount of all hydrophilic colloids in the present invention means the sum of all the hydrophilic colloids on each side of the photographic material.

In the present invention, the hydrophilic colloid layer means a layer containing a hydrophilic colloid, and all hydrophilic colloid layers means the total of those layers.

If the swelling rate of the hydrophilic colloid layer is high, a large amount of water is absorbed by the film layer in the processing solution, which results in unfavorable deterioration of the drying property. The swelling rate of all the hydrophilic colloid layers present is therefore preferably 200% or less, and more preferably 170% or less.

The swelling rate is determined by (a) incubating the photographic material at a temperature of 38°C at a relative humidity of 50% for 3 days, (b) measuring the thickness of the layers, (c) immersing the photographic material in distilled water at a temperature of 21°C for 3 minutes, and (d) measuring the thickness of the layers thus treated to express changes in thickness in percentage, compared to the thickness measured in step (b). However, if the swelling rate is too low, the processing solution may have difficulty penetrating the film layer which introduces the problems of deteriorated rate of development and rate of fixing. Accordingly, the swelling rate is required to be at least 120%.

As the hydrophilic colloid, gelatin is typical. However, other colloids which are known in the art as suitable for photographic material can be used.

As the silver halide emulsions used in the present invention, emulsions comprising silver bromide, silver iodobromide, silver iodochlorobromide or silver chlorobromide are preferably used.

The silver halide grains used in the present invention may have a regular crystal form such as a cubic, an octahedral or a tetradecahedral form, an irregular crystal form such as a spherical or a plate (tabular) form, or a composite form thereof. Further, mixtures of grains having various crystal forms may also be used. It is preferred, however, that silver halide grains having a regular crystal form are used.

The silver halide grains used in the present invention may have different phases in the interior and the surface layers, respectively, or may have homogeneous phases. Further, the grains in which latent images are mainly formed on the surfaces (for example, negative type emulsions) may be used, or the grains in which latent images are mainly formed in the interiors (for example, internal latent image type emulsions or previously fogged direct reversal type emulsions) may be used. Preferably, the grains in which latent images are mainly formed on the surfaces are used.

The silver halide emulsions used in the present invention are preferably plate form grain emulsions which contain grains having a thickness of 0.5 µm or less, preferably 0.3 µm or less, and a diameter of preferably 0.6 µm or more, and in which 50% or more of the projected area of all grains are composed of grains having a mean aspect ratio of at least 5, or monodisperse emulsions having a statistical coefficient of variation (the value $s/\overline{d}$ is obtained by dividing the standard deviation S by the diameter $\overline{d}$ in distribution of grains when the grain diameter is represented by the diameter of circles approximated by the projected area of the grains) of 20% or less. In addition, at least two kinds of plate form grain emulsions and monodisperse emulsions may be mixed.

Plate form grains are high in covering power, so that the amount of silver required to obtain a particular density is reduced. The plate form grains are therefore preferably used to decrease the amount of silver applied in X-ray photographic materials which typically are coated with a large amount of silver.

The photographic emulsions used in the present invention can be prepared according to the methods described in 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).

In forming the silver halide grain emulsions, solvents for silver halides are used to control the growth of the grains. Examples of such solvents include ammonia, potassium rhodanide, ammonium rhodanide and thioether compounds (for example, described in U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439 and 4,276,374), thione compounds (for example, described in JP-A-53-144319, JP-A-53-82408 and JP-A-55-77737) and amine compounds (for example, described in JP-A-54-100717).

Cadmium salts, zinc salts, thallium salts, iridium salts or complex salts thereof, rhodium salts or complex salts thereof, iron salts or complex salts thereof may be present during the formation of the silver halide grains or during physical ripening.

Gelatin can be advantageously used as a binder or as a protective colloid for the emulsion layers or the intermediate layers of the photographic material of the present invention. However, hydrophilic colloids other than gelatin may also be used. For example, various synthetic hydrophilic polymers can be used. Examples of such polymers include proteins such as gelatin compounds, graft polymers of gelatin and other polymers, albumin and casein; cellulose compounds such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfate; saccharide compounds such as sodium alginate and starch compounds; and homopolymers or copolymers such as polyvinyl alcohol, partially acetalized polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinylpyrazole.

As gelatin, acid-treated gelatin or enzyme-treated gelatin described in Bull. Soc. Sci. Phot. Japan, 16, 30 (1966), as well as general purpose lime-treated gelatin, may also be used. Further, hydrolyzed products of gelatin can be used.

In the photographic materials of the present invention, inorganic or organic hardening agents may be added to any hydrophilic colloid layers, including photographic light-sensitive layers or back layers. Specific examples of hardening agents include chromium salts, aldehydes (such as formaldehyde, glyoxal and glutaraldehyde) and N-methylol compounds (such as dimethylolurea). Active halogen compounds (such as 2,4-dichloro-6-hydroxy-1,3,5-triazine) and active vinyl compounds (such as 1,3-bis(vinylsulfonyl)-2-propanol, 1,2-bis(vinylsulfonylacetamido)ethane, bis(vinylsulfonylmethyl)ether and vinyl polymers having vinylsulfonyl groups at their side chains) are preferable because they rapidly harden the hydrophilic colloids such as gelatin to provide stable photographic characteristics. In particular, N-carbamoylpyridinium salts (such as (1-morpholinocarbonyl-3-pyridinio)methanesulfonate) and haloamidinium salts (such as 1-(1-chloro-1-pyridinomethylene)pyrrolidinium and 2-naphthalenesulfonate) are high in hardening rate.

The silver halide photographic emulsions used in the present invention may be spectrally sensitized with methine dyes or the like. Dyes used for spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. In particular, cyanine dyes, merocyanine dyes and complex merocyanine dyes are useful. Any nucleus usually employed in cyanine dyes as a basic heterocyclic nucleus can be present in these dyes. Such basic heterocyclic nuclei include pyrroline, oxazoline, thiazoline, pyrrole, oxazole, thiazole, selenazole, imidazole, tetrazole and pyridine nuclei; nuclei in which alicyclic hydrocarbon rings are fused together with these nuclei; nuclei in which aromatic hydrocarbon rings are fused together with these nuclei, such as indolenine, benzindolenine, indole, benzoxazole, naphthoxazole, benzothiazole, naphthothiazole, benzoselenazole, benzimidazole and quinoline nuclei. These nuclei may have substituent groups on the carbon atoms.

5-Membered or 6-membered heterocyclic nuclei such as pyrazoline-5-one, thiohydantoin, 2-thiooxazolidine-2,4-dione, thiazolidine-4-dione, rhodanine and thiobarbituric acid nuclei may be present in the merocyanine dyes or the complex merocyanine dyes as nuclei that have a ketomethylene structure.

These sensitizing dyes may be used separately or in combination. In particular, they are frequently used in combination for supersensitization. The emulsions may contain dyes which themselves have no spectral sensitization action, or substances which do not substantially absorb visible light and exhibit supersensitization. For example, the emulsions may contain aminostilbene compounds substituted with nitrogen-containing heterocyclic nucleus groups (for example, described in U.S. Patents 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensation products (for example, described in U.S. Patent 3,743,510), cadmium salts and azaindene compounds. The combination of the sensitizing dyes described in U.S. Patents 3,615,613, 3,615,641, 3,617,295 and 3,635,721 is particularly useful.

The silver halide photographic emulsions used in the present invention may contain various compounds to prevent fogging during manufacturing stages, storage or photographic processing of the light-sensitive materials or to stabilize photographic properties thereof. Specifically, many compounds known as antifoggants or stabilizers can be added. Examples of such compounds include azoles such as benzothiazolium salts, nitroindazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles and mercaptotetrazoles (particularly, 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; thioketo compounds such as oxazolinethione; azaindenes such as triazaindenes, tetraazaindenes (particularly, 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes) and pentaazaindenes; benzenethiosulfonic acid; benzenesulfinic acid; and benzenesulfonic acid amide.

The photographic material of the present invention may contain at least one surface active agent for various purposes such as for use as a coating assistant, the prevention of static charge, improvements in slip properties, the promotion of emulsification and dispersing, the prevention of adhesion and improvements in photographic characteristics (for example, development acceleration, contrast enhancement and sensitization).

In the photographic materials of the present invention, the hydrophilic colloid layers may contain water-soluble dyes as filter dyes, for the purpose of preventing irradiation or halation or for other various purposes. Such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, anthraquinone dyes and azo dyes. In addition, cyanine dyes, azomethine dyes, triarylmethane dyes and phthalocyanine dyes are also useful. Oil-soluble dyes emulsified by oil-in-water dispersing methods can also be added to the hydrophilic colloid layers.

The present invention can be applied to a multilayer multicolor photographic material having at least two different color sensitivities on a support. The multilayer color photographic material usually has at least one layer for each red-sensitive, green-sensitive and blue-sensitive emulsion layer on the support. The order of arrangement of these layers can be arbitrarily selected as required. The preferred order of the layers arranged from the support side is the red-sensitive layer, the green-sensitive layer and the blue-sensitive layer, the blue-sensitive layer, the green-sensitive layer and the red-sensitive layer, or the blue-sensitive layer, the red-sensitive layer and the green-sensitive layer.

Emulsion layers having the same color sensitivity but which differ from each other in light sensitivity may be formed and used in a combination of at least two emulsion layers to improve the range of sensitivity, or may be formed in a three-layer structure to improve the graininess. A light-insensitive layer may be interposed between two or more layers having the same color sensitivity. Between emulsion layers having the same color sensitivity, an emulsion layer having a different color sensitivity may be inserted. A reflecting layer of a finely divided silver halide or the like may be provided under a high-sensitive layer, particularly under a high-sensitive blue-sensitive layer to improve the sensitivity.

In general, the red-sensitive emulsion layer contains a cyan-forming coupler, the green-sensitive emulsion layer contains a magenta-forming coupler, and the blue-sensitive emulsion layer contains a yellow-forming coupler. However, different combinations may also be used if circumstances require. For example, the red-sensitive layers may be incorporated into the photographic material of the present invention to use for pseudo color photographs or semiconductor laser exposure.

In the photographic materials of the present invention, the photographic emulsion layers and other layers are coated on a flexible support usually employed such as a plastic film, paper or cloth, or a rigid support such as a glass, a ceramic or a metal. Useful flexible supports include films formed of semisynthetic or synthetic polymers such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate and polycarbonates, and paper coated or laminated with a baryta layer or an α-olefin polymer (for example, polyethylene, polypropylene or an ethylene-butene copolymer). The supports may be colored by using dyes or pigments. They may be colored black to shield the light.

In order to improve adhesion of the support with the hydrophilic colloid layer, the surface of the support is preferably subjected to corona discharge treatment, glow discharge treatment or ultraviolet irradiation treatment. The support may be provided with an underlayer composed of a styrene-butadiene latex, a vinylidene chloride latex or the like, and a gelatin layer may be further formed thereon.

In printing sensitive materials, it is desirable to use a hydrophobic polymer as an underlayer to prevent deterioration of dimensional stability caused by absorption of water by the support on processing. A vinylidene chloride polymer is preferably used as such a polymer.

Further, an underlayer comprising an organic solvent containing a polyethylene swelling agent and gelatin may be provided. These underlayers can further improve adhesion with the hydrophilic colloid layer by adding a surface treatment.

Various known coating methods such as a dip coating method, a roller coating method, a curtain coating method and an extrusion coating method can be utilized for the coating of the photographic emulsion layers and other hydrophilic colloid layers. Multilayers may be simultaneously formed by coating methods described in U.S. Patents 2,681,294, 2,761,791, 3,526,528 and 3,508,947, as required.

The present invention can be applied to various color photographic materials and black-and-white materials. Typical examples thereof include negative color films for movies, reversal color films for slides or for television, color paper, color positive films, color reversal paper, color diffusion transfer photographic materials and thermal developing type color photographic materials.

The present invention can also be applied to black-and-white materials such as photographic materials for X-ray photography by employing mixtures of three color couplers described in Research Disclosure, No. 17123 (July, 1978) or black color developing couplers described in U.S. Patent 4,126,461 and British Patent 2,102,136. The present invention can also be applied to films for plate making such as lithographic films and scanner films, direct X-ray films or indirect medical or industrial X-ray films, negative black-and-white films, black-and-white photographic paper, COM or normal microfilms, silver salt diffusion transfer photographic materials and print-out type photographic materials.

When the photographic materials of the present invention are applied to the color diffusion transfer photographic method, film units of a peel-apart type, an integrated type as described in JP-B-46-16356 (the term "JP-B" as used herein refers to an "examined Japanese patent publication"), JP-B-48-33697, JP-A-50-13040 and British Patent 1,330,524, or a non-peeling type structure as described in JP-A-57-119345 can be formed.

The photographic materials of the present invention can be exposed by various means. Any light source emitting radiation corresponding to the light-sensitive wavelengths of the photographic materials can be used as an illuminating light source or a write-in light source. Natural light (sunlight), an incandescent lamp, a halogen atom-enclosed lamp, a mercury lamp, a fluorescent lamp and a flash light source such as an electronic flash or a metal burning flash valve are generally used. A gas, a dye solution, a semiconductor laser, a light emitting diode and a plasma light source which emit light in the wavelength range extending from the ultraviolet region to the infrared region can also be used. Further, fluorescence emitted from a fluorescent material excited with electron beams or X-rays (for example, CRT and fluorescent sensitized paper), and exposure means in which a linear or plane light source is combined with microshutter arrays utilizing lead titanium zirconate (PLZT) doping a liquid crystal display (LCD) or lanthanum can also be used. The spectral distribution used for exposure is adjustable with color filters, if necessary.

Any of known methods and processing solutions which are described in, for example, Research Disclosure, No. 176, pages 28 to 30 (RD-17643) can be applied to the photographic processing of the photographic materials of the present invention. This photographic processing may be either photographic processing for forming silver images (black-and-white photographic processing) or photographic processing for forming dye images (color photographic processing), depending on their purposes. The processing temperature is usually selected within the range of 18 to 50°C.

Developing solutions used for black-and-white photographic processing may contain conventional developing agents such as dihydroxybenzenes (for example, hydroquinone), 3-pyrazolidones (for example, 1-phenyl-3-pyrazolidone) and aminophenols (for example, N-methyl-p-aminophenol). These developing agents may be used separately or in combination. In addition, the developing solutions generally contain conventional preservatives, alkali agents, pH buffers and antifoggants, and may further contain dissolving assistants, color tone agents, development accelerators (for example, quaternary salts, hydrazine and benzyl alcohol), surface active agents, antifoaming agents, water softeners, hardening agents (for example, glutaraldehyde) and tackifiers (viscosity imparting agents) as so desired.

Any of known processing methods for forming positive silver images by reverse development can be used for the black-and-white reversal photographic processing of the photographic materials of the present invention. The processing can be conducted by using conventional processing solutions. The processing temperature is usually selected within the range of 18 to 65°C. However, the temperature may be lower than 18°C or may exceed 65°C.

Reversal processing generally comprises the following stages:

First Development - Washing - Bleaching - Cleaning - Whole Exposure - Second Development - Fixing - Washing - Drying.

Developing solutions for the first development for black-and-white photographic processing may contain conventional developing agents such as dihydroxybenzenes (for example, hydroquinone), 3-pyrazolidones (for example, 1-phenyl-3-pyrazolidone), aminophenols (for example, N-methyl-p-aminophenol), 1-phenyl-3-pyrazolines, ascorbic acid and heterocyclic compounds such as a product obtained by condensation of a 1,2,3,4-tetrahydroquinoline ring and an indolene ring which is described in U.S. Patent 4,067,872. These developing agents may be used separately or in combination. In particular, it is preferred to use pyrazolidones and/or aminophenols in combination with dihydroxybenzenes. In addition, the developing solutions for the first development generally contain conventional preservatives, alkali agents, pH buffers and antifoggants, and may further contain dissolving assistants, color tone agents, development accelerators, surface active agents, antifoaming agents, water softeners, hardening agents and tackifiers, as required. The photographic materials of the present invention are usually processed with first developing solutions containing sulfite ions in an amount of 0.15 mol/liter as the preservative.

The pH of the developing solution for the first development is preferably 8.5 to 11, and more preferably 9.5 to 10.5.

Solvents for silver halides such as NaSCN are used in an amount of 0.5 to 6 g/liter in the first developing solutions.

As second developing solutions, ordinary black-and-white processing solutions can be used. Specifically, they have the same composition as with the first developing solutions with the exception that the solvents for silver halides are removed therefrom. The pH of the second developing solutions is preferably 9 to 11, and more preferably 9.5 to 10.5.

Bleaching agents such as potassium bichromate or cerium sulfate are used in bleaching solutions.

Thiosulfates or thiocyanates are preferably used in fixing solutions, which may contain water-soluble aluminum salts, if necessary.

As a special processing form, the developing agent may be added to the photographic material, for example, to the emulsion layer, and the photographic material containing the developing agent may be processed in an alkali solution to develop it. Of the developing agents, the hydrophobic agents can be added to the emulsion layers by various methods described in Research Disclosure, No. 169 (RD-16928), U.S. Patent 2,739,890, British Patent 813,253 and West German Patent 1,547,763.

As the fixing solutions, fixing solutions having the composition generally used can be employed. As the fixing agents, organic sulfur compounds whose fixing effect is known can be used in addition to thiosulfates and thiocyanates. The fixing solutions may contain water-soluble aluminum salts as hardening agents.

Color developing solutions used for processing the photographic materials of the present invention are preferably aqueous alkaline solution mainly containing aromatic primary amine color developing agents.

Although the aminophenol compounds are also useful as the color developing agents, p-phenylenediamine compounds are preferably used. Typical examples thereof include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, and sulfates, hydrochlorides and p-toluenesulfonates thereof. These diamines are preferably used in the form of salts, because they are generally more stable in the form of salts than in the free state.

The color developing solutions generally contain pH buffers such as alkali metal carbonates, borates and phosphates, and developing inhibitors or antifoggants such as bromides, iodides, benzimidazoles, benzothiazoles and mercapto compounds. Further, the color developing solutions may contain various preservatives such as hydroxylamines, dialkylhydroxylamines, hydrazines, triethanolamine, triethylenediamine and sulfites, organic solvents such as triethanolamine and diethylene glycol, development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines, dye forming couplers, competitive couplers, nucleating agents such as sodium borohydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, tackifiers, various chelating agents represented by aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, and antioxidants described in German Patent Application (OLS) 2,622,950, as required.

In processing reversal color photographic materials, color development is usually conducted after black-and-white development. Black-and-white developing solutions used here may contain known black-and-white developing agents such as dihydroxybenzenes (for example, hydroquinone), 3-pyrazolidones (for example, 1-phenyl-3-pyrazolidone) and aminophenols (for example, N-methyl-p-aminophenol). These developing agents may be used separately or in combination.

Not only the color developing solutions, but also any photographic developing methods can be applied to the photographic materials of the present invention. Developing agents used in developing solutions include dihydroxybenzene developing agents, 1-phenyl-3-pyrazolidone developing agents and p-aminophenol developing agents. These developing agents may be used alone or in combination (for example, 1-phenyl-3-pyrazolidones and dihydroxybenzenes, or p-aminophenols and dihydroxybenzenes). Furthermore, the photographic materials of the present invention may be processed by an infectious developing solution containing hydroquinone and a sulfite ion buffer such as carbonyl bisulfite.

Examples of the dihydroxybenzene developing agents include hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone and 2,5-dimethylhydroquinone. The 1-phenyl-3-pyrazolidone developing agents include 1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone, 4-hydroxymethyl-4'-methyl-1-phenyl-3-pyrazolidone and 4,4-dihydroxymethyl-1-phenyl-3-pyrazolidone. The p-aminophenol developing agents include p-aminophenol and N-methyl-p-aminophenol.

Compounds providing free sulfite ions, such as sodium sulfite, potassium sulfite, potassium metabisulfite and sodium bisulfite, are added to the developing solutions as the preservatives. In the case of the infectious developing solution, sodium formaldehydebisulfite, which hardly provides any sulfite ions in the developing solution, may be used.

The alkali agents contained in the developing solutions used in the present invention include potassium hydroxide, sodium hydroxide, potassium carbonate, sodium carbonate, sodium acetate, potassium tertiary phosphate, diethanolamine and triethanolamine. The pH of the developing solution is usually 8.5 or more, and preferably 9.5 or more.

The developing agents may contain organic compounds known as antifoggants or development inhibitors. Examples thereof include azoles such as benzothiazolium salts, nitroindazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles and mercaptotetrazoles (particularly, 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; thioketo compounds such as oxazolinethione; azaindenes such as triazaindenes, tetraazaindenes (particularly, 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes) and pentaazaindenes; benzenethiosulfonic acid; benzenesulfinic acid; benzenesulfonic acid amide; and sodium 2-mercaptobenzimidazole-5-sulfonate.

The developing solutions used in the present invention may contain polyalkylene oxide as a development inhibitor. For example, polyethylene oxide having a molecular weight of 1,000 to 10,000 can be added in an amount ranging from 0.1 to 10 g/liter.

It is preferred to add water softeners to the developing solutions used in the present invention. Such water softeners include nitrilotriacetic acid, ethylenediaminetetraacetic acid, triethylenetetraminehexaacetic acid and diethylenetetraminepentaacetic acid.

In the developing solutions used in the present invention, compounds described in JP-A-56-24347 can be used as silver stain-proofing agents, compounds described in JP-A-62-212651 as uneven developmentproofing agents, and compounds described in JP-A-61-267759 as dissolving assistants.

In the developing solutions used in the present invention, boric acid described in JP-A-62-186259, saccharides (for example, saccharose) described in JP-A-60-93433, oximes (for example, acetoxime), phenols (for example, 5-sulfosalicylic acid) and tertiary phosphates (for example, sodium salts and potassium salts) are used as the buffers.

Various compounds may be used as development accelerators in the present invention, and may be added either to the photographic materials or to any of the processing solutions. Preferred examples of the development accelerators include amine compounds, imidazole compounds, imidazoline compounds, phosphonium compounds, sulfonium compounds, hydrazine compounds, thioether compounds, thione compounds, certain kinds of mercapto compounds, meso-ionic compounds and thiocyanates.

The development accelerator is necessary to conduct rapid processing within a short period of time. It is desirable to add the development accelerator to the color developing solution. However, the development accelerator can be added to the photographic material depending on the kind of development accelerator or the position at which a light-sensitive layer to be accelerated in development is formed. Further, they may be added to both the color developing solution and the photographic material. Furthermore, a preceding bath can be provided prior to a color developing bath to add the development accelerator thereto.

As development accelerator amine compounds, inorganic amines such as hydroxylamine and organic amine are both useful. The organic amines may be aliphatic, aromatic, cyclic, aliphatic-aromatic mixed or heterocyclic amines, and primary, secondary and tertiary amines and quaternary ammonium compounds are all effective.

After color development, the photographic emulsion layers are generally bleached. Bleaching may be carried out simultaneously with fixing or separately. Further, bleaching-fixing treatment may be conducted after bleaching to expedite processing. As bleaching agents, for example, compounds of polyvalent metals such as iron(III), cobalt(III), chromium(IV) and copper(II), peracids, quinones and nitrone compounds are used. Typical examples of the bleaching agents include ferricyanides; bichromates; organic complex salts of iron(III) or cobalt(III), for example, complex salts of iron(III) or cobalt(III) with aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid and 1,3-diamino-2-propanoltetraacetic acid, or with organic acids such as citric acid, tartaric acid and maleic acid; persulfates; manganates; and nitrosophenol. Of these, the salt of iron(III) with ethylenediaminetetraacetic acid, the salt of iron(III) with diethylenetriaminepentaacetic acid and persulfates are preferable from the viewpoints of rapid processing and environmental pollution. Further, the complex salts of iron(III) with ethylenediaminetetraacetic acid is also particularly useful for both independent bleaching solutions and combined bleaching-fixing solutions.

Bleaching promoters may be added to the bleaching solutions, the bleaching-fixing solutions and the preceding baths thereof, as required. Specific examples of the useful bleaching promoters include compounds having mercapto groups or disulfide groups described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-65732, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426 and Research Disclosure, No. 17129 (July, 1978); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent 3,706,561; iodides described in West German Patent 1,127,715 and JP-A-58-16235; polyethylene oxides described in West German Patents 966,410 and 2,748,430; polyamine compounds described in JP-B-45-8836; other compounds described in JP-A-49-42434, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and iodine and bromine ions. In particular, the compounds having mercapto groups or disulfide groups are preferable from the viewpoint of high promoting effect, and particularly the compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are preferable. In addition, the compounds described in U.S. Patent 4,552,834 are also preferable. These bleaching promoters may be added to the photographic materials. When color photographic picture-taking materials are subjected to the bleaching-fixing, these bleaching promoters are particularly effective.

Fixing agents include thiosulfates, thiocyanates, thioether compounds and large quantities of iodides. The thiosulfates are generally used. As preservatives for the bleaching-fixing solutions or the fixing solutions, sulfites, bisulfites or carbonyl bisulfite addition compounds are preferably used.

The photographic materials are usually subjected to washing and stabilizing stages after bleaching-fixing or fixing. In the washing and stabilizing stages, various known compounds may be added to prevent precipitation or to save water. For example, in order to prevent precipitation, various compounds can be added as required which include water softeners such as inorganic phosphoric acids, aminopolycarboxylic acids, organic aminopolyphosphonic acids and organic phosphoric acids; disinfectants or antifungal agents for preventing various bacteria, duckweeds or molds from being produced; metal salts represented by magnesium salts, aluminum salts and bismuth salts; surface active agents for preventing the load and unevenness of drying; and various hardeners. Also, compounds described in L.E. West, Phot. Sci. Eng., Vol. 6, pages 344 to 359 (1965) may be added. The addition of chelating agents or the antifungal agents is particularly effective.

In the washing stage, a countercurrent washing system using two or more tanks is usually employed to save water. Further, a multistage countercurrent stabilizing stage described in JP-A-57-8543 may be carried out instead of the washing stage. This stage requires 2 to 9 countercurrent baths. In addition to the above described additives, various compounds are added to these stabilizing baths to stabilize images. Typical examples thereof include various buffers for adjusting the pH of films, for example, to pH 3 to 9. Examples of buffers are borates, metaborates, borax, phosphates, carbonates, potassium hydroxide, sodium hydroxide, aqueous ammonia, monocarboxylic acids, dicarboxylic acids and polycarboxylic acids used in combination of two or more and aldehydes such as formalin. In addition, various additives may be used, if necessary, and two or more compounds which are the same or different in their object may be used in combination. Such additives include chelating agents (such as inorganic phosphoric acids, aminopolycarboxylic acids, organic phosphoric acids, organic phosphonic acids, aminopolyphosphonic acids and phosphonocarboxylic acids), disinfectants (such as benzoisothiazolinone, irithiazolone, 4-thiazolinebenzimidazole halogenated phenol, sulfanilamide and benzotriazole), surface active agents, fluorescent brightening agents and hardeners.

After processing, various ammonium salts are preferably added as film pH adjusting agents. Such ammonium salts include ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium phosphate, ammonium sulfite and ammonium thiosulfate.

As for the color photographic picture-taking materials, the washing-stabilizing stage usually carried out after fixing can also be replaced by the above described stabilizing stage and washing stage (water saving treatment). In this case, when 2 equivalents of a magenta coupler is used, formalin contained in the stabilizing bath may be removed.

In the present invention, the washing time and the stabilizing time are each usually 20 seconds to 10 minutes, and preferably 20 seconds to 5 minutes, though they vary depending on the kind of photographic material and processing conditions.

The silver halide color photographic materials of the present invention may contain the color developing agents in order to simplify and expedite processing. It is preferred to use various precursors of the color developing agents for this purpose. Examples of such precursors include indoaniline compounds described in U.S. Patent 3,342,597, Schiff base type compounds described in U.S. Patent 3,342,599, Research Disclosure, No. 14850 and ibid., No. 15159, aldol compounds described in Research Disclosure, No. 13924, metal salt complexes described in U.S. Patent 3,719,492, urethane compounds described in JP-A-53-135628, and various salt type precursors described in JP-A-56-6235, JP-A-56-16133, JP-A-56-59232, JP-A-56-67842, JP-A-56-83734, JP-A-56-83735, JP-A-56-83436, JP-A-56-89735, JP-A-56-81837, JP-A-56-54430, JP-A-56-106241, JP-A-56-107236, JP-A-57-97531 and JP-A-57-83565.

The silver halide color photographic materials of the present invention may contain various 1-phenyl-3-pyrazolidones for the purpose of promoting color development, as required. Typical compounds thereof are described in JP-A-56-64339, JP-A-57-144547, JP-A-57-211147, JP-A-58-50532, JP-A-58-50536, JP-A-58-50533, JP-A-58-50534, JP-A-58-50535 and JP-A-58-115438.

Various processing solutions in the present invention are used at a temperature of 10 to 50° C. The standard temperature is usually 33 to 38° C. However, the temperature may be elevated higher to expedite processing, whereby the processing time can be shortened. On the contrary, the temperature can be decreased lower to achieve improvements in image qualities and in stability of the processing solutions. In addition, processing may be conducted using cobalt intensification or hydrogen peroxide intensification described in West German Patent 2,226,770 and U.S. Patent 3,674,499 to save silver of the photographic materials.

Various processing baths may be provided with heaters, temperature sensors, level sensors, circulating pumps, filters, floating covers and squeegees, if necessary.

In continuous processing, a constant finish is obtained by preventing the fluctuation of the solution composition, using the replenisher of each processing solution. The replenishment rate can be reduced to one half or less of the standard replenishment rate for cost reduction.

When the photographic materials of the present invention are color paper, the bleaching-fixing processing can be generally carried out. Also when they are photographic materials for taking pictures, the bleaching-fixing processing can be conducted, as so desired.

The development processing time in the present invention means a period from the time when a leading end of a photographic material reaches a developing solution to the time when the leading end is discharged from a final drying zone in automatic processing.

As methods for increasing the drying speed in automatic developing machines, the following methods are proposed, but the scope of the present invention is not limited thereto:

(a) a method for detecting the temperature and humidity and controlling the drying temperature thereby (JP-A-1-237659);

(b) a method for drying with dehumidifying (JP-A-1-260444);

(c) a method for drying while irradiating far infrared radiation microwaves (JP-A-1-260445); and

(d) a method using heated transfer rollers (JP-A-1-260448).

EXAMPLE 1

Preparation of Support (1)

A 175 µm thick polyethylene terephthalate film dyed blue and biaxially oriented was submitted to corona discharge and a first undercoat solution was applied to the film with a wire bar coater so as to give the following coated amounts, followed by drying at 175° C for 1 minute. Then, the solution was also similarly applied to the opposite surface to form a first underlayer.

First Underlayer

Butadiene-Styrene Copolymer Latex (solid content: 40; weight ratio of butadiene/styrene: 31/69)	0.16 g/m^2
2,4-Dichloro-6-Hydroxy-s-Triazine Sodium Salt	3.2 mg/m^2

Second underlayers were formed on the above described first underayers on both surfaces so as to give the following coated amounts by drying at 150° C for 1 minute.

Second Underlayer

Gelatin	0.08 g/m^2
$C_{12}H_{25}O(CH_2CH_2O)_{10}H$	7.5 g/m^2

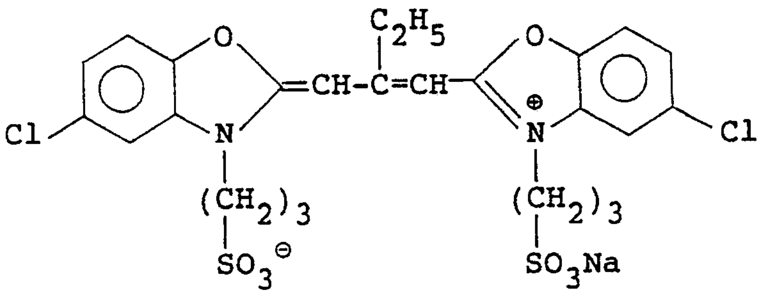
1 Preparation of Emulsion (1)

5 g of potassium bromide, 0.05 g of potassium iodide, 25.5 g of gelatin and 2.5 cc of a 5% aqueous solution of thioether $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OH$ were added to 1 liter of water, and an aqueous solution containing 8.35 g of silver sulfate and an aqueous solution containing 5.94 g of potassium bromide and 0.726 g of potassium iodide were added to the solution maintained at 69° C with stirring by the double jet method for 45 seconds. Subsequently, 2.9 g of potassium bromide was added thereto, and then a solution containing 8.35 g of silver nitrate was added thereto for 26 minutes so that the flow rate at the time when the addition was completed was increased to twice that at the time when the addition was started. Then, 20 cc of a 25% ammonia solution and 10 cc of 50% NH_4NO_3 were added thereto, and physical ripening was carried out for 20 minutes, followed by addition of 240 cc of 1 N sulfuric acid for neutralization. Subsequently, an aqueous solution containing 149.9 g of silver nitrate and an aqueous solution of potassium bromide were added thereto by the control double jet method for 40 minutes, keeping the potential at pAg 8.2. The flow rate at this time was accelerated so that the flow rate at the time then the addition was completed was increased to 9 times that at the time when the addition was started. After the addition was completed, 15 cc of a 2 N potassium thiocyanate solution was added, and 25 cc of a 1% potassium iodide

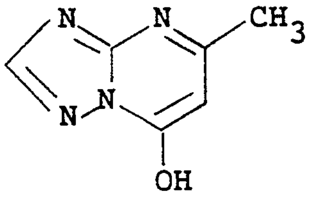
solution was further added thereto for 30 seconds. The temperature was thereafter lowered to 35° C, and soluble salts were removed by the precipitation method. Then, the temperature was elevated to 40° C, and 74.5 g of gelatin and 1.2 g of Proxel were added, followed by adjustment with sodium hydroxide and potassium bromide to pH 6.40 and pAg 8.10.

After the temperature was elevated to 65° C, 600 mg of a sensitizing dye having the following structure and 150 mg of a stabilizer were added. After 10 minutes, 2.4 mg of sodium thiosulfate pentahydrate, 140 mg of potassium thiocyanate and 2.1 mg of chloroauric acid were added to each emulsion. After 80 minutes, the mixture was solidified by rapid cooling to form an emulsion. 95% of the sum of the projected areas of all grains contained in the resulting emulsion consisted of grains having an aspect ratio of at least 3. For all grains having an aspect ratio of at least 2, the mean projected diameter was 1.4 µm, the standard deviation was 15%, the mean thickness was 0.190 µm, and the aspect ratio was 7.4.

Sensitizing Dye

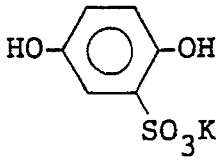


Stabilizer



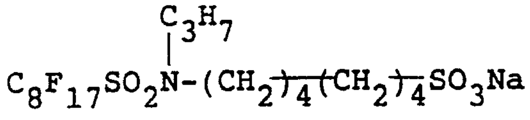
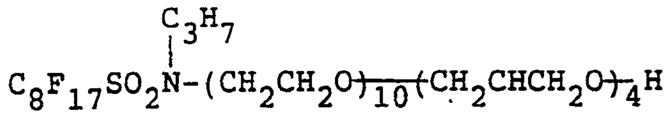
2 Preparation of Emulsion Coating Solution

The following agents were added to the emulsion per mol of silver halide to prepare a coating solution.

Polymer Latex (poly(ethylacrylate/methacrylic acid) 97/3)	25.0 g
Hardener (1,2-bis(sulfonylacetamido)-ethane)	Coated amounts described in Table 1
	12.0 g
2,6-Bis(hydroxyamino)-4-Diethylamino-1,3,5-Triazine	80 mg
Sodium Polyacrylate (mean molecular weight: 41,000)	4.0 g
Potassium Polystyrenesulfonate (mean molecular weight: 600,000)	1.0 g

3 Preparation of Coating Solution for Surface Protective Layer and Preparation of Antihalation Layer

A coating solution for a surface protective layer was prepared so as to give the following coated amounts of respective components:

Component of Surface Protective Layer	Coated Amount (g/m^2)
Gelatin	0.7
Polyacrylamide (mean molecular weight: 45,000)	0.2
Sodium Polyacrylate (mean molecular weight: 400,000)	0.02
Sodium Salt of p-t-Octylphenoxy-diglycerylbutylsulfonate	0.02
Poly(polymerization degree 10)-oxyethylene Cetyl Ether	0.035
Poly(polymerization degree 10)-oxyethylene-Poly(polymerization degree 3)oxyglyceryl-p-Octylphenoxy Ether	0.01
$C_8F_{17}SO_3K$	0.003
 $C_8F_{17}SO_2\overset{\overset{C_3H_7}{\vert}}{N}\text{-}(CH_2)_4(CH_2)_4SO_3Na$	0.001
 $C_8F_{17}SO_2\overset{\overset{C_3H_7}{\vert}}{N}\text{-}(CH_2CH_2O)_{10}(CH_2CHCH_2O)_4H$	0.003
Polymethyl Methacrylate (mean grain size: 3.5 µm)	0.025
Poly(methyl Methacrylate/ Methacrylate) (mole ratio: 7:3, mean grain size: 2.5 µm)	0.020

An antihalation layer was prepared using the following amounts of the respective components.

Antihalation (AH) Layer

Gelatin	0.2 g/m^2
Dye III-3	15 mg/m^2
1,2-Bis(sulfonylacetamido)-ethane	0.013 $mmol/m^2$

(The dispersion of the dyes was carried out as described in Examples 1 to 7 of PCT International Publication No. WO 88/04794.)

4 Preparation of Photographic Materials

The layers were formed on the support in the order of the AH layer, the emulsion layer and the surface protective layer, and dried to obtain Photographic Materials 1-1 to 1-4 shown in Table 1.

In these photographic materials the coated amount of emulsion was 1.6 g/m^2 as silver and that of gelatin was as indicated in Table 1.

5 Evaluation of Photographic Properties

GRENEX orthoscreen HR-4 (Fuji Photo Film Co., Ltd.) was brought into close contact with both sides of the photographic material by using a cassette to carry out X-ray sensitometry. The amount of exposure was adjusted by varying the distance between an X-ray tube and the cassette. After exposure, automatic processing A-1(a) was conducted using the following developing solution and fixing solution.

Automatic Processing A-1(a)

Processing Stage	Temperature (°C)	Time (second)
Development	35	9.5
Fixing	31	10
Washing	15	6
Squeeze		6
Drying	50	12

Dry to dry processing time: 45 seconds

(When an undried sample was obtained, it was subjected to air drying after processing.)

The compositions of the developing solution and the fixing solution were as follows:

Devoloping Solution:

Potassium Hydroxide	29 g
Potassium Sulfite	44.2 g
Sodium Hydrogencarbonate	7.5 g
Boric Acid	1.0 g
Diethylene Glycol	12.0 g
Ethylenediaminetetraacetic Acid	1.7 g
5-Methylbenzotriazole	0.06 g
Hydroquinone	25.0 g
Glacial Acetic Acid	18.0 g
Triethylene Glycol	12.0 g
5-Nitroindazole	0.25 g
1-Phenyl-3-Pyrazolidone	2.8 g
Glutaraldehyde (50 wt/wt%)	9.86 g
Sodium Methabisulfite	12.6 g
Potassium Bromide	3.7 g
Water to make	1.0 liter

Fixing Solution

Ammonium Thiosulfate (70 wt/vol%)	200.0 ml
Disodium Ethylenediaminetetraacetate Dihydrate	0.02 g
Sodium Sulfite	15.0 g
Boric Acid	10.0 g
Sodium Hydroxide	6.7 g
Glacial Acetic Acid	15.0 g
Aluminum Sulfate	10.0 g
Sulfuric Acid (36 N)	3.9 g
Water to make	1.0 liter

The pH was adjusted to 4.25

Measurement of Sharpness (MTF)

The MTF was measured in the combination of the above described HR-4 screen and automatic processing. The measurement was conducted through an aperture with a size of 30 µm x 500 µm, and the evaluation was carried out at the portion whose optical density was 1.0, using the MTF value at a spatial frequency of 1.0 cycle/mm.

Evaluation of Drying Property

The film with a size of 24.5 cm x 30.5 cm was subjected to automatic processing A-1(a) and A-1(b), and the film discharged from the drying zone was immediately touched by hand to confirm the dried state. The respective results are summarized in Table 1. The evaluation standard is as follows:

o: sufficiently dried.
x: the films discharged are wettish and insufficiently dried.
x x: the films discharged are wet, and adhere to each other.

Automatic Processing A-1(b)

Processing Stage	Temperature (°C)	Time (second)
Development	35	6.3
Fixing	31	6.7
Washing	15	4
Squeeze		4
Drying	60	8

Dry to dry processing time: 29 seconds

The developing solution and the fixing solution were prepared as in automatic processing A-1(a).

Evaluation of Swelling Rate

For the photographic materials not subjected to photographic processing, the swelling percentage was measured 7 days after coating. Each photographic material was incubated at a temperature of 38° C at a relative humidity of 50% for 3 days. The thickness of all hydrophilic colloid layers of each photographic material was first measured, and then, each sample was immersed in distilled water at 21° C for 3 minutes. Then, the change in the thickness thereof was measured. The thickness was measured by freezing each sample with liquid N_2 and observing a cross section thereof with a scanning electron microscope having a liquid N_2 stage.

T A B L E 1

	Amount of Gelatin in Emulsion Layer (g/m^2)	Amount of Hydrophilic Colloid (g/m^2)	Coated Amount of 1,2-Bis(sulfonylacetamido)ethane (mg/m^2)	Drying Property		
				Swelling Rate (%)	Automatic Processing A-1(a)	Automatic Processing A-1(b)
Photographic Material 1-1 (Comparison)	1.72	2.7	43	230	xx	xx
Photographic Material 1-2 (Comparison)	1.72	2.7	72	190	x	x
Photographic Material 1-3 (Comparison)	1.42	2.4	39	235	x	x
Photographic Material 1-4 (Invention)	1.42	2.4	65	185	o	o

The MTF of Photographic Materials 1-1 to 1-4 was 0.71.

The results shown in Table 1 reveal that the photographic material excellent in sharpness and drying property can be obtained by the present invention.

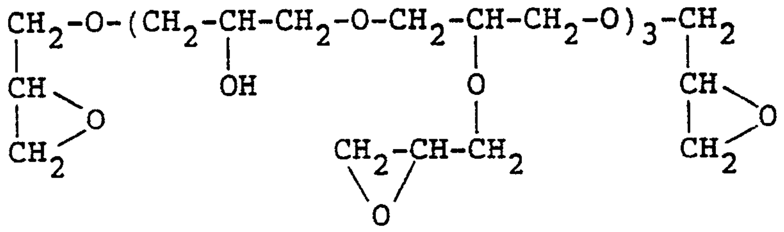
EXAMPLE 2

Both surfaces of a 100 µm thick biaxially oriented polyethylene terephthalate film were coated with a first underlayer of the following formulation (1) and a second underlayer of the following formulation (2) in turn.

Formulation (1) for First Underlayer	part by weight
Aqueous Dispersion of Vinylidene Chloride/Methyl Methacrylate/Acrylonitrile/Methacrylic Acid Copolymer (weight ratio: 90/8/1/1)	15
2,4-Dichloro-6-Hydroxy-s-Triazine	0.25
Fine Polystyrene Particles (mean grain size: 3 µm)	0.05
Compound (a)	0.02
Water to make	100

The coating solution to which 10% by weight of KOH was further added and which was adjusted to pH 6 was applied so as to give a dried film thickness of 0.9 µm by drying at 180° C for 2 minutes.

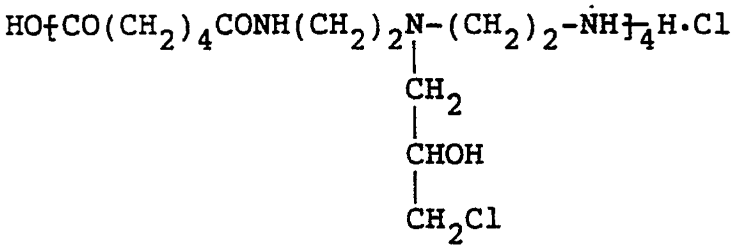
Compound (a)



Formulation (2) for Second Underlayer	part by weight
Gelatin	1
Methyl Cellulose	0.05
Compound (f)	0.02
$C_{12}H_{25}O(CH_2CH_2O)_{10}H$	0.03
Compound (b)	3.5×10^{-3}
Acetic Acid	0.2
Water to make	100

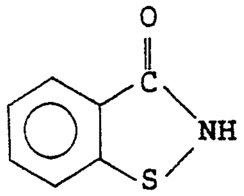
This coating solution was applied so as to give a gelatin amount of 0.08 g/m² by drying at 170° C for 2 minutes.

Compound (f)



$$HO\left[CO(CH_2)_4CONH(CH_2)_2\underset{\substack{|\\ CH_2\\ |\\ CHOH\\ |\\ CH_2Cl}}{N}-(CH_2)_2-NH\right]_4H\cdot Cl$$

Compound (b)



One surface of the support thus obtained was undercoated with a conductive layer of the following formulation (3) and a back layer of the following formulation (4).

Formulation (3) for Conductive Layer

SnO_2/Sb (weight ratio: 9/1, mean grain size: 0.25 μm)	300 mg/m^2
Gelatin	170 mg/m^2
Compound (b)	7 mg/m^2
Sodium Dodecylbenzenesulfonate	10 mg/m^2
Sodium Dihexyl-α-Sulfosuccinate	40 mg/m^2
Sodium Polystyrenesulfonate	9 mg/m^2

Formulation (4) for Back Layer

Gelatin	1.9 g/m^2
Compound (b)	10 g/m^2
Sodium Dodecylbenzenesulfonate	70 g/m^2
Sodium Dibenzyl-α-Sulfosuccinate	15 g/m^2
1,2-Bis(vinylsulfonylacetamido)ethane	150 g/m^2
Ethyl Acrylate Latex (mean grain size: 0.05 μm)	500 g/m^2
Lithium Perfluorooctanesulfonate	10 g/m^2
Finely Divided Silicon Dioxide Particles (mean grain size: 4 μm, pore diameter: 170 Å, surface area: 300 m^2/g)	35 g/m^2

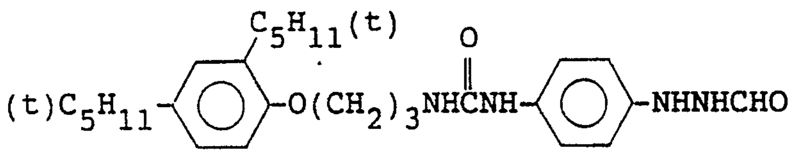
The opposite surface thereof was further coated in the following manner.

Emulsion A (Br: 1 mol%, grain size: 0.20 μm, Rh: 1.0 x 10^{-5} mol/mol Ag) was prepared by the following method using the following Solutions I, II and III:

Solution I: 600 ml of water, 18 g of gelatin, pH 3.0
Solution II: 200 g of $AgNO_3$, 800 ml of water
Solution III: 1.4 g of KBr, 76 g of NaCl, 4 mg of $(NH_4)_3RhCl_6$, 800 ml of water

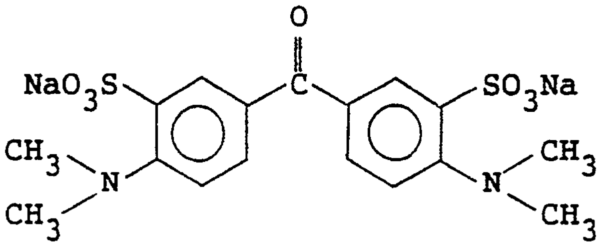
Solutions II and III were added to Solution I maintained at 40 °C, keeping the speed constant for 20 minutes, by double jet method. Soluble salts were removed from the resulting emulsion by a conventional method well known in the art, followed by addition of gelatin. Then, 2-methyl-4-hydroxy-1,3,3a,7-tetraazaindene was added thereto as a stabilizer without chemical ripening. The mean grain size of the resulting emulsion was 0.20 μm, the yield thereof was 1 kg, and the amount of gelatin contained therein was 45 g. The following hydrazine compound (Hz) was added to this emulsion in an amount of 4 X 10^{-4} mol/mol Ag to prepare an emulsion.

Hydrazine Compound (Hz)



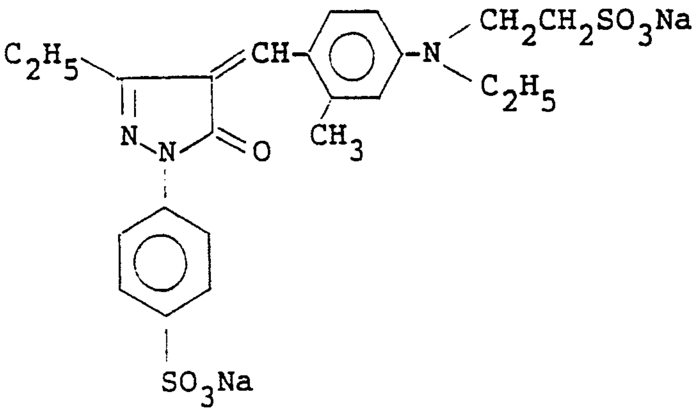
After the following ultraviolet light absorber (UV absorber) was added thereto in an amount of 100 mg/m^2, polyethyl acrylate latex was added in an amount of 30% by weight as a solid based on gelatin, and 1,3-bis-(vinylsulfonyl)-2-propanol was added thereto in the amount described in Table 2 as the hardener. The resulting coating solution was applied so as to give a coated silver amount of 2 g/m^2 and the coated gelatin amount described in Table 2.

Ultraviolet Light Absorber (UV Absorber)



A protective layer to which the following yellow dye for improving safelight safety was added so as to give an amount of 120 mg/m^2 was formed thereon so as to contain gelatin in an amount of 0.9 g/m^2. An anti-halation layer (AH layer), to which a dispersion (prepared by dispersing a dye as shown in Table 2 in the same manner as described in Examples 1 to 7 of PCT International Publication No. WO 88/04794) was added, was formed under the emulsion layer so as to give a coated gelatin amount of 0.30 g/m^2.

Yellow Dye



Photographic Materials 2-1 to 2-16 were prepared as described above.

The Photographic Materials 2-1 to 2-16 were subjected to the following processing.

An original constitution consisting of (a) this sample, (b) a dot original, (c) a transparent or translucent strip-in base, (d) a line original and (e) a transparent or translucent strip-in base was exposed at the (d) side to the light emitted from a P-607 extra high pressure mercury lamp (ORC-CHM-1000, Dainippon Screen Mfg. Co., Ltd.), so as to be exposed for the same period of time for each sample by adjusting the exposure with a neutral density filter (ND filter). Then, the following automatic processing A-2(a) was conducted using the following developing solution A to evaluate the image quality of extracted characters. RC-F1 was used as the fixing solution.

Automatic Processing A-2(a)

Processing Stage	Temperature (°C)	Time (second)
Development	38	15
Fixing	37	10
Washing	15	10
Drying	45	10

Dry to dry processing time: 45 seconds

(When an undried sample was obtained, it was subjected to air drying after processing.)

The composition of the developing solution used was as follows:

Developing Solution

Hydroquinone	45.0 g
N-Methyl-p-Aminophenol 1/2 Sulfate	0.8 g
Sodium Hydroxide	18.0 g
Potassium Hydroxide	55.0 g
5-Sulfosalicylic Acid	45.0 g
Boric Acid	25.0 g
Potassium Sulfite	110.0 g
Disodium Ethylenediaminetetraacetate	1.0 g
Potassium Bromide	6.0 g
5-Methylbenztriazole	0.6 g
n-Butyl-Diethanolamine	15.0 g
Water to make	1.0 liter
pH	11.6

An image quality of extracted characters "5" means such an image quality of extracted characters that 30 µm wide characters are reproduced when normal exposure is given so that 50% dot area forms 50% dot area on a photographic material for dot to dot work using a document. This image quality is very good. In contrast, an image quality of "1" means that only a character width of 150 µm or more can be reproduced when similar normal exposure is given. This image quality is poor. The image quality of "4", "3", and "2" are between "5" and "1". The image quality of "3" or more is on the practical level.

Evaluation of Drying Property

The film with a size of 24.5 cm × 30.5 cm was subjected to automatic processing A-2(a) and A-2(b), and evaluated as in Example 1.

Automatic Processing A-2(b)

Processing Stage	Temperature (°C)	Time (second)
Development	38	10
Fixing	37	7
Washing	25	6
Drying	60	6

Dry to dry processing time: 29 seconds

(When an undried sample was obtained, it was subjected to air drying after processing.)

The developing solution and the fixing solution used were similar to those used in automatic processing A-2(a).

Evaluation of Swelling Rate

The swelling rate was evaluated as in Example 1.

TABLE 2(a)

	Automatic Hydrophilic Colloid (g/m^2)	Dye	Coated Amount (mg/m^2)	Coated Amount of 1,3-Bis(vinylsulfonyl)-2-propanol (mg/m^2)	Swelling Rate (%)	Drying Property	
						Automatic Processing A-2(a)	Automatic Processing A-2(b)
Photographic Material 2-1 (Comparison)	2.6	III-1	80	41	232	xx	xx
Photographic Material 2-2 (Comparison)	2.6	III-1	80	92	165	x	x
Photographic Material 2-3 (Comparison)	1.8	III-1	80	29	230	x	x
Photographic Material 2-4 (Invention)	1.8	III-1	80	64	155	o	o

The image quality of Photographic Materials 2-1 to 2-4 was 3.5, and satisfactory.

TABLE 2(b)

	Automatic Hydrophilic Colloid (g/m^2)	Dye	Coated Amount (mg/m^2)	Coated Amount of 1,3-Bis(vinylsulfonyl)-2-propanol (mg/m^2)	Swelling Rate (%)	Drying Property	
						Automatic Processing A-2(a)	Automatic Processing A-2(b)
Photographic Material 2-5 (Comparison)	2.6	VII-1	64	41	235	xx	xx
Photographic Material 2-6 (Comparison)	2.6	VII-1	64	92	160	x	x
Photographic Material 2-7 (Comparison)	1.8	VII-1	64	29	225	x	x
Photographic Material 2-8 (Invention)	1.8	VII-1	64	64	165	o	o

The image quality of Photographic Materials 2-5 to 2-8 was 3.5, and satisfactory.

T A B L E 2(c)

	Automatic Hydrophilic Colloid (g/m^2)	Dye	Coated Amount (mg/m^2)	Coated Amount of 1,2-Bis(sulfonyl-acetamido)ethane (mg/m^2)	Swelling Rate (%)	Drying Property	
						Automatic Processing A-2(a)	Automatic Processing A-2(b)
Photographic Material 2- 9 (Comparison)	2.6	VII-2	64	41	227	xx	xx
Photographic Material 2-10 (Comparison)	2.6	VII-2	64	92	162	x	x
Photographic Material 2-11 (Comparison)	1.8	VII-2	64	29	231	x	x
Photographic Material 2-12 (Invention)	1.8	VII-2	64	64	159	o	o

The image quality of Photographic Materials 2-9 to 2-12 was 3.5, and satisfactory.

T A B L E 2(d)

	Automatic Hydrophilic Colloid (g/m^2)	Dye	Coated Amount (mg/m^2)	Coated Amount of 1,2-Bis(sulfonyl-acetamido)ethane (mg/m^2)	Swelling Rate (%)	Drying Property	
						Automatic Processing A-2(a)	Automatic Processing A-2(b)
Photographic Material 2-13 (Comparison)	2.6	I-28	80	41	228	xx	xx
Photographic Material 2-14 (Comparison)	2.6	I-28	80	92	165	x	x
Photographic Material 2-15 (Comparison)	1.8	I-28	80	29	230	x	x
Photographic Material 2-16 (Invention)	1.8	I-28	80	64	158	o	o

The image quality of Photographic Materials 2-13 to 2-16 was 3.5, and satisfactory.

The results shown above reveal that the photographic materials excellent in image quality and in drying property can be obtained according to the present invention.

EXAMPLE 3

A 100 µm thick biaxially oriented polyethylene terephthalate film was submitted to corona discharge and a first undercoat solution was applied to the film with a wire bar coater so as to give the following coated amounts, followed by drying at 170° C for 1 minute.

First Underlayer

Butadiene-Styrene Copolymer Latex (weight ratio of butadiene/styrene: 31/69)	0.16 g/m^2
2,4-Dichloro-6-Hydroxy-s-Triazine Sodium Salt	4.2 mg/m^2

A second underlayer was formed on the above described first underlayer so as to give the following coated amounts by drying at 175° C for 1 minute.

Second Underlayer

Gelatin	0.08 g/m^2
$C_{12}H_{25}O(CH_2CH_2O)_{10}H$	7.5 g/m^2

Preparation of Emulsion (2)

Solution I: 75°C

Inactive Gelatin	24 g
Distilled Water	900 ml
KBr	4 g
10% Aqueous Solution of Phosphoric Acid	2 ml
Sodium Benzenesulfinate	5×10^{-2} mol
1,2-Bis(2-Hydroxyethylthio)ethane	2.5×10^{-3} mol

Solution II: 35°C

Silver Nitrate	170 g
Distilled Water to make	1,000 ml

Solution III: 35°C

KBr	230 g
Distilled Water to make	1,000 ml

Solution IV: room temperature

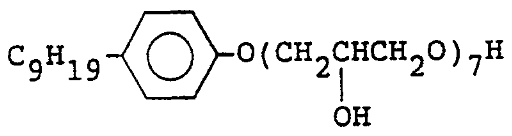
Potassium Hexacyanoferrate(II)	3.0 g
Distilled Water to make	100 ml

Solutions II and III were simultaneously added to Solution I for 5 minutes. When octahedral grains having a mean grain size of 0.1 µm were formed, the addition of Solutions II and III was temporarily stopped, and each of sodium thiosulfate and chloroauric acid tetrahydrate was added in an amount of 115 mg per mol of silver. Subsequently, chemical ripening was conducted at 75°C for 60 minutes. Solutions II and III were simultaneously added again to the chemically ripened grains thus obtained. Five minutes after the addition of Solution II was started again, Solution IV was added thereto for 5 minutes. While adjusting the addition rate of Solution III so that the pAg value of the mixed solution reached 7.50, all of Solution II was added at 75°C for 40 minutes. Thus, an emulsion containing cubic core/shell grains having a mean grain size of 0.28 µm was finally obtained. After washing and desalting by the precipitation method, the emulsion was dispersed in an aqueous solution containing 90 g of inactive gelatin. To this emulsion, each of sodium thiosulfate and chloroauric acid tetrahydrate was added in an amount of 34 mg per mol of silver to adjust it to pH 8.9 and pAg 7.0 (40°C), followed by chemical ripening at 75°C for 60 minutes.

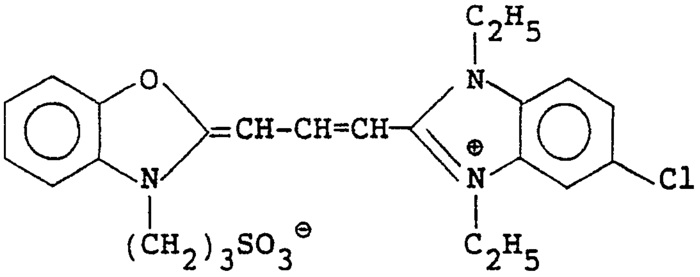
Antihalation Layer (AH Layer)

Gelatin	0.3 g/m^2
Dye III-1	150 mg/m^2
Dye III-3 (The dyes were dispersed as in Example 1)	150 mg/m^2
1,3-Bis(vinylsulfonyl)-2-Propanol	53.7 mg/m^2
Phenoxyethanol	1.9 mg/m^2

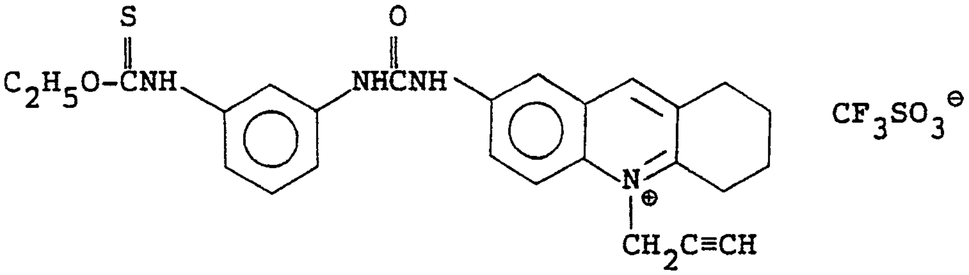
Emulsion Layer

Silver Halide Emulsion (as the amount of silver)	1,400 mg/m^2
Gelatin	Amounts described in Table 3
Sensitizing Dye (Compound (a))	23.8 mg/m^2
Nucleating Agent (Compound (b))	394 mg/m^2
5-Methylbenzenetriazole	4.1 mg/m^2
Sodium Dodecylbenzenesulfonate	5 mg/m^2
1,3-Bis(vinylsulfonyl)-2-propanol	Amounts described in Table 3
Sodium Polystyrenesulfonate	35 mg/m^2
	15 mg/m^2

Sensitizing Dye (Compound (a))



Nucleating Agent (Compound (b))



Protective Layer

Inactive Gelatin	700 mg/m^2
Colloidal Silica	249 mg/m^2
Fluid Paraffin	60 mg/m^2
Barium Strontium Sulfate (mean grain size: 1.5 μm)	32 mg/m^2
Proxel	4.3 mg/m^2
N-Perfluorooctanesulfonyl-N Propylglycine Potassium Salt	5.0 mg/m^2

The layers were formed on the above described support in the order of the AH layer, the emulsion layer and the protective layer, and dried to obtain Photographic Materials 3-1 to 3-4.

Evaluation of Photographic Properties

Image-like exposure was conducted from the emulsion-coated surface under a safety lamp through a continuous density wedge by using a xenon flash sensitometer (Mark-II, manufactured by E.G. & G., U.S.A.) for 10^{-3} second.

Each of the samples was subjected to automatic processing A-3 under the following conditions by using the general purpose processing solution for microfilms (FR-537 developing solution, manufactured by FR Chemicals, U.S.A.).

Automatic Processing A-3

Processing Stage	Processing Solution	Temperature (°C)	Time (second)
Development	FR-537 (1:3)	44	9
Washing	Flowing Water	44	9
Fixing	FR-535 (1:3)	44	9
Washing	Spray	44	9
Drying	Hot Air	50	9

The results are shown in Table 3.

Evaluation of Sharpness

The sharpness was evaluated by the MTF. Each of the photographic materials was exposed to white light for 1/100 second by using an MTF measuring wedge, and then subjected to the above described automatic processing A-3.

The MTF was measured through an aperture with a size of 400 x 2 μm^2, and the evaluation was carried out at the portion whose optical density was 1.0, using the MTF value at a spatial frequency of 20 cycles/mm.

The results are shown in Table 3.

Evaluation of Drying Property

The photographic materials were subjected to the above described automatic processing A-3, and evaluated according to the evaluation standard used in Example 1.

The results are shown in Table 3.

Evaluation of Swelling Rate

The swelling rate was evaluated as in Example 1.

TABLE 3

	Amount of Gelatin in Emulsion Layer (g/m^2)	Amount of Hydrophilic Colloid (mg/m^2)	1,3-Bis(vinylsulfonyl)-2-propanol (%)	Drying Property	
				Swelling Rate	Automatic Processing A-3
Photographic Material 3-1 (Comparison)	1.52	2.6	41	228	xx
Photographic Material 3-2 (Comparison)	1.52	2.6	69	190	x
Photographic Material 3-3 (Comparison)	1.02	2.1	34	230	x
Photographic Material 3-4 (Invention)	1.02	2.1	57	185	o

The MTF of Photographic Materials 1-1 to 1-4 was 1.0.

The results shown in Table 3 reveal that the photographic material excellent in sharpness and drying property can be obtained by the present invention.

According to the present invention, the silver halide photographic materials excellent in sharpness and drying property can be provided, and it becomes possible to process the photographic materials rapidly within a time of 45 seconds or less.

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

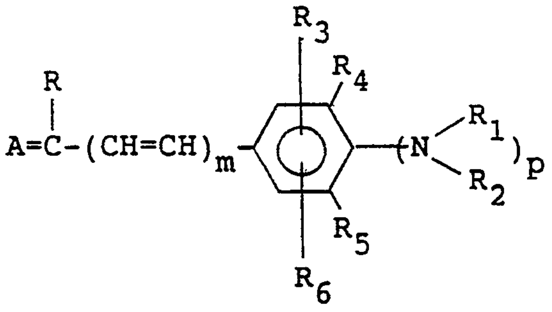
1. A silver halide photographic material having on a support at least one hydrophilic colloid layer containing a solid disperse dye and at least one silver halide emulsion layer provided thereon, wherein the amount of all the hydrophilic colloids present on each side of said photographic material is 2.5 g/m^2 or less, and all the hydrophilic colloid layers present are hardened to a degree sufficient to attain a swelling rate of less than 200%.

2. A silver halide photographic material as in claim 1, wherein all the hydrophilic colloid layers are hardened to a degree sufficient to attain a swelling rate of less than 170%.

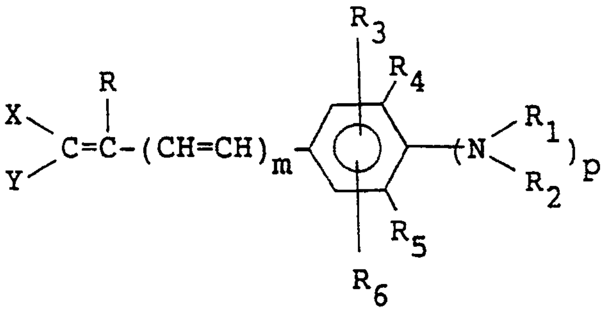
3. A silver halide photographic material as in claim 1, wherein the total amount of hydrophilic colloid applied to said one surface of said photographic material is 2.0 g/m^2 or less.

4. A silver halide photographic material as in claim 2, wherein the total amount of hydrophilic colloid applied to one surface of said photographic material is 2.0 g/m^2 or less.

5. A silver halide photographic material as in claim 1, wherein the dye is represented by general formulae (I) to (VII):



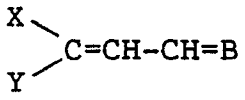
(I)



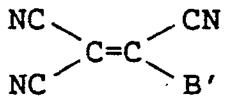
(II)

$$A=L_1-(L_2=L_3)_n-A'$$ (III)

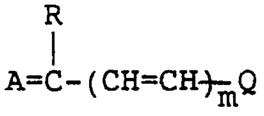
$$A=(L_1-L_2)_{2-q}=B$$ (IV)



$$\begin{matrix}X\\Y\end{matrix}{>}C=CH-CH=B$$ (V)



$$\begin{matrix}NC\\NC\end{matrix}{>}C=C{<}\begin{matrix}CN\\B'\end{matrix}$$ (VI)



$$A=\overset{\overset{R}{|}}{C}-(CH=CH)_m Q$$ (VII)

wherein A and A' may be the same or different and each represents acidic nuclei; B represents a basic nucleus; X and Y may be the same or different and each represents electron attractive groups;

R represents a hydrogen atom or an alkyl group; each of R_1 and R_2 represents an alkyl group, an aryl group, an acyl group or a sulfonyl group, and R_1 and R_2 may combine together to form a 5-membered or 6-membered ring; each of R_3 and R_6 represents a hydrogen atom, a hydroxyl group, a carboxyl group, an alkyl group, an alkoxy group or a halogen atom; each of R_4 and R_5 represents a hydrogen atom or a nonmetallic atom; R_1 can combine with R_4 to form a 5-membered or 6-membered ring wherein R_4 is a nonmetallic atom necessary to form such a ring; or R_2 can combine with R_5 to form a 5-membered or 6-membered ring wherein R_5 is a nonmetallic atom necessary to form such a ring;

each of L_1, L_2 and L_3 represents a methine group; m represents 0 or 1; each of n and q represents 0, 1 or 2; p represents 0 or 1; when p is 0, R_3 represents a hydroxyl group or a carboxyl group and each of R_4 and R_5 represents a hydrogen atom;

B' represents a heterocyclic group having a carboxyl group, a sulfamoyl group or a sulfonamido group;

Q represents a heterocyclic group;

and compounds represented by general formulae (I) to (VII) contain at least one dissociative group per molecule which has a pKa of from 4 to 11 in a mixed solution of water and methanol in a volume ratio of 1:1.

6. A silver halide photographic material as in claim 1, wherein the dye is present in an amount of 5 to 400 mg/m^2.

7. A silver halide photographic material as in claim 1, wherein the dye is present in an amount of 10 to 250 mg/m^2.

8. A silver halide photographic material as in claim 1, wherein the swelling rate is at least 120%.

9. A method for processing a silver halide photographic material having on a support at least one hydrophilic colloid layer containing a solid dye dispersed therein and at least one silver halide emulsion layer provided thereon, wherein the amount of all the hydrophilic colloids present on each side of said photographic material is 2.5 g/m^2 or less, and all the hydrophilic colloid layers present are hardened to a degree enough to obtain a swelling rate of less than 200%, wherein the developing time is 45 seconds or less.

10. A method for processing a silver halide photographic material having on a support at least one hydrophilic colloid layer containing a solid dye dispersed therein and at least one silver halide emulsion layer provided thereon, wherein the amount of all the hydrophilic colloids present on each side of said photographic material is 2.0 g/m^2 or less, and all the hydrophilic colloid layers present are hardened to a degree enough to obtain a swelling rate of less than 200%, wherein the developing time is 45 seconds or less.

11. A method for processing a silver halide photographic material having on a support at least one hydrophilic colloid layer containing a solid dye dispersed therein and at least one silver halide emulsion layer provided thereon, wherein the amount of all the hydrophilic colloids present on each side of said photographic material is 2.0 g/m^2 or less, and all the hydrophilic colloid layers present are hardened to a degree enough to obtain a swelling rate of less than 170%, wherein the developing time is 45 seconds or less.

12. A method for processing a silver halide photographic material as in claim 9, wherein the developing time is 30 seconds or less.

13. A method for processing a silver halide photographic material as in claim 10, wherein the developing time is 30 seconds or less.

14. A method for processing a silver halide photographic material as in claim 11, wherein the developing time is 30 seconds or less.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 7343

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	DE-A-3 241 640 (EASTMAN KODAK COMPANY) * claims * – – –	1-14	G 03 C 1/83 G 03 C 1/30 G 03 C 1/005
D,Y,D,D	EP-A-0 276 566 (EASTMAN KODAK COMPANY) * page 10, line 14 & WO-A-8804794 & US-A-4803150 * – – – – –	1-14	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	21 August 91	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
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