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(54) Silver halide photographic materials.

(57) A silver halide photographic material which provides good clear image quality, is suitable for rapid processing without adverse effect on film strength, and which has excellent handling properties with respect to safe-light safety and cule and dimensional changes, comprising a transparent support, having thereon at least one silver halide emulsion layer, at least one hydrophilic colloid layer which contains at least one type of solid dispersed dye between said support and said silver halide emulsion layer and at least one hydrophilc collid layer which contains at least one type of water soluble dye on the opposite side of the support to the side having said silver halide emulsion layer, wherein the coated weight of the hydrophilic colloid in the hydrophilic colloid layer which contains said solid dispersed dye is not more than 0.5 g/m^2 and the ratio by weight of the solid dispersed dye/hydrophilic colloid is not more than 0.4.

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FIELD OF THE INVENTION

The present invention concerns silver halide photographic materials which have colored hydrophilic colloid layers, and it particularly concerns silver halide photographic materials which have hydrophilic colloid layers which contains a dye which is photographically inactive and which is decolorized and/or washed out in the course of photographic processing

BACKGROUND OF THE INVENTION

Photographic emulsion layers or other layers in silver halide photographic materials are often colored with a view to absorbing light of a specified wavelength.

A colored layer is established on the side on which the light is incident (the exposure surface) of the photographic emulsion layer in a photographic material (this is generally the side further from the support than the photographic emulsion layer) when it is necessary to control the spectral composition of the light which should fall on the photographic emulsion layer. Such a colored layer is called a filter layer. In cases where there is a plurality of photographic emulsion layers, as in the case of a multi-layer color photosensitive material for example, filter layers are also located between these layers.

Colored layers are also established between the photographic emulsion layer and the support or on the surface of the support other than that on which the emulsion layer is established as a means of preventing the blurring of the image, the so-called halation, which is caused by light which has been scattered on passing through a photographic emulsion layer or after being reflected at the boundary between the emulsion layer and the support or at the surface of the photosensitive material on the side opposite to the emulsion layer and re-entering the photographic emulsion layer. Such a colored layer is called an anti-halation layer. Anti-halation layers can also be established between the various layers in the case of a multi-layer color photosensitive material.

Moreover, colored layers are also established in X-ray photosensitive materials as cross-over cut out filters for minimizing cross-over light with a view to increasing sharpness.

Photographic emulsion layers are also colored in order to prevent the loss of image sharpness which is caused by the scattering of light within a photographic emulsion layer (this phenomenon is generally called irradiation).

In many cases, the layers which are to be colored are composed of a hydrophilic colloid and so dyes are generally included in such layers in order to provide the coloration. These dyes must satisfy conditions such as those indicated below.

(1) They must have the appropriate spectral absorbance for the intended purpose.

(2) They must be inactive photographically. Thus, they must have no adverse effect in the chemical sense on the performance of the silver halide emulsion, which is to say, for example, that they must not lower the photographic speed, cause regression of the latent image or cause fogging to occur.

(3) They must be decolorized in the course of photographic processing and/or they must be dissolved out and eliminated and leave no harmful residual coloration in the photographic material after processing.

Much effort has been put into the discovery of dyes which satisfy these conditions in the industry and a great many dyes have been suggested.

However, some of these dyes have little effect on the photographic emulsion itself but cause spectral sensitization in unwanted regions in a spectrally sensitized emulsion, and there is a further disadvantage in that they result in a loss of photographic speed which is thought to be due to the fact that sensitizing dyes are desorbed.

Further, in those cases where the colored layer is a filter layer or an anti-halation layer which is located on the same side of the support as the photographic emulsion layer, the layers generally have to be colored selectively to ensure that there is essentially no coloration of layers other than these layers. This is not simply because this would result in a lowering of the effectiveness of the filter layer or anti-halation layer but also because of the harmful spectral action which arises in the other layers. There are various methods for selectively coloring specified hydrophilic colloid layers, and in many cases methods in which hydrophilic polymers which contain a part which has the opposite charge to the dye ion are included as a mordant in the hydrophilic colloid layer and the dye is localized in the specified layer by the interaction between the polymer and the dye molecule (attraction due to the charge and hydrophobic bonding can be considered) are used.

However, when this method of mordanting is used and the layer to which the dye has been added and other hydrophilic colloid layers are brought into contact in a wet state, some of the dye often diffuses from the former to the latter. Such diffusion of the dye is, of course, dependent on the chemical structure of the mordant and also on the chemical structure of the dyes which are used.

Furthermore, residual coloration is especially liable to arise in the photosensitive material after photographic processing, and especially after photographic processing where the processing time is short, and in cases where a high polymer mordant has been used. It is thought that this is because even though the affinity of the mordant for the dye is quite weak in an alkaline liquid such as a developer, there is some residual affinity and so the dye or a reversibly decolorization product thereof remains in the layer which contains the mordant.

Furthermore, other known means of retaining a dye in a specified layer of a photographic material involve the presence of the dye as a dispersed solid, as disclosed in JP-A-56-12639, JP-A-55-155350, JP-A-55-155351, JP-A-52-92716, JP-A-63-197943, JP-A-63-27838, JP-A-64-40827, European Patents 0015601B1 and 0276566A1, and International Patent Laid Open 88/04794. The term "JP-A" as used herein signifies an "unexamined published Japanese patent application". With photographic materials in which a conventional water soluble dye is established on the opposite side of the support to the silver halide emulsion layer using this method there is no adverse effect of the type mentioned earlier and the dye is adjacent to the silver halide emulsion layer and has an anti-halation effect, and it is possible to improve the image quality in this way.

However, the establishment of a new layer as an anti-halation layer is certainly an undesirable step from the viewpoint of rapid processing which has come into great demand in recent years. Reduction of the amount of hydrophilic colloid in the solid dispersed dye layer increases the solid dispersed dye/hydrophilic colloid ratio and has the disadvantage of greatly reducing the film strength in the wet state during processing. Moreover, when a dye layer which has been established on the opposite side of the support is established on the silver halide emulsion side there is a further disadvantage in that the curl balance is not always established.

Moreover, it is desirable that demands such as those for ensuring safe-light safety so that the silver halide photographic material can be exposed and handled easily prior to processing, and the need for retaining the ease of reverse side discrimination when handling under safe-lighting, should also be satisfied at the same time.

SUMMARY OF THE INVENTION

The first aim of the present invention is to provide silver halide photographic materials which have excellent sharpness.

The second aim of the present invention is to provide silver halide photographic materials which have excellent film strength.

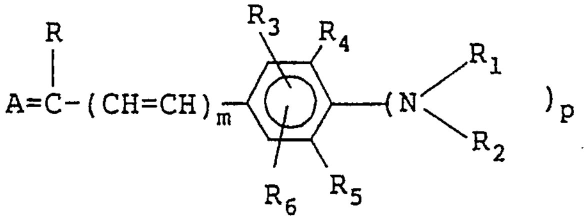
The third aim of the present invention is to provide silver halide photographic materials which have a curl balance.

A further aim of the present invention is to provide silver halide photographic materials which have excellent handlability under safe-lighting.

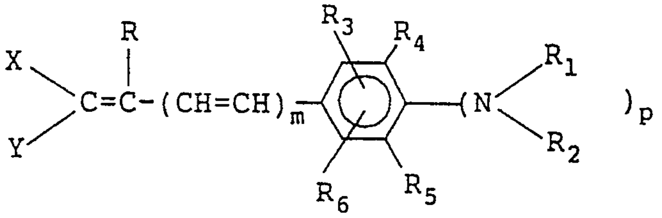
As a result of thorough research, the inventors have discovered that the above mentioned aims can be realized by means of a silver halide photographic material comprising a support, having thereon at least one silver halide emulsion layer, at least one hydrophilic colloid layer which contains at least one type of solid dispersed dye between the support and the silver halide emulsion layer and at least one hydrophilic colloid layer which contains at least one type of water soluble dye on the opposite side of the support to the side having the silver halide emulsion layer, wherein the coated weight of the hydrophilic colloid in the hydrophilic colloid layer which contains the solid dispersed dye (hereinafter referred to as the solid dye dispersed layer) is not more than 0.50 g/m^2 and the ratio by weight of the solid dispersed dye/hydrophilic colloid is not more than 0.4.

DETAILED DESCRIPTION OF THE INVENTION

The dyes in Tables I to X of International Patent WO88/04794, the dyes represented by formulae (I) to (VII) indicated below and other dyes can be used as the dyes which are used in the present invention.



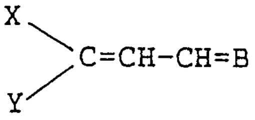
(I)



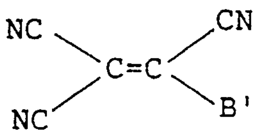
(II)

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

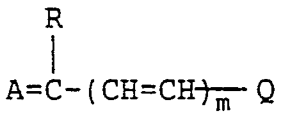
$$A=(L_1-L_2)_{2-q}=B \qquad (IV)$$



(V)



(VI)



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

(VII)

In these formulae, A and A' may be the same or different, each representing an acidic nucleus, B represents a basic nucleus, and X and Y may be the same or different, each representing an electron withdrawing group. R represents a hydrogen atom or an alkyl group, R_1 and R_2 each represent an alkyl group, an aryl group, an acyl group or a sulfonyl group, and R_1 and R_2 may be joined together to form a five or six membered ring. R_3 and R_6 each represent a hydrogen atom, a hydroxy group, a carboxyl group, an alkyl group, an alkoxy group or a halogen atom, and R_4 and R_5 each represent a hydrogen atom or they represent a group of non-metal atoms which is required to form a five or six membered ring when R_1 and R_4, or R_2 and R_5, are joined together. L_1, L_2 and L_3 each represent a methine group. Moreover, m represents 0 or 1, n and q each represent 0, 1 or 2 and p represents 0 or 1, and when p represents 0 then R_3 represents a hydroxy group or a carboxyl group and R_4 and R_5 represent hydrogen atoms. B' represents a heterocyclic group which has a carboxyl group, a sulfamoyl group or a sulfonamido group. Q represents a heterocyclic group.

However, the compounds represented by general formulae (I) to (VII) have within the molecule at least one dissociable group of which the pKa value in a mixed solvent comprised of water and ethanol in the ratio by volume of 1 : 1 is from 4 to 11.

The compounds represented by general formula (I) to (VII) will be described in detail first of all.

The acidic nucleus represented by A or A' is preferably a 2-pyrazolin-5-one, rhodanine, hydantoin, thiohydantoin, 2,4-oxazolinedione, isooxazolidione, barbituric acid, thiobarbituric acid, indanedione, pyrazolopyridine or hydroxypyridone nucleus.

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

Examples of heterocyclic nuclei for B' include pyrrole, indole, thiophene, furan, imidazole, pyrazole, indolidine, quinoline, carbazole, phenothiazine, phenoxazine, indoline, thiazole, pyridine, pyridazine, thiadiazine, pyran, thiopyran, oxadiazole, benzoquinolidine, thiadiazole, pyrrolothiazole, pyrrolopyridazine and tetrazole.

The heterocyclic ring represented by Q is preferably a five membered heterocyclic ring which may have a condensed benzo group, and it is most desirably a five membered nitrogen containing heterocyclic ring which may have a condensed benzo group. Examples of heterocyclic groups for Q include pyrrole, indole, pyrazole, pyrazolopyrimidone and benzoindole.

The group which has a dissociable proton of which the pKa (acid dissociation constant) value in a mixed solvent comprised of water and ethanol in the ratio 1 : 1 by volume is within the range from 4 to 11 is unlimited in respect of type and the position at which it is substituted onto the dye molecule provided that it renders the dye molecule essentially insoluble in water at pH 6 or below and essentially water soluble at pH 8 or above, but it is preferably a carboxyl group, a sulfamoyl group, a sulfonamido group or a hydroxy group, and it is most desirably a carboxyl group. The dissociable group may be substituted directly onto the dye molecule but it may also be substituted via a divalent linking group (for example, an alkylene group or a phenylene group). Examples of linkage via a divalent linking group include the 4-carboxyphenyl, 2-methyl-3-carboxyphenyl,2,4-dicarboxyphenyl, 3,5-dicarboxyphenyl, 3-carboxyphenyl, 2,5-dicarboxyphenyl, 3-ethylsulfamoylphenyl, 4-phenylsulfamoylphenyl, 2-carboxyphenyl, 2,4,6-trihydroxyphenyl, 3-benzenesulfonamidophenyl, 4-(p-cyanobenzenesulfonamido)phenyl, 3-hydroxyphenyl, 2-hydroxy-phenyl, 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 groups.

The alkyl groups represented by R, R_3 and R_6 are preferably alkyl groups which have from 1 to 10 carbon atoms (for example, methyl, ethyl, n-propyl, isoamyl, n-octyl)

The alkyl groups represented by R_1 or R_2 are preferably alkyl groups which have from 1 to 20 carbon atoms (for example, methyl, ethyl, n-propyl, n-butyl, n-octyl, n-octadecyl, iso-butyl, iso-propyl) and they may have substituent groups (for example, halogen such as chlorine and bromine, nitro, cyano, hydroxy, carboxyl, alkoxy (for example, methoxy, ethoxy), alkoxycarbonyl (for example, methoxycarbonyl, isopropoxycarbonyl), aryloxy (for example, phenoxy), phenyl, amido (for example, acetylamino, methanesulfonamido), carbamoyl (for example, methylcarbamoyl, ethylcarbamoyl) and sulfamoyl (for example, methylsulfamoyl, phenylsulfonyl)).

The aryl groups represented by R_1 or R_2 are preferably phenyl groups or naphthyl groups, and they may have substituent groups (the groups cited as substituent groups for the alkyl groups represented by R_1 and R_2 and alkyl groups (for example, methyl, ethyl) are included as substituent groups).

The acyl groups represented by R_1 or R_2 are preferably acyl groups which have from 2 to 10 carbon atoms, for example acetyl, propionyl, n-octanoyl, n-decanoyl, iso-butanoyl and benzoyl. The alkylsulfonyl groups and arylsulfonyl groups represented by R_1 or R_2 are groups such as methanesulfonyl, ethanesulfonyl, n-butanesulfonyl, n-octanesulfonyl, benzene-sulfonyl, p-toluenesulfonyl and o-carboxybenzenesulfonyl.

The alkoxy groups represented by R_3 or R_4 are preferably alkoxy groups which have from 1 to 10 carbon atoms, for example methoxy, ethoxy, n-butoxy, n-octyloxy, 2-ethylhexyloxy, iso-butoxy and iso-propoxy. The halogen atoms represented by R_3 or R_6 are chlorine, bromine and fluorine.

Examples of the ring formed when R_1 and R_4 or R_2 and R_5 join together include julolidine ring.

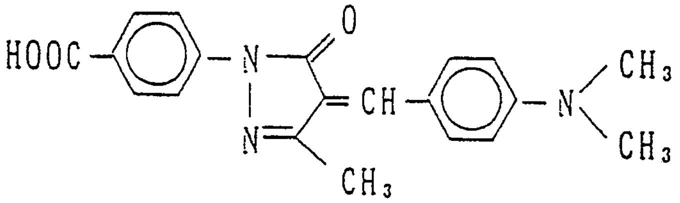
The five or six membered rings which are formed when R_1 and R_2 are joined together are, for example piperidine, morpholine or pyrrolidine rings.

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

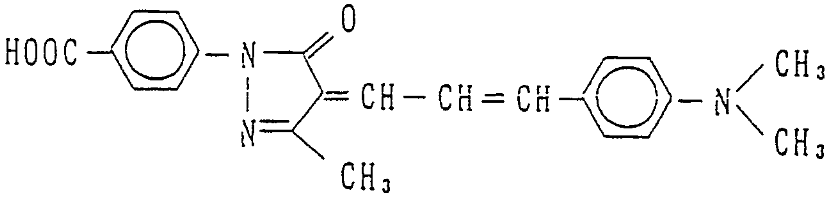
The electron withdrawing groups represented by X or Y may be the same or different, being cyano groups, carboxy groups, alkylcarbonyl groups (which may be substituted alkylcarbonyl groups, for example acetyl, propionyl, heptadecanoyl, dodecanoyl, hexadecanoyl, 1-oxy-7-chloroheptyl), arylcarbonyl groups (which may be substituted arylcarbonyl groups, for example benzoyl, 4-ethoxycarbonylbenzoyl, 3-chlorobenzoyl), alkoxycarbonyl groups (which may be substituted alkoxycarbonyl groups, for example methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, tert-amyloxycarbonyl, hexyloxycarbonyl, 2-ethylhexyloxycarbonyl, octyloxycarbonyl, decyloxycarbonyl, dodecyloxycarbonyl, hexadecyloxycarbonyl, octadecyloxycarbonyl, 2-butoxyethoxycarbonyl, 2-methylsulfonylethoxycarbonyl, 2-cyanoethoxycarbonyl, 2-(2-chloroethoxy)ethoxycarbonyl, 2-(2-(2-chloroethoxy)ethoxy)ethoxycarbonyl), aryloxycarbonyl groups (which may be substituted aryloxycarbonyl groups, for example phenoxycarbonyl, 3-ethylphenoxycarbonyl, 4-ethylphenoxy-carbonyl, 4-fluorophenoxycarbonyl, 4-nitrophenoxycarbonyl, 4-methoxyphenoxycarbonyl, 2,4-di(tert-amyl)phenoxycarbonyl), carbamoyl groups (which may be substituted carbamoyl groups, for example carbamoyl, ethylcarbamoyl, dodecylcarbamoyl, phenylcarbamoyl, 4-methoxyphenylcarbamoyl, 2-bromophenylcarbamoyl, 4-chlorophenylcarbamoyl, 4-ethoxycarbonylphenylcarbamoyl, 4-propylsulfonylphenylcarbamoyl, 4-cyanophenylcarbamoyl, 3-methylphenylcarbamoyl, 4-hexyloxyphenylcarbamoyl, 2,4-di-(tert-amyl)phenylcarbamoyl, 2-chloro-3-(dodecyloxycarbamoyl)phenylcarbamoyl, 3-(hexyloxycarbonyl)-phenylcarbamoyl), sulfonyl groups (for example, methylsulfonyl, phenylsulfonyl), and sulfamoyl groups (which may be substituted sulfamoyl groups, for example sulfamoyl, methylsulfamoyl).

Actual examples of dyes which can be used in the present invention are indicated below.

I − 1


HOOC
N
N
O
CH
CH₃
N
CH₃
CH₃

I − 2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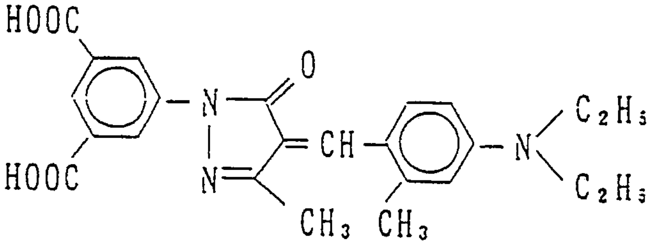
N
O
CH − CH = CH
CH₃
N
CH₃
CH₃

I − 3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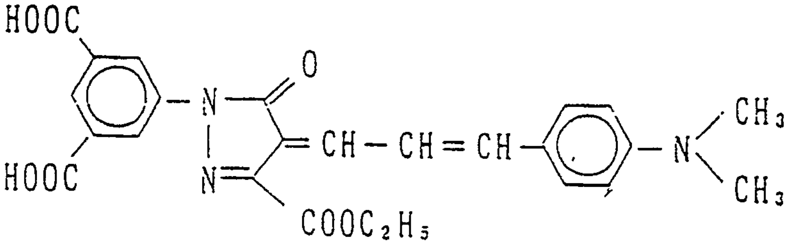
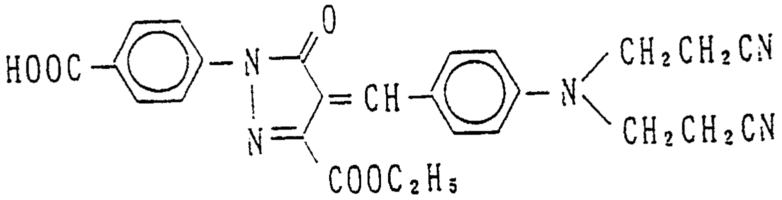
N
O
CH
CH₃
CH₃
N
C₂H₅
C₂H₅

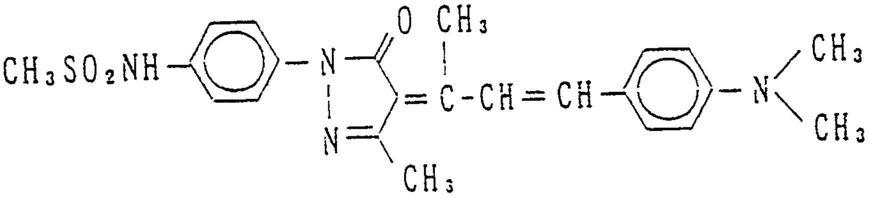
I − 4


HOOC
HOOC
N
N
O
CH − CH = CH
COOC₂H₅
N
CH₃
CH₃

I − 5



I − 6



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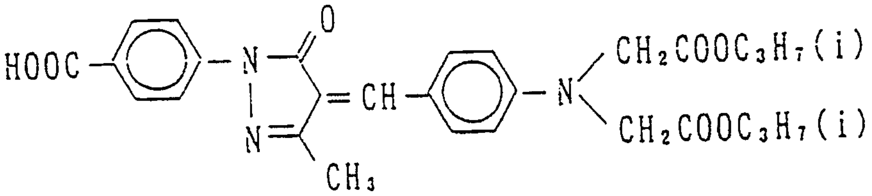

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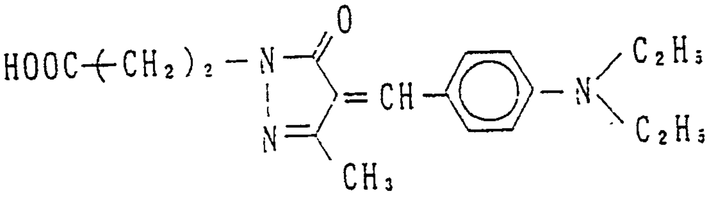
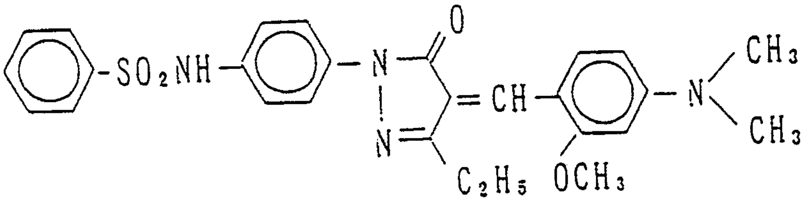
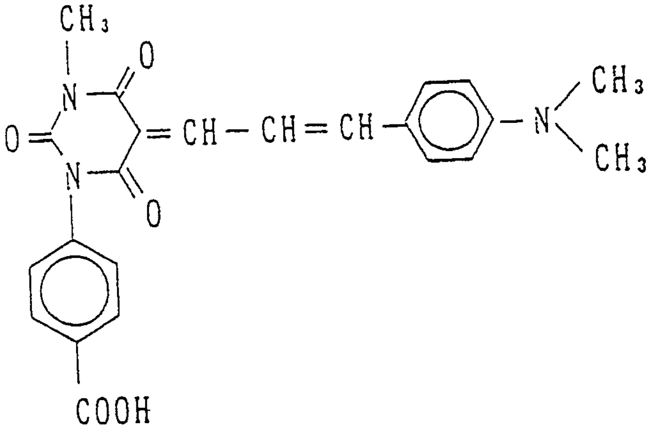


I－9



I－10



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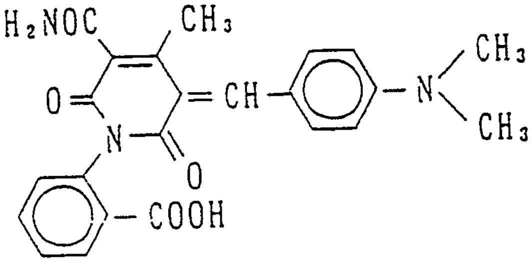
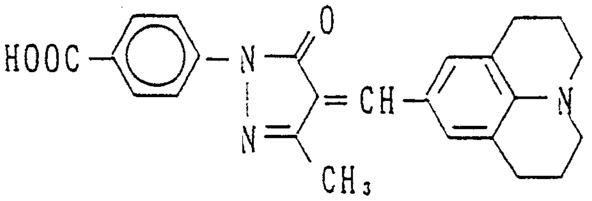
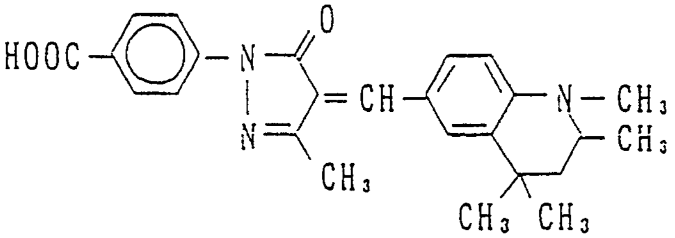


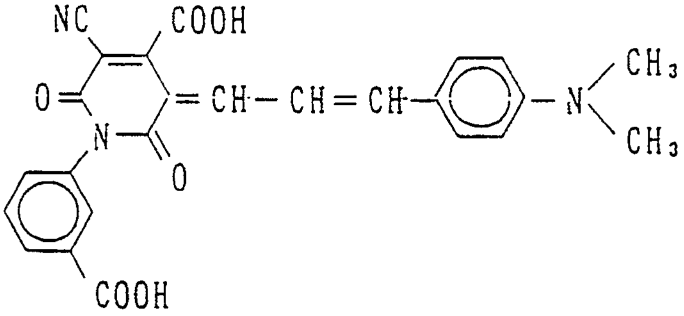
I－１２



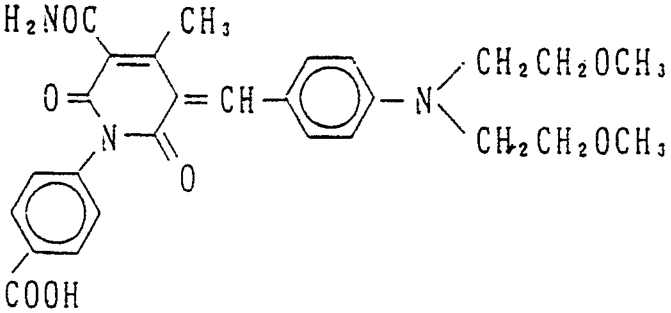
I－１３



I－１４



I－１５



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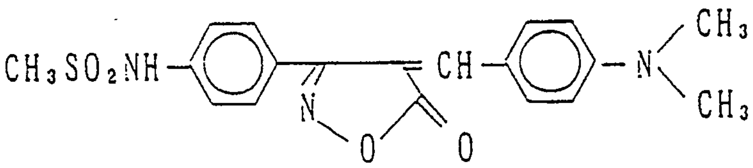

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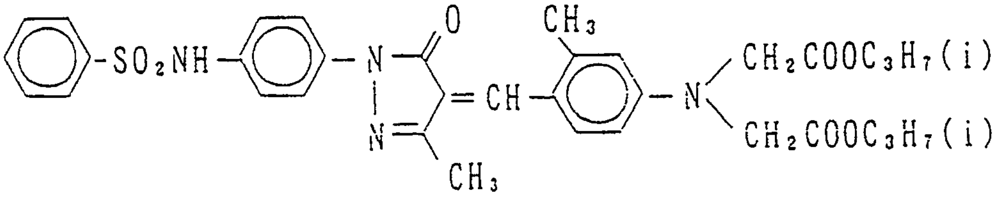
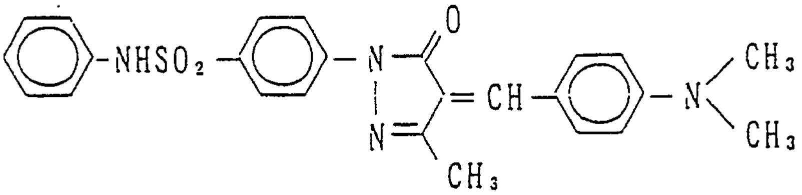


I－18



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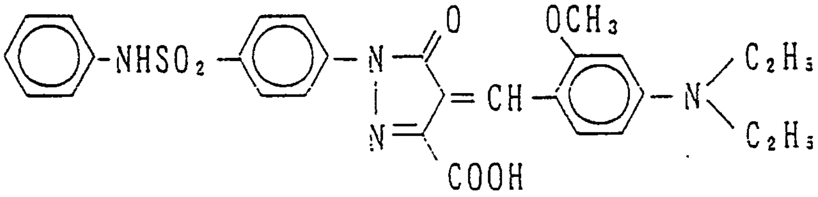
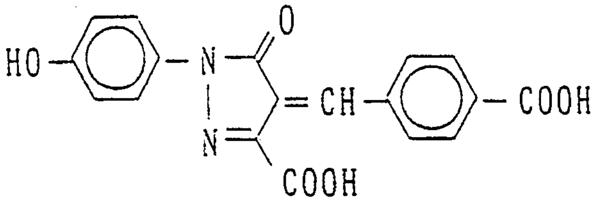
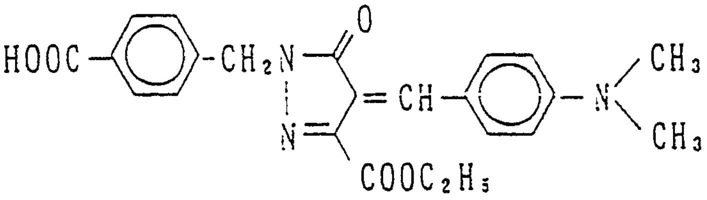


I－２０



I－２１



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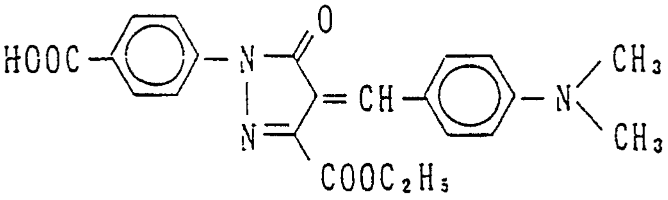
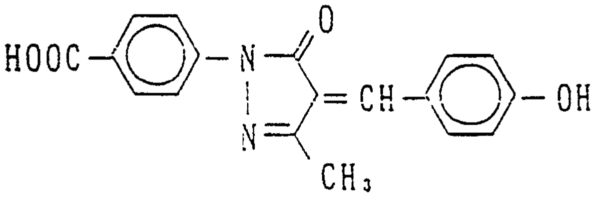
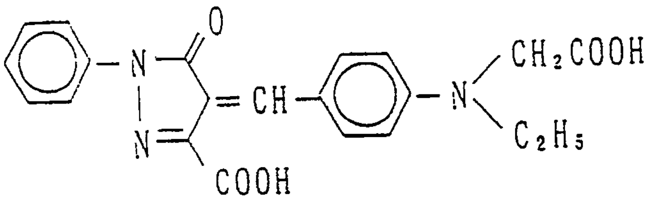


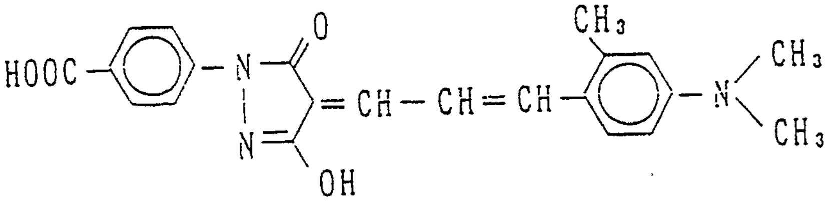
I－２５



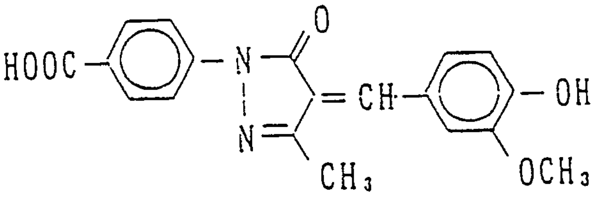
I－２６



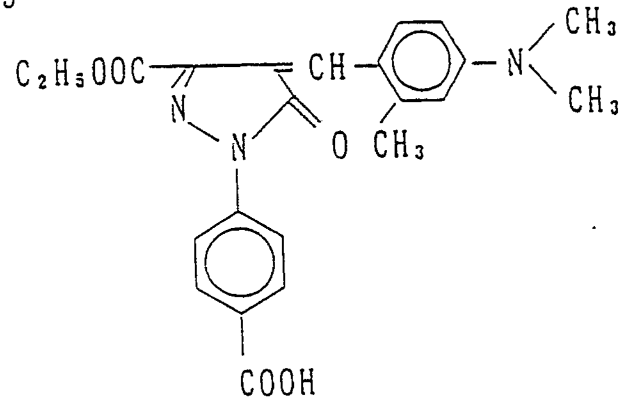
I－２７



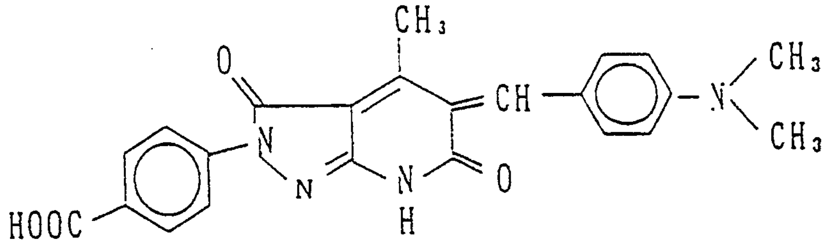
I－２８



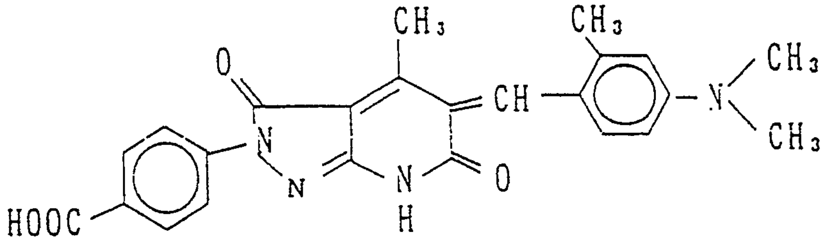
I－２９



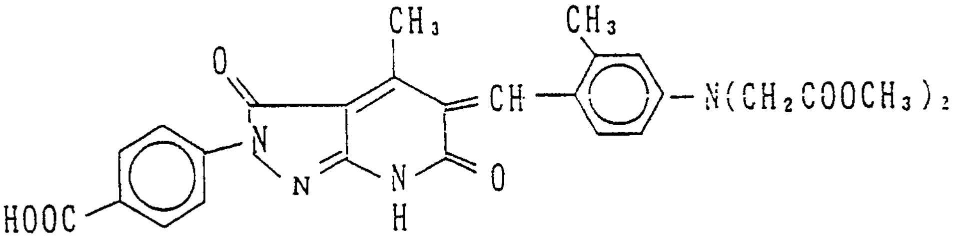
I－３０



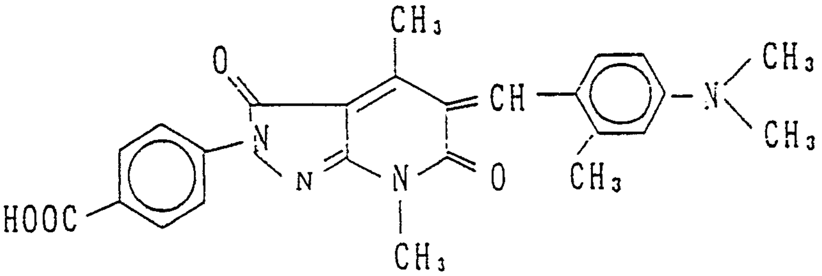
I－３１



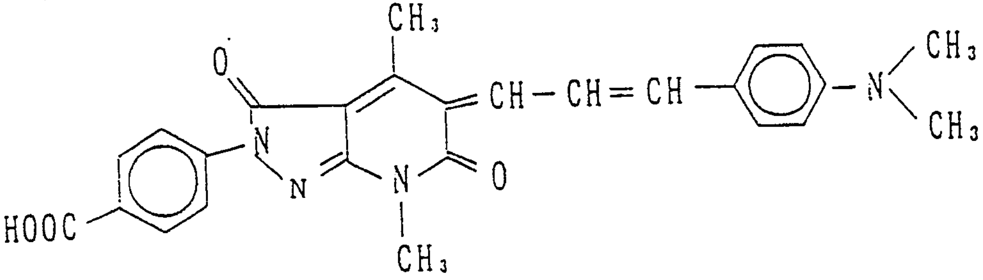
I－３２



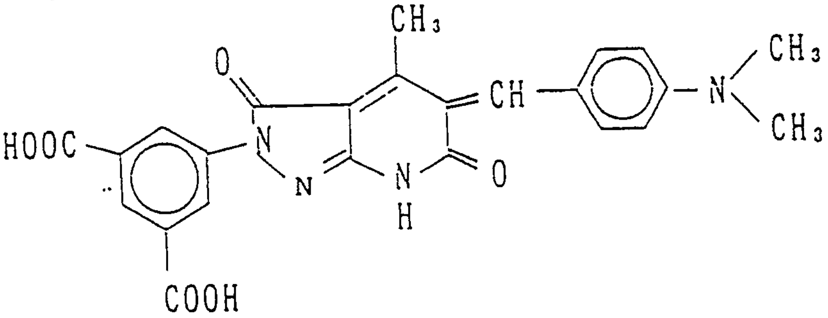
I－３３



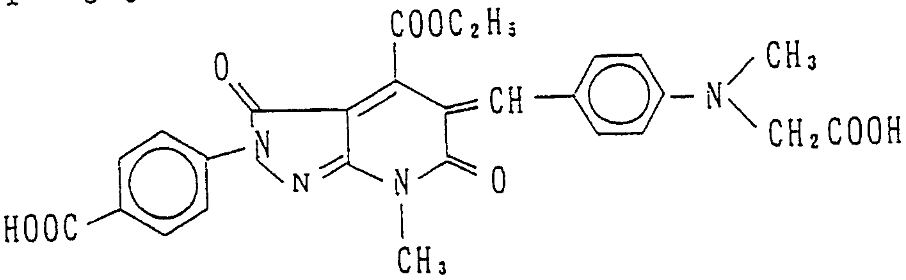
I－３４



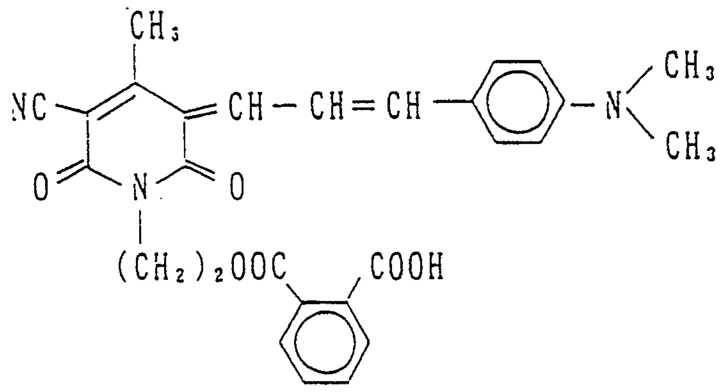
I－３５



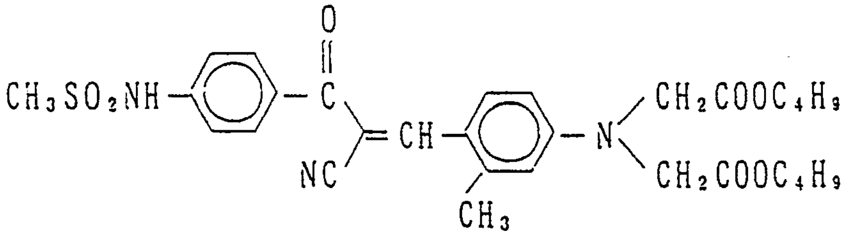
I－３６



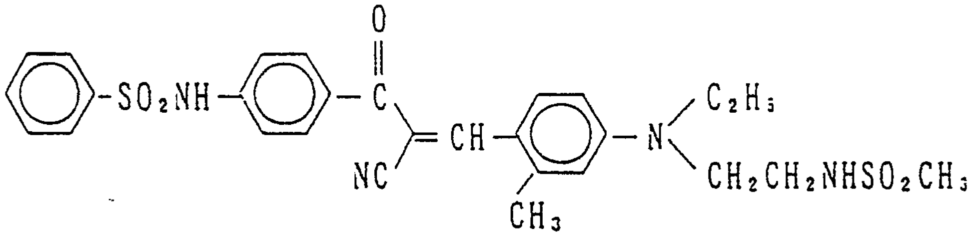
I－37



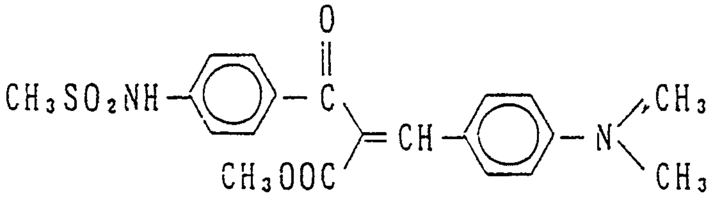
II－1



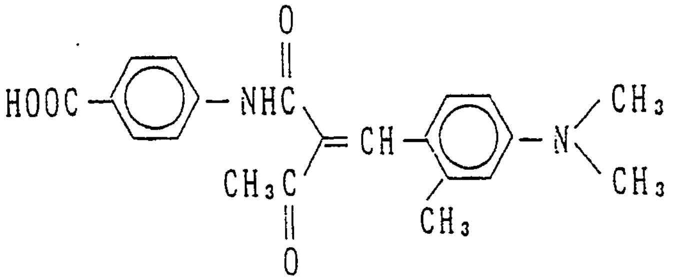
II－2



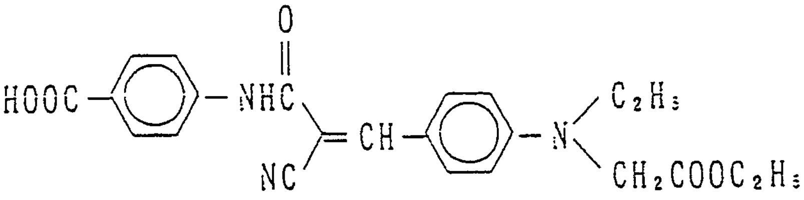
II－3



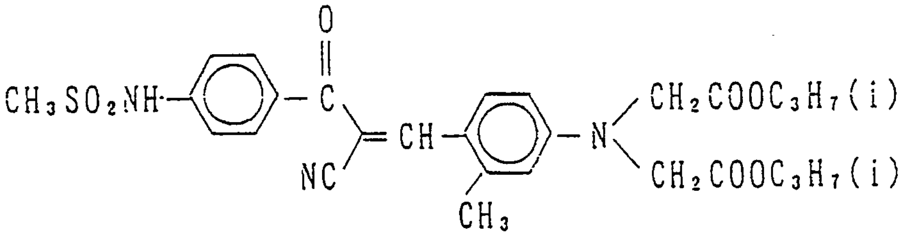
Ⅱ－4



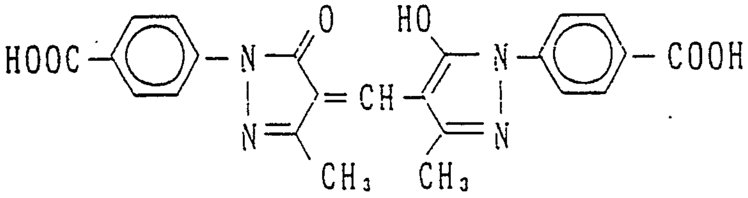
Ⅱ－5



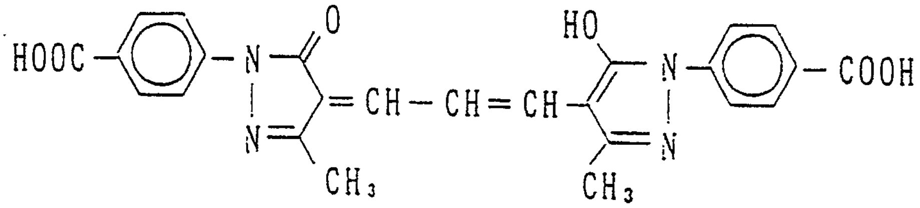
Ⅱ－6



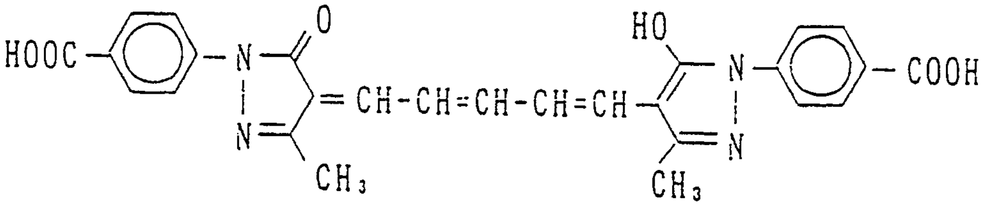
Ⅲ－1



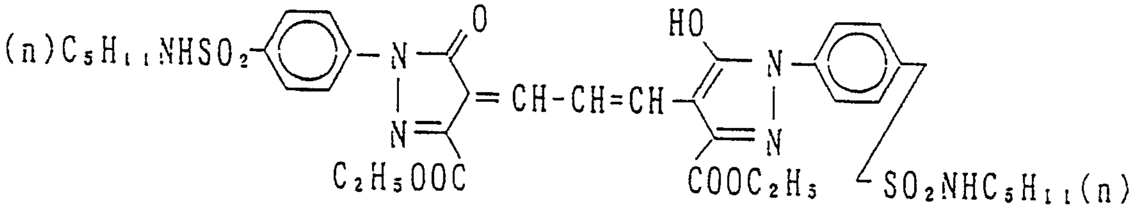
Ⅲ - 2


HOOC
O
N
N
CH₃
=CH-CH=CH
HO
N
N
CH₃
COOH

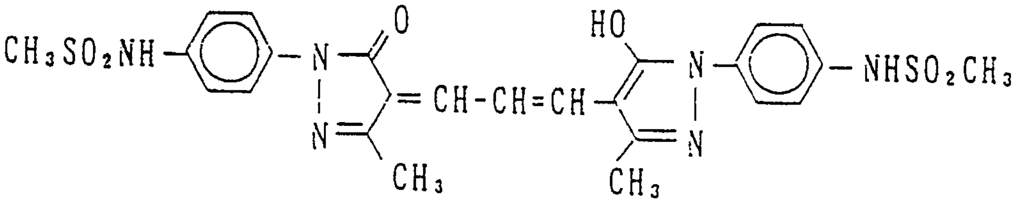
Ⅲ - 3


HOOC
O
N
N
CH₃
=CH-CH=CH-CH=CH
HO
N
N
CH₃
COOH

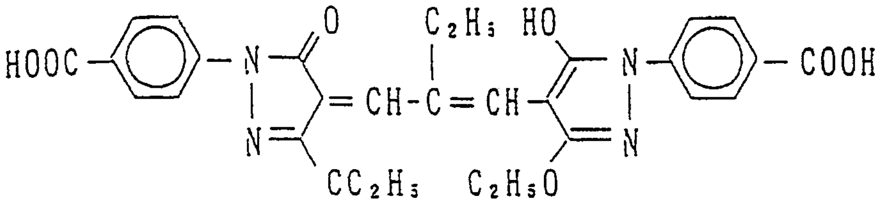
Ⅲ - 4


(n)C₅H₁₁NHSO₂
O
N
N
C₂H₅OOC
=CH-CH=CH
HO
N
N
COOC₂H₅
SO₂NHC₅H₁₁(n)

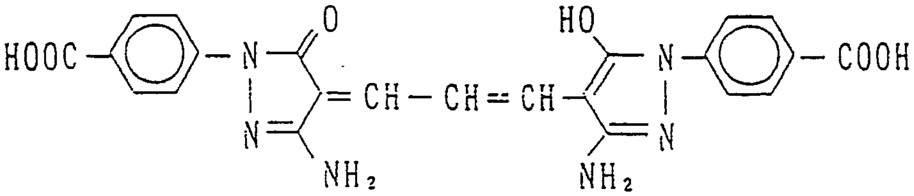
Ⅲ - 5


CH₃SO₂NH
O
N
N
CH₃
=CH-CH=CH
HO
N
N
CH₃
NHSO₂CH₃

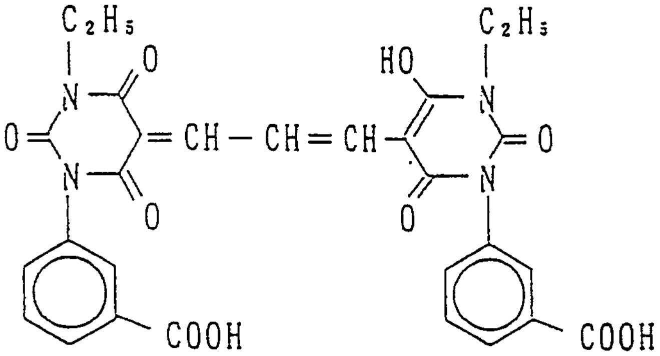
Ⅲ－6


HOOC
O
C2H5
HO
N
COOH
N
CH-C=CH
N
N
CC2H5
C2H5O

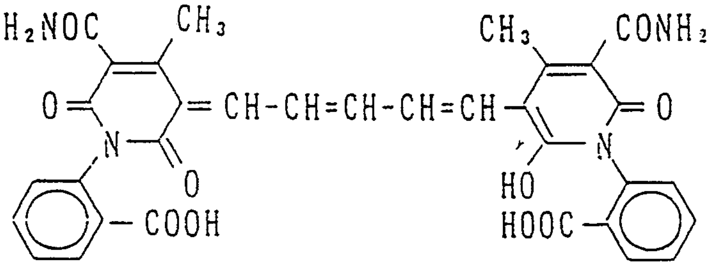
Ⅲ－7


HOOC
O
HO
N
N
COOH
CH－CH=CH
N
N
NH2
NH2

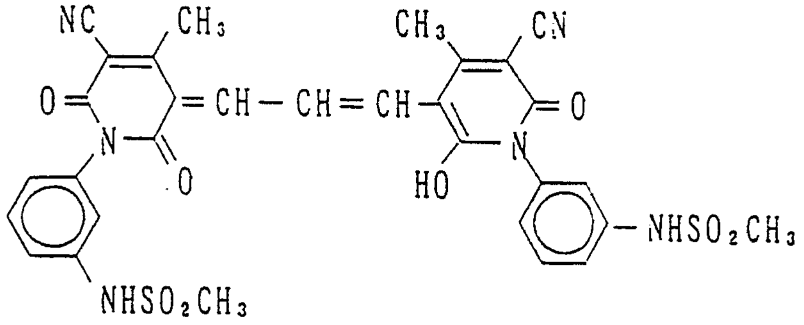
Ⅲ－8


C2H5
C2H5
O
HO
N
N
O
CH－CH=CH
O
N
N
O
O
COOH
COOH

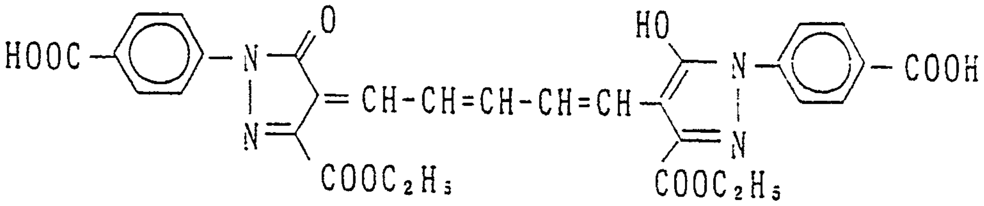
Ⅲ－9


H2NOC
CH3
CH3
CONH2
O
CH-CH=CH-CH=CH
O
N
N
O
HO
COOH
HOOC

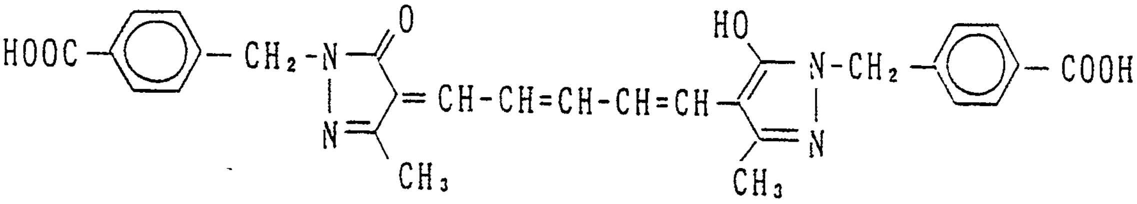
Ⅲ－１０



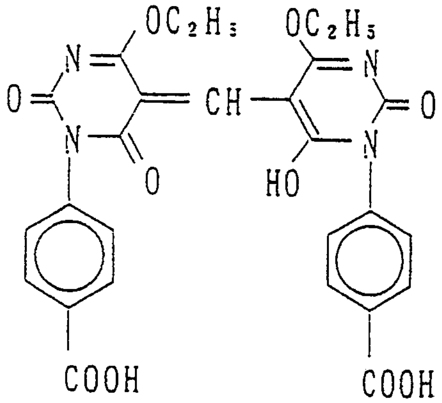
Ⅲ－１１



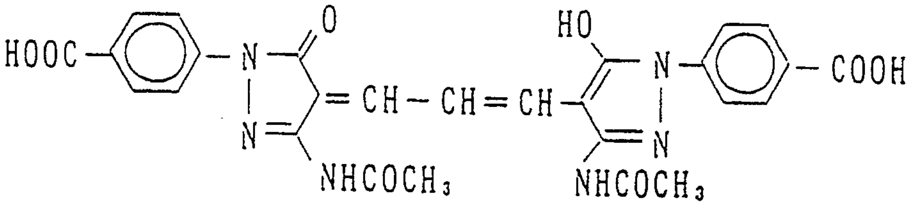
Ⅲ－１２



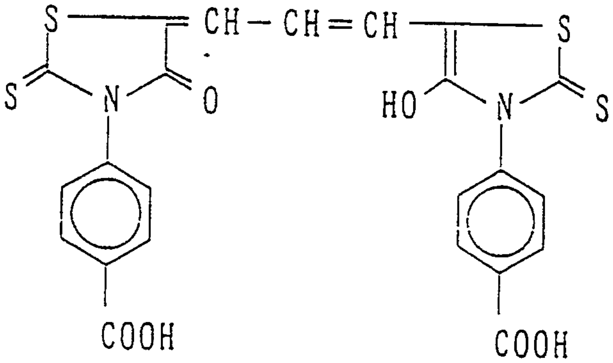
Ⅲ－１３


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

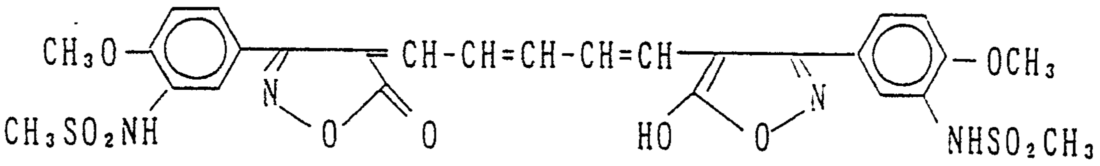
Ⅲ－１４


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

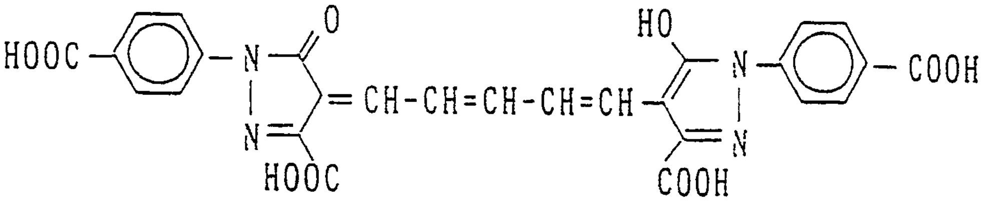
Ⅲ－１５


S
CH－CH＝CH
S
S
N
O
HO
N
S
COOH
COOH

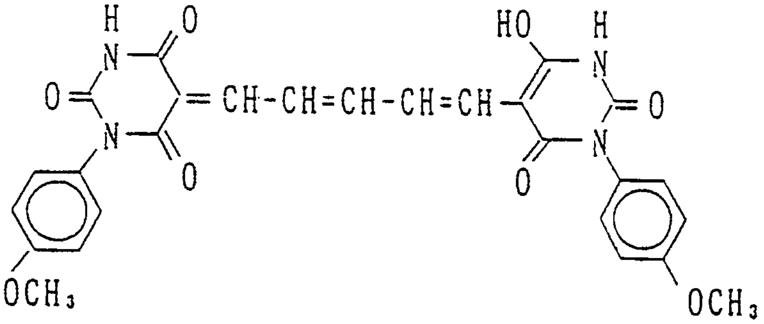
Ⅲ－１６



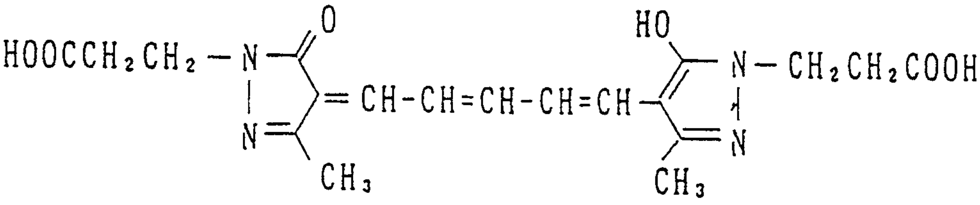
Ⅲ－１７



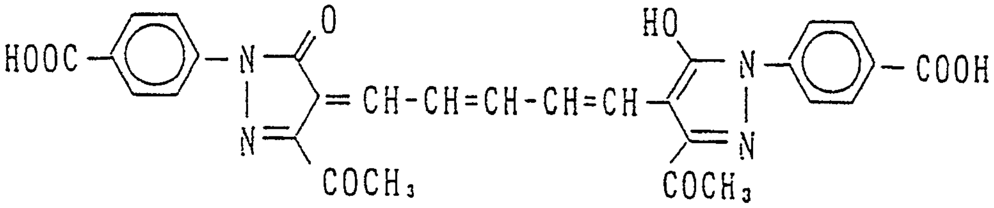
Ⅲ－１８



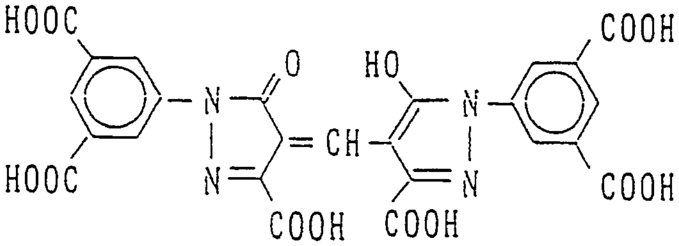
Ⅲ－１９



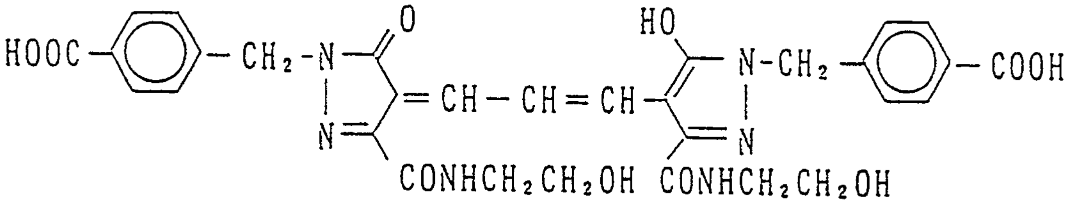
Ⅲ－２０



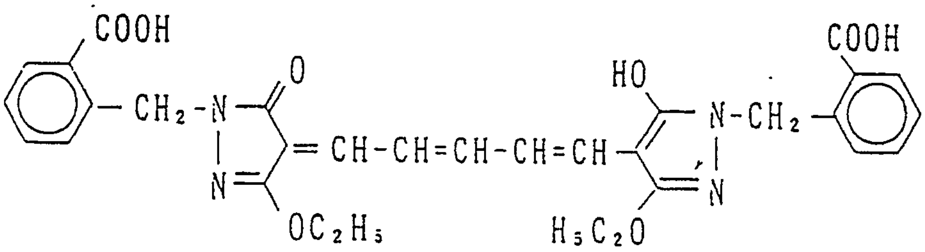
Ⅲ－２１



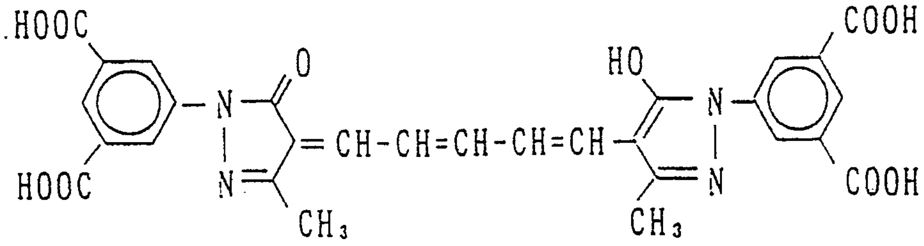
Ⅲ－２２



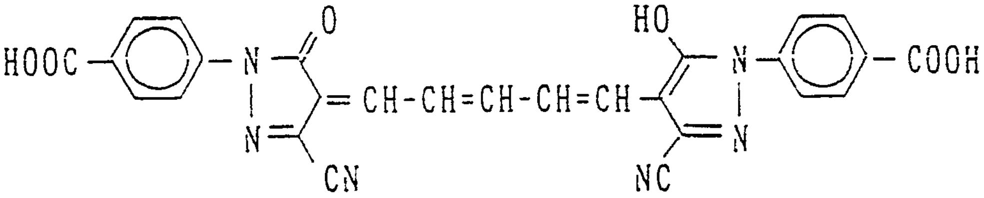
Ⅲ－２３



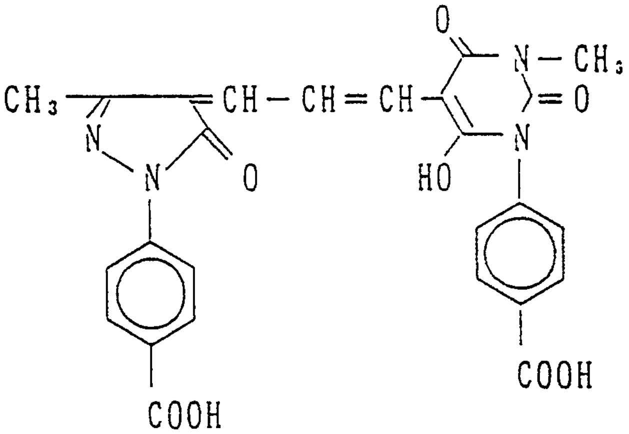
Ⅲ－２４



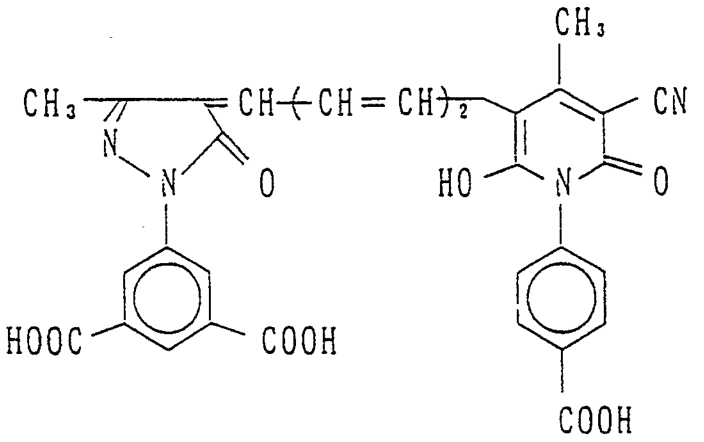
Ⅲ－２５



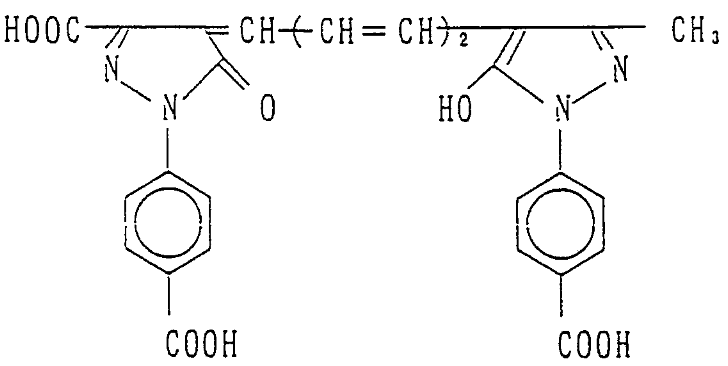
Ⅲ－２６



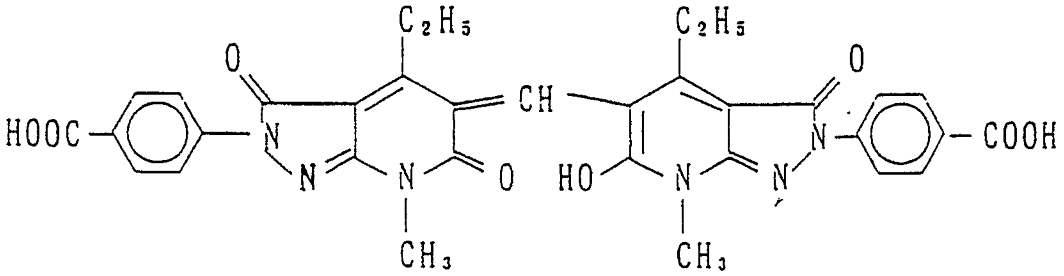
Ⅲ－２７


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

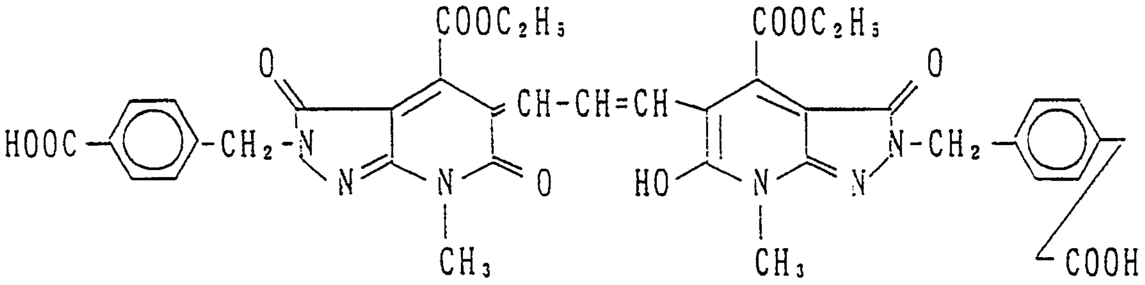
Ⅲ－２８


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

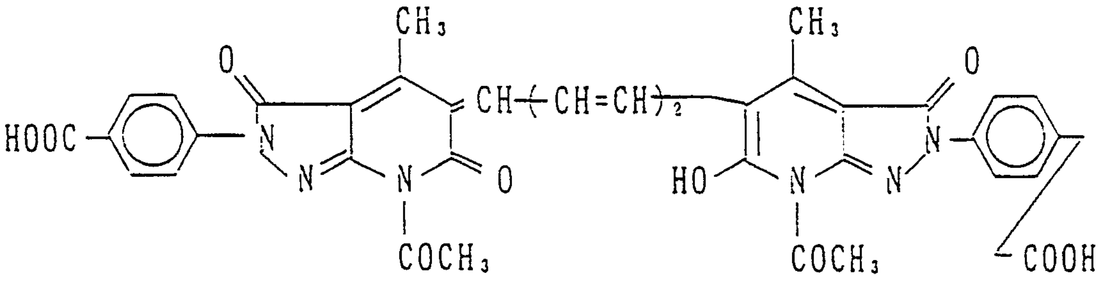
Ⅲ－２９


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

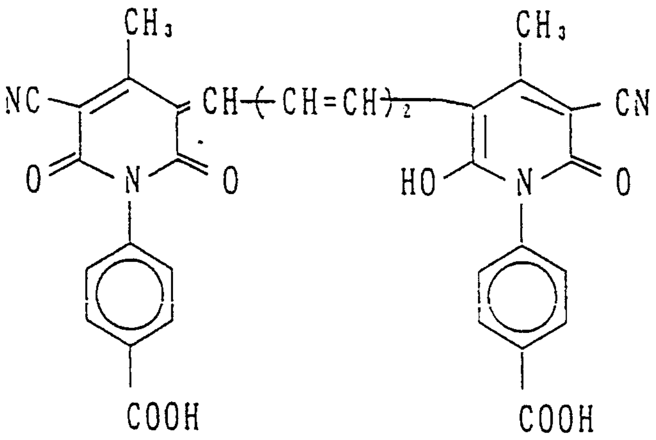
Ⅲ－３０



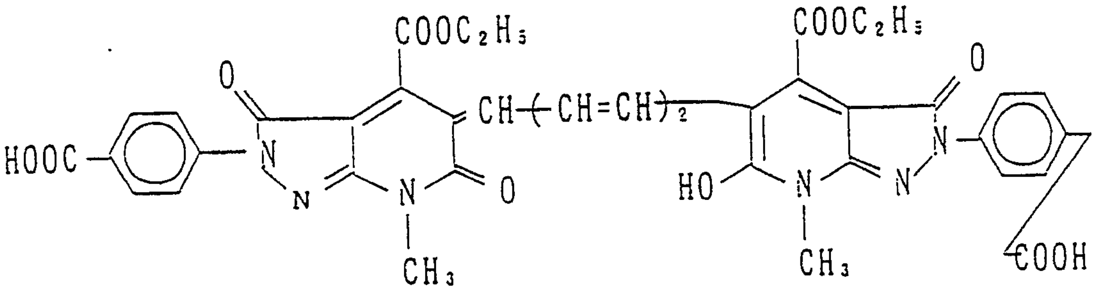
Ⅲ－３１



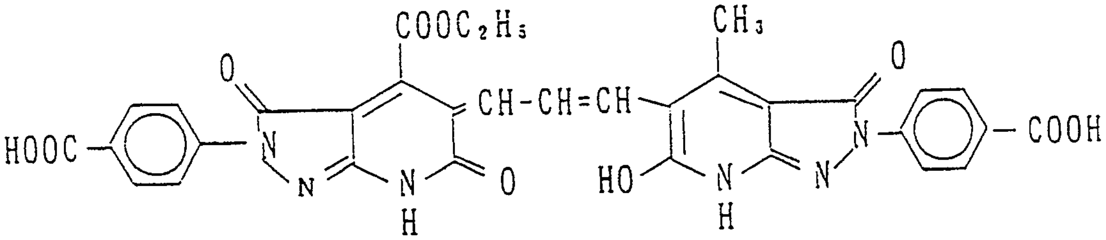
Ⅲ－３２



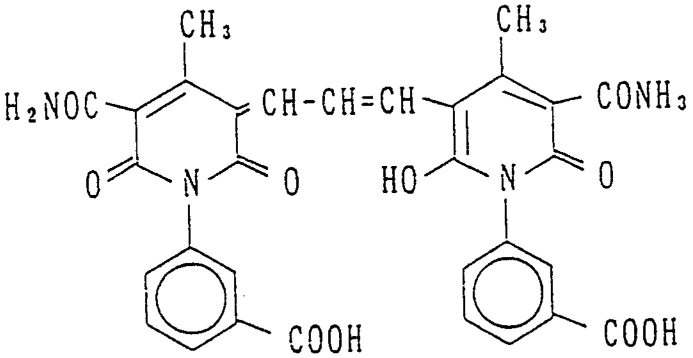
Ⅲ－３３



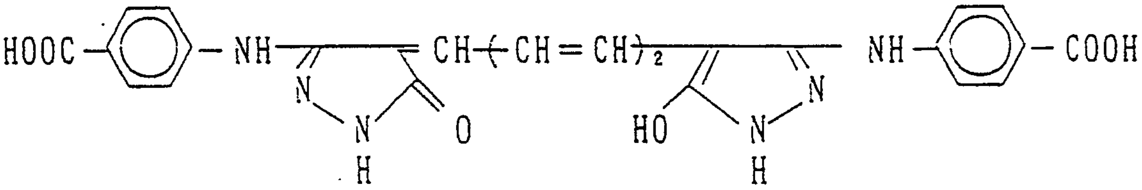
Ⅲ－３４



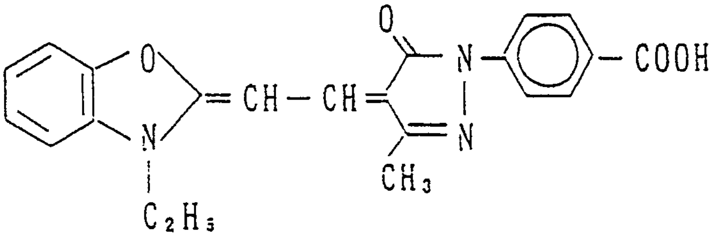
Ⅲ－３５



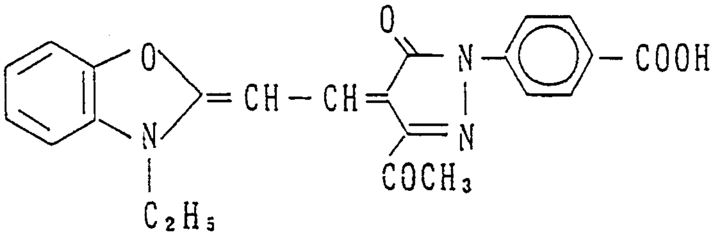
Ⅲ－３６



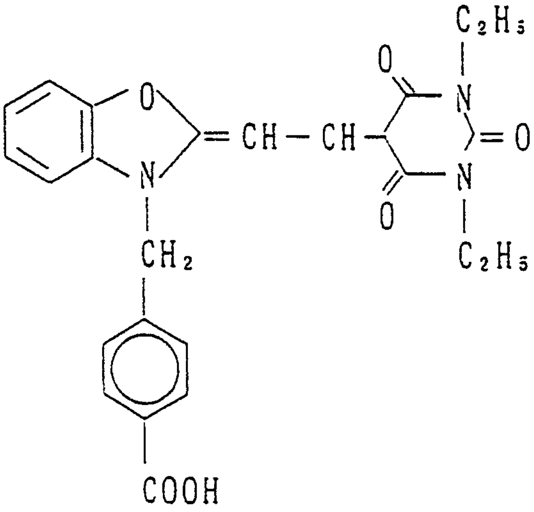
Ⅳ－１



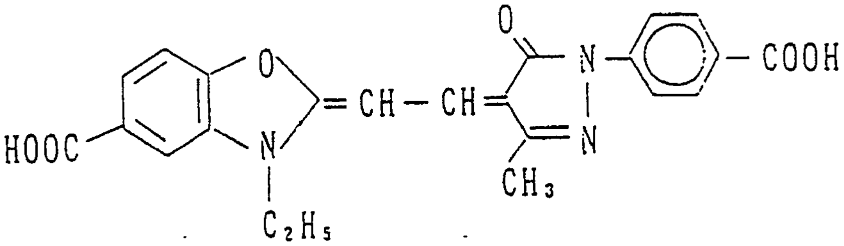
Ⅳ－２



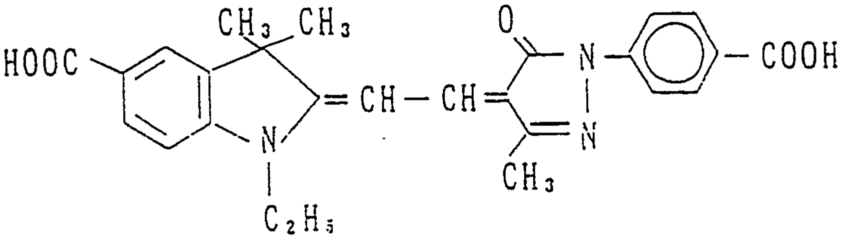
Ⅳ－３



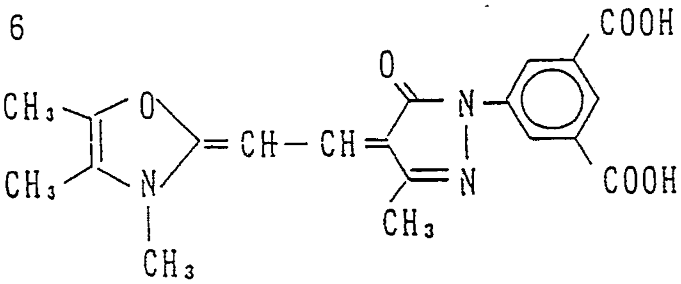
IV－4



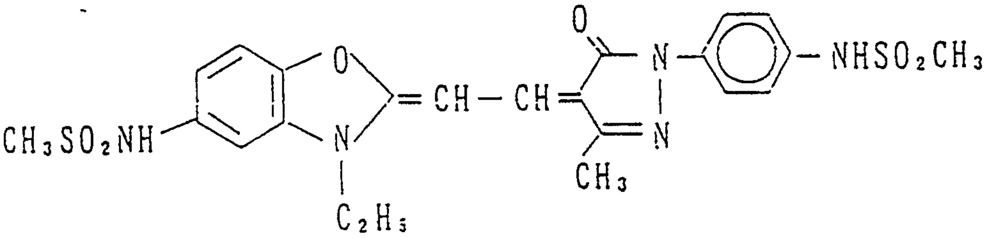
IV－5



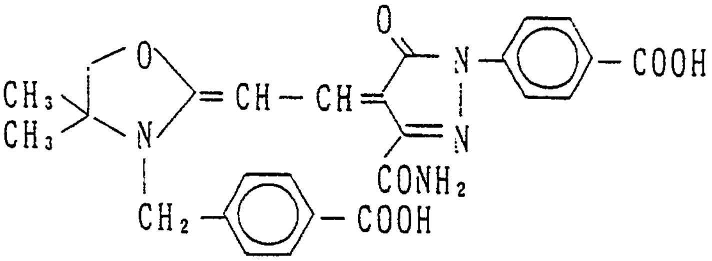
IV－6



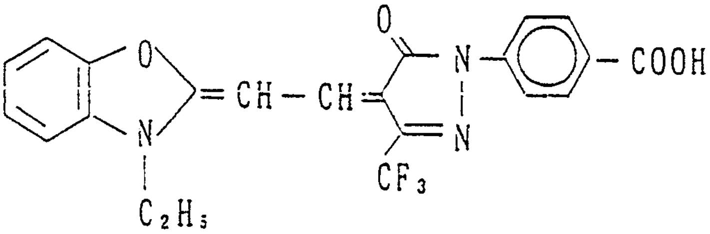
IV－7



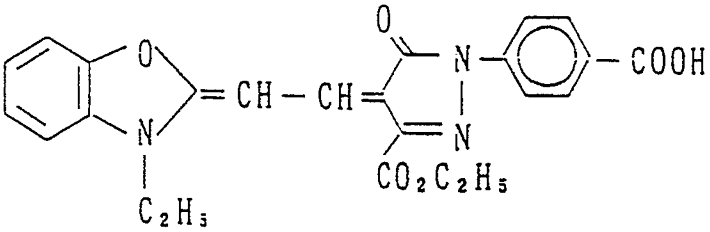
IV－8



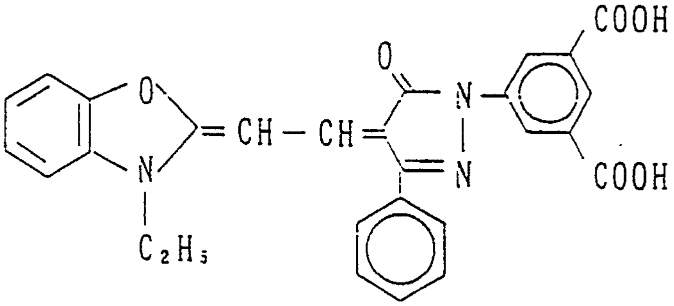
IV－9



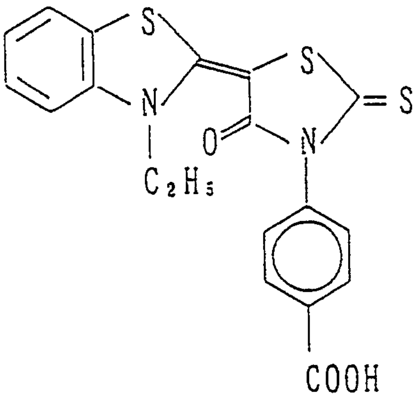
IV－10



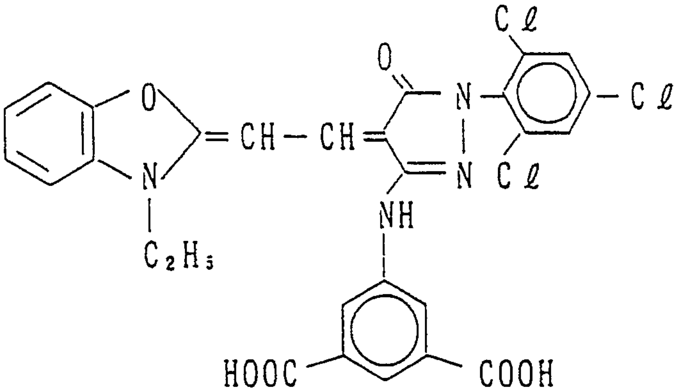
IV－11



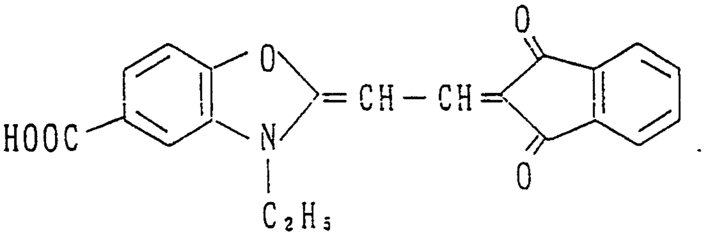
IV－１２



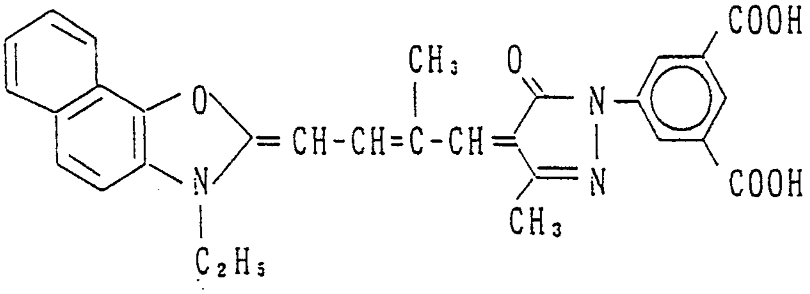
IV－１３



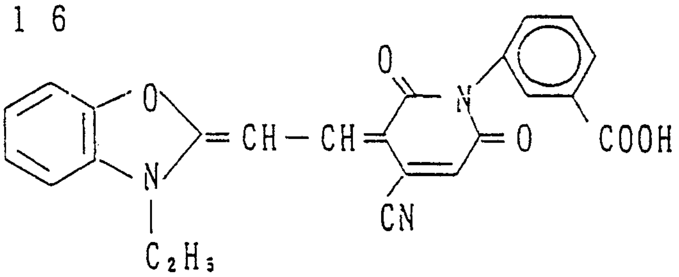
IV－１４



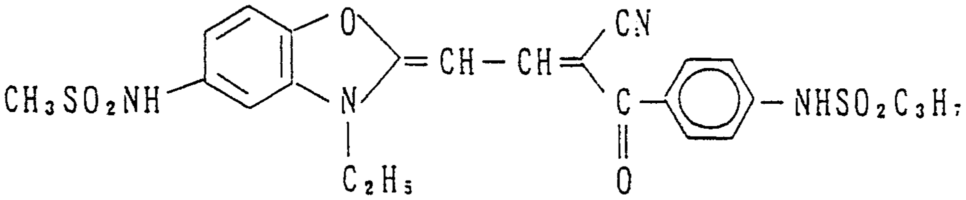
IV－15



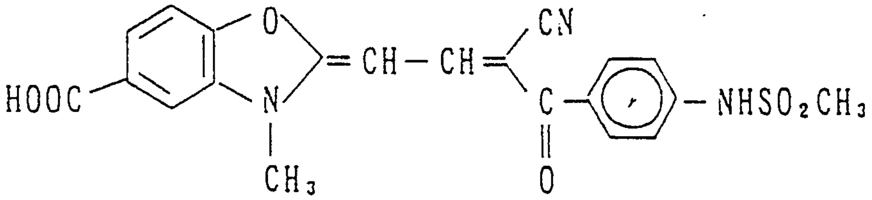
IV－16



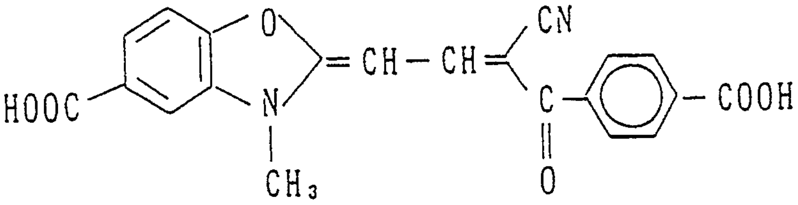
V－1



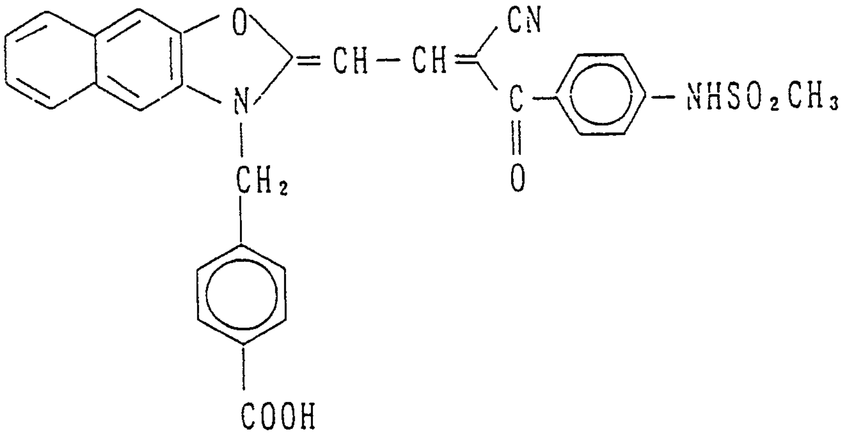
V－2



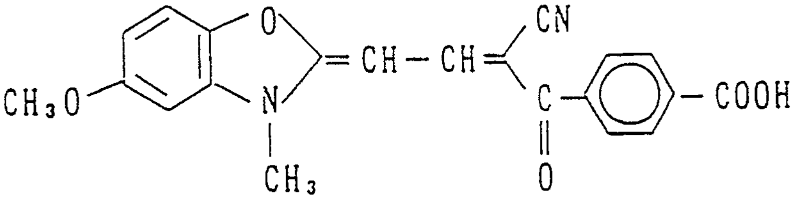
V − 3



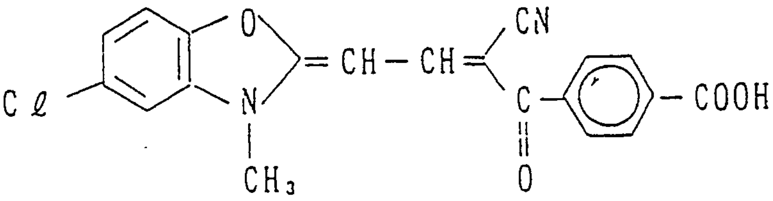
V − 4



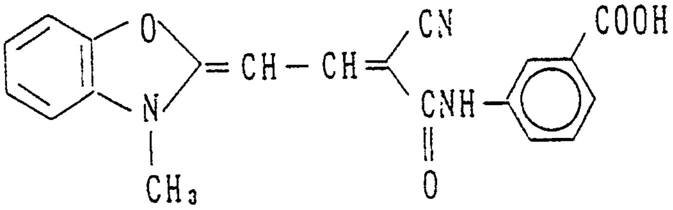
V − 5



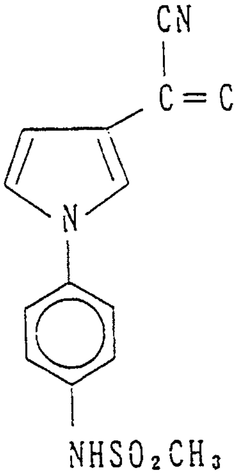
V − 6



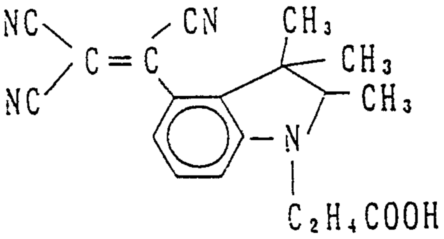
V－7



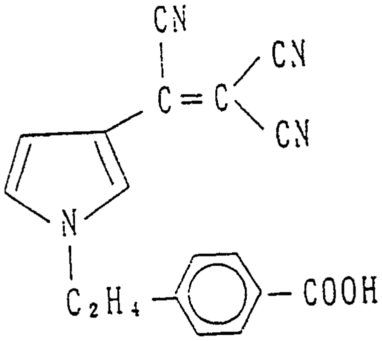
Ⅵ－1



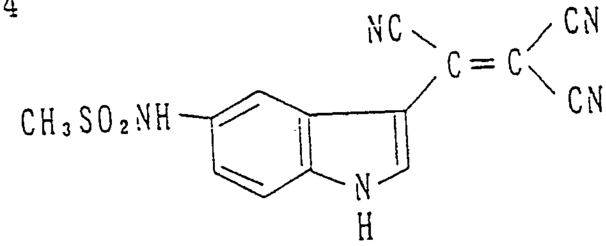
Ⅵ－2



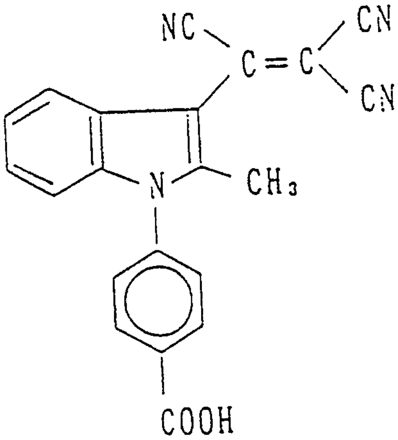
VI − 3


CN
C = C
CN
CN
N
C₂H₄
COOH

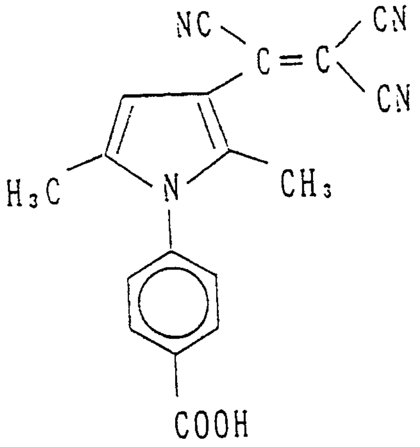
VI − 4


NC
C = C
CN
CN
CH₃SO₂NH
N
H

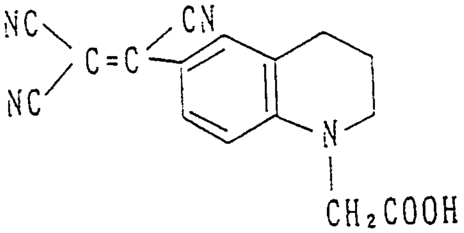
VI − 5


NC
C = C
CN
CN
N
CH₃
COOH

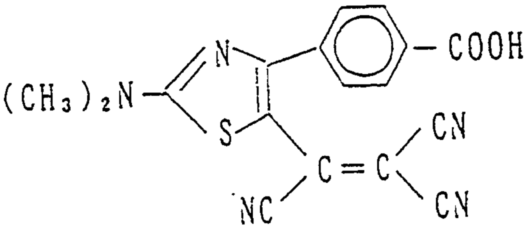
VI − 6


NC
CN
CN
C=C
H₃C
N
CH₃
COOH

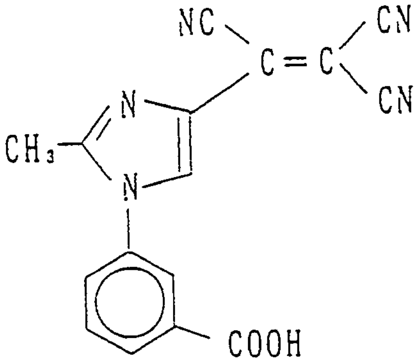
VI − 7


NC
CN
NC
C=C
N
CH₂COOH

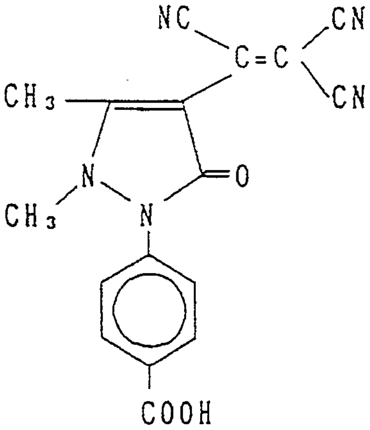
VI − 8


(CH₃)₂N
N
S
COOH
CN
C=C
NC
CN

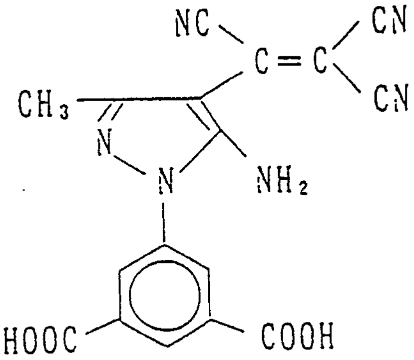
VI－9



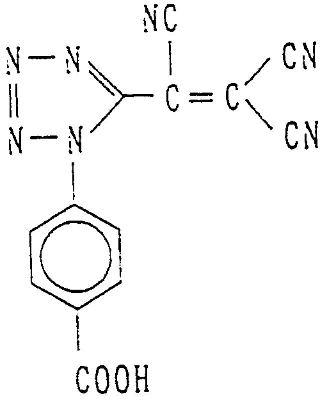
VI－10



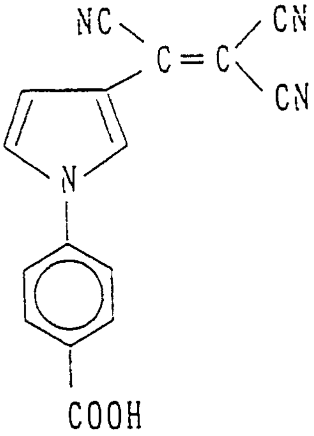
VI－11



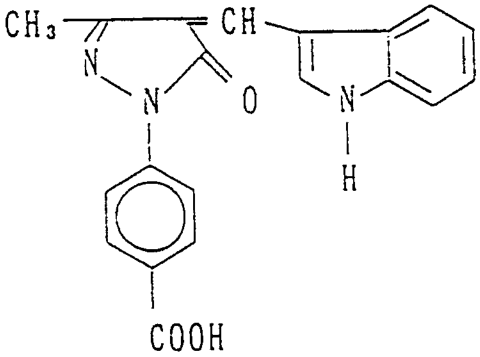
Ⅵ－１２



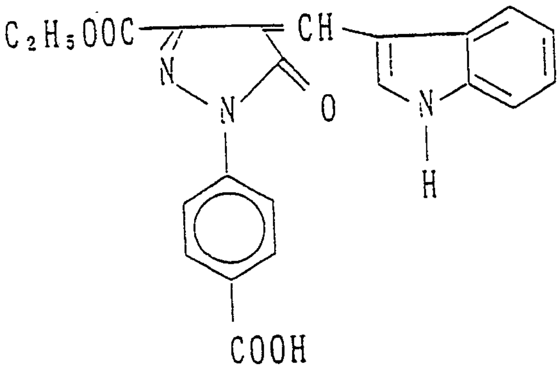
Ⅵ－１３



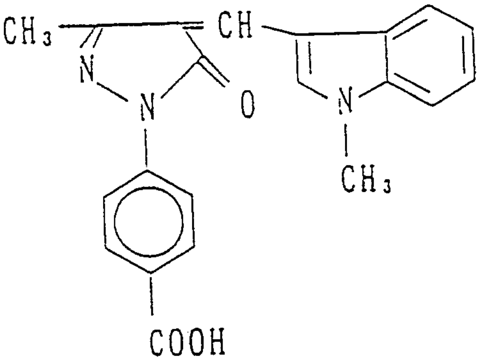
Ⅶ－１



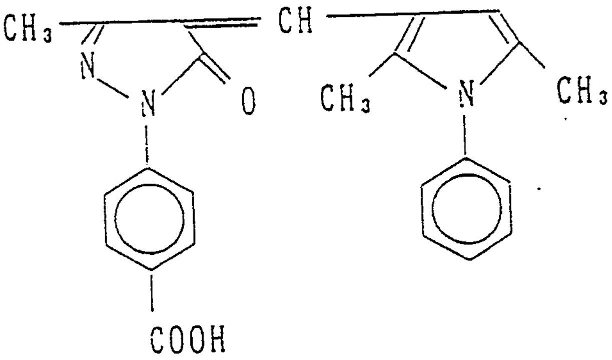
VII − 2



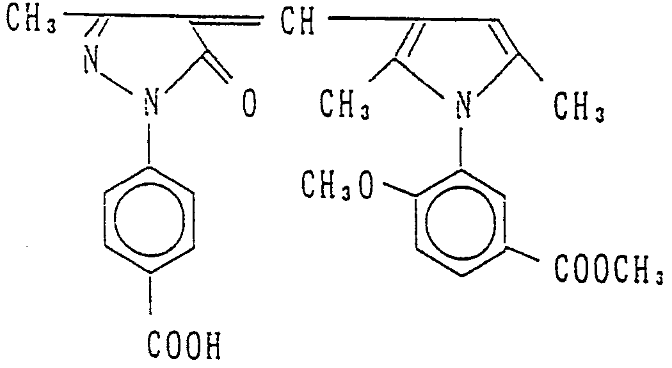
VII − 3



VII − 4



VII − 5



The dyes used in this present invention can be prepared easily using the methods disclosed, for example, in International Patent WO88/04794, European Patent EP 0274723A1, European Patents 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, 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 Applications 1-50874, 1-103751 and 1-307363, and on the basis of these methods.

This present invention is not limited to the dyes indicated above.

In this present invention the term solid dispersed dyes signifies the presence of the dye as a solid of a size such that diffusion within the layers is essentially impossible, their presence in a molecular state within the intended colored layer being impossible because the solubility of the dyes themselves is inadequate.

Methods of preparation have been disclosed, for example, in International Patent Laid Open (WO)-88/04794, European Patent (EP) 0276566A1 and JP-A-63-197943, but use of the method in which the dye is pulverized in a ball mill and stabilized with surfactant and gelatin, and the method in which the dye is dissolved in an alkaline solution and precipitated by lowering the pH are preferred. However, this present invention is not limited to these methods of preparation.

Moreover, combinations of two or more types of solid dispersed dye which have different hues can be used in accordance with the spectral sensitivity region of the silver halide emulsion or the application and method of use of the photosensitive material.

These solid dispersed dyes can be used not only between the support and the silver halide emulsion layer but also in other layers, for example silver halide emulsion layers for anti-irradiation purposes or between the silver halide emulsion layer and the exposing light source, for example in certain cases in a protective layer, as a safe-light filter, as required.

The hydrophilic colloids generally known in the field of photographic materials can be used in a layer which contains the solid dispersed dye which is located between the support and a silver halide emulsion layer in this present invention, which is to say that the hydrophilic colloid can be selected from among, for example, gelatin, gelatin derivatives, poly(vinyl alcohol), cellulose derivatives, starch derivatives, and polyacrylamides. As well a lime treated gelatin, acid treated gelatins, for example, can be used as gelatin. The amount of hydrophilic colloid coated in the solid dispersed dye layer in this present invention is preferably from 0.05 g/m^2 to 0.50 g/m^2, and most desirably from 0.10 g/m^2 to 0.50 g/m^2. If the coated weight of hydrophilic colloid is too high then the total amount of hydrophilic colloid including that in the silver halide emulsion layer which is required to provide a satisfactorily high maximum density after development processing and in the protective layer which is required to provide the film properties required for handling becomes high and the suitability for rapid processing is lost.

The proportions (by weight) of dye/hydrophilic colloid in the solid dispersed dye layer is not more than 0.4, and preferably not more than 0.3. The lower limits of the propotion are not limited but preferably about 0.01.

The total hydrophilic colloid coated weight on the silver halide emulsion layer side, including that in the solid dispersed dye containing layer, is not more than 3.0 g/m^2, and preferably not more than 2.5 g/m^2. The lower limits are not limited but preferably about 1.0 g/m^2.

The coated weight of hydrophilic colloid which contains solid dispersed dye in this present invention is not more than 0.50 g/m^2 and so the average particle size is less than 3 μm and preferably not more than 1 μm. It is most desirably not more than 0.5 μm.

The solid dispersed layer may be coated independently or at the same time as the silver halide emulsion layer, for example, on a support which has been provided with an under-layer, or it can be coated as an under-layer or as part of an under-layer. In those cases where it is coated as part of an under-layer, this layer can be established as a second layer after the high temperature coating and drying of a vinylidene chloride aqueous latex, an aqueous vinyl polymer latex or an aqueous polyester as a first under-layer, or it can be established as a third under-layer via a thin gelatin layer.

Under-layer polymers which can be used conjointly in an under-layer include, for example, halogen containing synthetic resins such as poly(vinyl chloride), poly(vinyl bromide), poly(vinyl fluoride), poly(vinylidene chloride), poly(vinyl acetate), chlorinated polyethylene, chlorinated polypropylene, brominated polyethylene, chlorinated rubber, vinyl chloride/ethylene copolymer, vinyl chloride/propylene copolymer, vinyl chloride/styrene copolymer, vinyl chloride/iso-butylene copolymer, vinyl chloride/vinylidene chloride copolymer, vinyl chloride/styrene/maleic anhydride terpolymer, vinyl chloride/styrene/acrylonitrile copolymer, vinyl chloride/butadiene copolymer, vinyl chloride/isoprene copolymer, vinyl chloride/chlorinated propylene copolymer, vinyl chloride/vinylidene chloride/vinyl acetate terpolymer, vinyl chloride/acrylic acid ester copolymer, vinyl chloride/ maleic acid ester copolymer, vinyl chloride/methacrylic acid ester copolymer, vinyl chloride/acrylonitrile copolymer, internally plasticized poly(vinyl chloride), vinyl chloride/ vinyl acetate copolymer, poly(vinylidene chloride), vinylidene chloride/methacrylic acid ester copolymer, vinylidene chloride/acrylonitrile copolymer, vinylidene chloride/acrylic acid ester copolymer, chloroethyl vinyl ether/acrylic acid ester copolymer, poly(vinylidene fluoride), polyolefins including α-olefin polymers such as polyethylene, polypropylene, polybutene, poly-3-methylbutene and ethylene/propylene copolymer, ethylene/propylene/1,4-hexadiene copolymer, ethylene/vinyl acetate copolymer, copoly(butene-1/propylene) and butadiene/acrylonitrile copolymer, and blends of these copolymers with halogen containing resins, acrylic resins such as acrylic acid ester/acrylonitrile polymer, acrylic acid ester/styrene copolymer, methacrylic acid ester/acrylonitrile copolymer, methacrylic acid ester/styrene copolymer, poly(alkyl acrylate), acrylic acid/butyl acrylate copolymer, acrylic acid ester/butadiene/styrene copolymer, or polymers of methyl methacrylate/ethyl acrylate/2-hydroxyethyl acrylate/methacrylic acid in the ratio by weight of 67/23/7/3, of methyl methacrylate/ethyl acrylate/2-hydroxyethyl acrylate/methacrylic acid in the ratio by weight of 72/17/7/3, of methyl methacrylate/ethyl acrylate/2-hydroxyethyl acrylate/methacrylic acid in the ratio by weight of 70/20/7/3 and of methyl methacrylate/butyl acrylate/2-hydroxyethyl acrylate/methacrylic acid in the ratio by weight of 70/20/7/3, and polystyrene, copolymers of styrene with other monomers (for example, maleic anhydride, butadiene, acrylonitrile), acrylonitrile/butadiene/ styrene copolymer and polyacetal resins, poly(vinyl alcohol) or blends, block copolymers or graft copolymers of these resins, polyamide resin, poly(vinyl butyrate), cellulose derivatives, polyester resin and other vinyl polymers such as poly(vinyl alcohol), and also condensation polymers such as polycarbonate and polyether, rubbers such as natural rubber, butyl rubber, neoprene rubber, styrene/butadiene copolymer rubber, natural or artificial rubbers such as silicone rubber and polyurethane, polyamide, urethane elastomer and nylon/silicone based resins and nitrocellulose/polyamide resins as acrylic based, methacrylic based, polyolefin based, polyamide based, polyester based, polyurethane based, polycarbonate based, rubber based and cellulose based resins and aqueous polyesters or blends, block copolymers or graft copolymers of these resins. Styrene/butadiene copolymer and vinylidene chloride copolymers are the most desirable polymers.

The use of hydrophobic polymers in the under-layer is desirable for preventing any worsening of dimensional stability caused by the support taking up water during development processing in sensitive materials for printing purposes, and the use of vinylidene chloride is preferred.

Latexes are preferred embodiments of the polymers used in this present invention.

In this present invention there is at least one hydrophilic colloid layer which contains at least one type of water soluble dye on the opposite side of the support to the side having the silver halide emulsion layer. Although the added amount of the water soluble dye depends on the required absorbance and kind of the water soluble dye, it is generally from 1 mg/m^2 to 1 g/m^2, preferably from 10 mg/m^2 to 500 mg/m^2. Water soluble dyes which are decolorized or dissolved out and removed in the development processing operations are preferred for the water soluble dye. The dyes indicated below are known. For example, there are the oxonol dyes which have a pyrazolone nucleus or barbituric acid nucleus disclosed, for example, in British Patents 506,385, 1,177,429, 1,311,884, 1,338,799, 1,385,371, 1,467,214, 1,433,102 and 1,553,516, JP-A-48-85130, JP-A-49-114420, JP-A-50-147712, JP-A-55-161233, JP-A-58-143,342, JP-A-59-38742, JP-A-59-111641, JP-A-59-111640, and U.S. Patents 3,247,127, 3,469,985 and 4,078,933, other oxonol dyes disclosed, for example, in U.S. Patents 2,533,472 and 3,379,533, and British Patent 1,278,621, the azo dyes disclosed, for example, in British Patents 575,691, 680,631, 599,623, 786,907, 907,125 and 1,045,609, U.S. Patent 4,255,326 and JP-A-59-211043, the azomethine dyes disclosed, for example, in JP-A-50-100116, JP-A-54-118247 and British Patents 2,014,598 and 750,031, the anthraquinone dyes disclosed in U.S. Patent

2,865,752, the arylidene dyes disclosed, for example, in U.S. Patents 2,538,009, 2,688,541 and 2,538,008, British Patents 584,609 and 1,210,252, JP-A-50-40625, JP-A-51-3623, JP-A-51-10927, JP-A-54-118247, JP-B-48-3286 and JP-B-59-37303, the styryl dyes disclosed, for example, in JP-B-28-3082, JP-B-44-16594 and JP-B-59-28898, the triarylmethane dyes disclosed, for example, in British Patents 446,583 and 1,335,422, and JP-A-59-228250, the merocyanine dyes disclosed, for example, British Patents 1,075,653, 1,153,341, 1,284,730, 1,475,228 and 1,542,807, and the cyanine dyes disclosed, for example, U.S. Patents 2,843,486 and 3,294,539. (The term "JP-B" as used herein signifies an "examined Japanese patent publication".)

From among these dyes, the arylidene dyes which have a pyrazolone nucleus and the oxonol dyes which have two pyrazolone nuclei are especially desirable, being decolorized in developers which contain sulfite.

The water soluble dyes which are used here are used for back-up purposes in cases where the anti-halation effect in the solid dispersed dye layer is inadequate, for providing safe-lighting safety, or for the purpose of reverse side discrimination and, although no limitation is imposed upon their absorption characteristics, the inclusion of at least one water soluble dye which has a peak absorption at a position at least 10 nm, and preferably at least 20 nm from the wavelength of the peak of the spectral sensitivity of the silver halide layer is desirable.

The hydrophilic colloids which can be used in the layer which contains the water soluble dye which is located on the opposite side of the support to the silver halide emulsion layer are the same as those in the aforementioned solid dispersed dye layer, and gelatin is preferred. In this case, there is not much need for fixing the water soluble dye in a specified position. The coated weight of hydrophilic colloid is determined by the curl balance and is preferably not too large from the point of view of dimensional stability, and it is preferably from 0.5 g/m^2 to 2.5 g/m^2, and most desirably from 0.5 g/m^2 to 2.0 g/m^2.

This present invention is preferably applied to rapid process photosensitive material, and the dry to dry processing time is not more than 60 seconds, and preferably not more than 45 seconds. In this case, the development time is not more than 20 seconds, preferably from 3 to 15 seconds, and most desirably from 3 to 10 seconds.

The silver halide photographic materials of the present invention can be used in various applications and no particular limitation is imposed, but the invention is preferably applied to black and white silver halide photographic materials, and most desirably to high contrast silver halide photographic materials intended for photographic plate making purposes, but of course it can also be applied to materials for micro-photography for example.

The silver halide grains used in this present invention may have a regular crystalline form such as a cubic or octahedral form, an irregular crystalline form such as a spherical or plate-like form, or they may have a crystalline form which is a composite of these crystalline forms. Furthermore, mixtures of grains which have various crystalline forms can also be used, but the use of grains which have a regular crystalline form is preferred.

The silver halide grains which are used in this present invention may be such that the interior and surface layer are comprised of different phases, or they may be comprised of a uniform phase.

Furthermore, they may be grains of the type with which the latent image is formed principally on the grain surface (for example negative type emulsions) or of the type with which the latent image is formed principally within the grains (for example an internal latent image type emulsion or pre-fogged direct reversal type emulsion). Grains with which the latent image is formed principally on the grain surface are preferred.

The silver halide emulsions which are used in this present invention are preferably tabular grain emulsions in which grains which have a thickness of not more than 0.5 microns, and preferably of not more than 0.3 microns, and which preferably have a diameter of 0.6 microns or more, and of which the aspect ratio is 5 or more, account for 50% or more of the total projected area, and mono-disperse emulsions of which the statistical variation coefficient (the value $s/\bar{d}$ obtained by dividing the standard deviation S by the diameter $\bar{d}$ in a distribution which represents the diameter when the projected areas are approximately circular) is not more than 20% are preferred. Mixtures of two or more types of tabular grain emulsion and mono-disperse emulsion can be used.

In a preferred embodiment, the grains of silver halide in this present invention are preferably fine grains (for example, having average grain size of not more than 0.7 μ), and they are most desirably not more than 0.5 μ. The grain size distribution is basically unlimited, but mono-dispersions are preferred.

The photographic emulsions used in the invention can be prepared using the methods described, for example, by P. Glafkides in Chimie et Physique Photographique, published by Paul Montel, 1967, by G. F. Duffin in Photographic Emulsion Chemistry, published by Focal Press, 1966, and by V. L. Zelikmann et al. in Making and Coating Photographic Emulsions, published by Focal Press, 1964.

Furthermore, ammonia, potassium thiocyanate, ammonium thiocyanate, thioether compounds (for example, those disclosed, for example, in U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439 and 4,276,374), thione compounds (for example, those disclosed, for example, in JP-A-53-144319, JP-A-53-82408 and JP-A-55-77737) and amine compounds (for example, those disclosed, for example, in JP-A-54-100717) can be used as silver halide solvents for controlling grain growth during silver halide grain formation.

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

Gelatin is useful as a binding agent or protective colloid which can be used in the emulsion layers and intermediate layers of a photosensitive material of this present invention, but other hydrophilic colloids can be used for this purpose. For example, gelatin derivatives, graft polymers of other polymers with gelatin, proteins such as albumin and casein, cellulose derivatives such as hydroxyethylcellulose, carboxymethylcellulose and cellulose sulfate esters, sodium alginate, sugar derivatives such as starch derivatives, and various synthetic hydrophilic polymeric materials, for example homopolymers or copolymers such as poly-(vinyl alcohol), partially acetalated poly (vinyl alcohol), poly (N-vinylpyrrolidone), poly(acrylic acid), poly-(methacrylic acid), polyacrylamide, polyvinylimidazole and polyvinylpyrazole, can be used for this purpose.

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

The photosensitive materials of the present invention may contain inorganic or organic film hardening agents in any of the hydrophilic colloid layers which form the photographic photosensitive layer or the backing layer. Chromium salts, aldehydes (for example, formaldehyde, glyoxal, glutaraldehyde) and N-methylol compounds (for example, dimethylolurea) can be cited as actual examples of such compounds. The use of active halogen compounds (for example, 2,4-dichloro-6-hydroxy-1,3,5-triazine and its sodium salt), and active vinyl compounds (for example, 1,3-bis-vinylsulfonyl-2-propanol, 1,2-bis-(vinylsulfonylacetamido)ethane, bis(vinylsulfonylmethy) ether or vinyl based polymers which have vinyl groups in side chains) is preferred for rapidly hardening the hydrophilic colloids such as gelatin and providing stable photographic characteristics. N-Carbamoylpyridinium salts (for example, (1-morpholinocarbonyl-3-pyridinio)methanesulfonate), and haloamidinium salts (for example, 1-(1-chloro-1-pyridinomethylene)pyrrolidinium 2-naphthalenesulfonate) are also excellent for providing rapid hardening rates.

The silver halide photographic emulsions used in the present invention may be spectrally sensitized using cyanine dyes or by other means. The dyes which can be used include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemi-cyanine dyes, styryl dyes and hemi-oxonol dyes. Dyes classified as cyanine dyes, merocyanine dyes and complex merocyanine dyes are especially useful dyes. All of the nuclei generally used in cyanine dyes can be used for the basic heterocyclic nuclei in these dyes. That is to say, the nucleus may be a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus or a pyridine nucleus; a nucleus in which one of these nuclei is fused with an aliphatic hydrocarbyl ring, or a nucleus in which one of these nuclei is fused with an aromatic hydrocarbyl ring, which is to say an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus or a quinoline nucleus for example. These nuclei may be substituted on the carbon atoms.

The nucleus which has a ketomethylene structure in the merocyanine dyes or complex merocyanine dyes may be a five or six membered heterocyclic nucleus, for example a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thio-oxazolidin-2,4-dione nucleus, a thiazolidin-2,4-dione nucleus, a rhodanine nucleus or a thiobarbituric acid nucleus.

These sensitizing dyes may be used individually or they may be used in combinations, and combinations of sensitizing dyes are often used in particular with the intention of achieving super-sensitization. Substances which exhibit supersensitization, being dyes which themselves have no spectrally sensitizing action or substances which essentially do not absorb visible light, can be included in the emulsion together with the sensitizing dyes. For example, substituted amino-stilbene compounds with a nitrogen containing heterocyclic group (for example, those disclosed in U.S. Patents 2,933,390 and 3,635,721), aromatic organic acid/formaldehyde condensates (for example, those disclosed in U.S. Patent 3,743,510), and cadmium salts and azaindene compounds, for example, may be included. The combinations disclosed in U.S. Patents 3,615,613, 3,615,641, 3,617,295 and 3,635,721 are especially useful.

Various compounds can be included in the silver halide photographic emulsions which are used in the present invention with a view, for example, to preventing the occurrence of fogging during the manufacture, storage or photographic processing of the photosensitive material, or with a view to stabilizing photographic performance. Thus, many compounds which are known as anti-fogging agents or stabilizers, including azoles, for example benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mecaptotetrazoles (especially 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines, thioketo compounds such as oxazolinethione for example; azaindenes, for example triazaindenes, tetra-azaindenes (especially 4-hydroxy substituted (1,3,3a,7)-tetra-azaindenes) and pentaazaindenes; benzenethiosulfonic acid; benzenesulfinic acid and benzenesulfonic acid amide, for example, can be added for this purpose.

One or more type of surfactant may be included in a photosensitive material of the present invention for various purposes, for example as coating promotors, as anti-static agents, for improving slip properties, for emulsification and dispersion purposes, for preventing the occurrence of sticking and for improving photographic characteristics (for example, for accelerating development, increasing contrast or increasing photographic speed).

Photosensitive materials which have been made using the present invention may contain water soluble dyes in the hydrophilic colloid layer as filter dyes, for the prevention of irradiation or halation, or for various other purposes. Oxonol dyes, hemi-oxonol dyes, styryl dyes, merocyanine dyes, anthraquinone dyes and azo dyes are preferably used as dyes of this type, but cyanine dyes, azomethine dyes, triarylmethane dyes and phthalocyanine dyes are also useful in this connection. Oil soluble dyes can be emulsified using the oil in water dispersion method and added to the hydrophilic colloid layers.

The present invention can be applied to multi-layer multi-color photographic materials which have at least two different spectral sensitivities on a support, but black an white photographic materials are preferred. When applied to a multi-layer natural color photographic material this generally has at least one red sensitive emulsion layer, at least one green sensitive emulsion layer and at least one blue sensitive emulsion layer on a support. The order of these layers can be changed optionally, as desired. The preferred layer arrangements are, from the support side, red sensitive layer, green sensitive layer, blue sensitive layer; from the support side, blue sensitive layer, green sensitive layer, red sensitive layer or, from the support side, blue sensitive layer, red sensitive layer, green sensitive layer. Furthermore, any of the emulsion layers of the same color sensitivity may be comprised of two or more emulsion layers which have different photographic speeds to improve the speed achieved, and graininess can be improved by using triple layer structures. Furthermore, non-photosensitive layers may be present between two or more emulsion layers which have the same color sensitivity. Structures in which an emulsion layer which has a different color sensitivity is introduced between certain emulsion layers which have the same color sensitivity can also be used. The establishment of a reflecting layer, such as a fine grained silver halide layer, below the highest speed layer, and especially below the highest speed blue sensitive layer, may be used to increase photographic speed.

Cyan forming couplers are generally included in the red sensitive emulsion layer, magenta forming couplers are generally included in the green sensitive emulsion layer and yellow forming couplers are generally included in the blue sensitive emulsion layer, but different combinations can be used, depending on the particular case. For example, with the incorporation of an infrared sensitive layer, the materials can be used for making false color photographs and as materials for use with semiconductor laser exposures.

The photographic emulsion layers and other layers in the photographic materials of the present invention can be coated onto a flexible support, such as a plastic film for example, or onto a transparent rigid support, such as glass for example, of the type generally used for photographic materials. Useful flexible supports include, for example, films made of semi-synthetic or synthetic polymers, such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, poly(vinyl chloride), poly(ethylene terephthalate) or polycarbonate for example, but poly(ethylene terephthalate) is preferred. The support may be colored using dyes or pigments.

The surface resistivity of at least one of the structural layers of a photosensitive material of the present invention is preferably not more than 10^{12} Ω under an atmosphere of 25% RH at 25° C.

That is to say, the photosensitive materials of the present invention preferably have an electrically conductive layer.

Electrically conductive metal oxides or electrically conductive polymer compounds, for example, can be used for the electrically conductive substances which are used in the electrically conductive layers used in the present invention.

Crystalline metal oxide particles are preferred as the electrically conductive metals oxide which can be used in the present invention, and those which contain oxygen deficiencies and those which contain a small amount of a different type of atom which forms a donor for the metal oxide which is being used generally have a higher electrical conductivity and are especially desirable, and the latter type are especially desirable because they do not cause fogging in silver halide emulsions. Examples of metal oxides include ZnO, TiO_2, SnO_2, Al_2O_3, In_2O_3, SiO_2, MgO, BaO, MoO3 and V_2O_5, or complex oxides thereof, and ZnO, TiO_2 and SnO_2 are especially desirable. Examples of the effective inclusion of different types of atoms in these oxides include the addition of Al and In, for example, to ZnO, the addition of Sb, Nb and halogen elements, for example, to SnO_2 and the addition of Nb and Ta, for example, to TiO_2. The amount of the different type of atom added is preferably within the range from 0.01 mol•% to 30 mol•%, and most desirably from 0.1 mol•% to 10 mol•%.

The fine metal oxide particles in the present invention are electrically conductive, and their volume resistivity is not more than 10^7 Ω•cm, and preferably not more than 10^5 Ω•cm.

These oxides have been disclosed, for example, in JP-A-56-143431, JP-A-56-120519 and JP-A-58-62647.

Moreover, electrically conductive materials in which the above mentioned metal oxides are deposited on other crystalline metal oxide particles or fibrous materials (for example titanium oxide), as disclosed in JP-B-59-6235, can also be used.

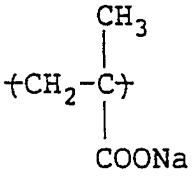
The size of the particles which can be used is preferably not more than 10 μ, but the stability after dispersion is better and the materials are easier to use if the particle size is not more than 2 μ. Furthermore, it is possible to form transparent photosensitive materials when electrically conductive particles of particle size not more than 0.5 μ are used to order to reduce light scattering as far as possible, and this is very desirable.

Furthermore, in those cases where the electrically conductive material is needle shaped or fibrous, the length is preferably not more than 30 μm and the diameter is preferably not more than 2 μm, and those which have a length of not more than 25 μm and a diameter of not more than 0.5 μ, and a length/diameter ratio of 3 or more, are especially desirable.

Preferred examples of the electrically conductive polymer compounds which can be used in the present invention include poly(vinylbenzenesulfonic acid salts), poly(vinylbenzyltrimethylammonium chloride), the quaternary salt polymers disclosed in U.S. Patents 4,108,802, 4,118,231, 4,126,467 and 4,137,217, and the polymer latexes disclosed, for example, in U.S. Patent 4,070,189, OLS 2,830,767, JP-A-61-296352 and JP-A-61-62033.

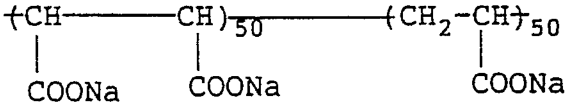
Actual examples of electrically conductive polymer compounds which can be used in the present invention are indicated below, but these compounds are not in any way limited by these examples.

P-1



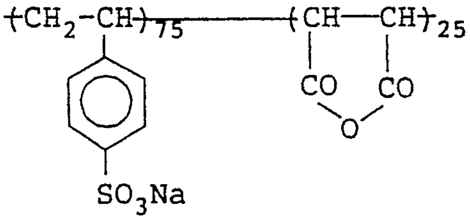
$-(CH_2-C(CH_3)(COONa))-$

P-2

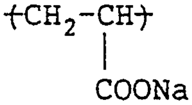


$-(CH(COONa)-CH(COONa))_{50}-(CH_2-CH(COONa))_{50}-$

P-3

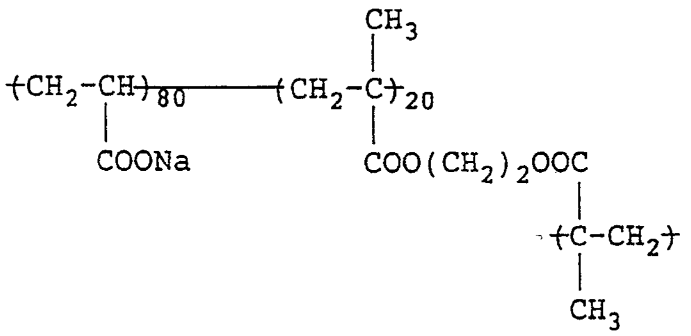


P-4

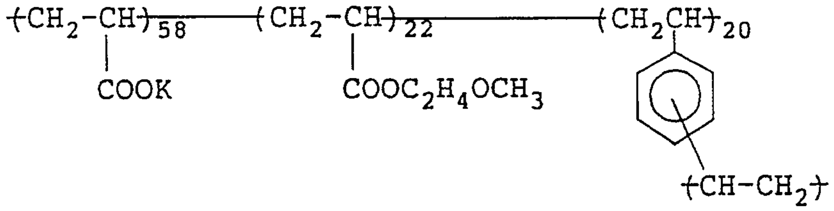


$-(CH_2-CH(COONa))-$

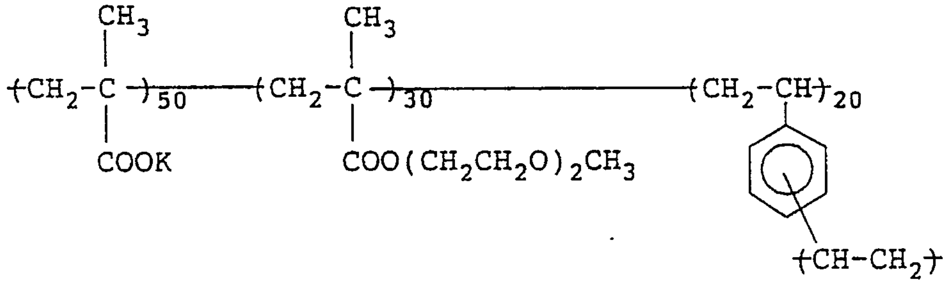
P-5



P-6



P-7



The electrically conductive metal oxides or electrically conductive polymer compounds which are used in the present invention are dispersed or dissolved in a binder for use.

No particular limitation is imposed upon the binder provided that it has film forming properties, and examples of such materials include gelatin, proteins such as casein, cellulose compounds such as carboxymethylcellulose, hydroxyethylcellulose, acetylcellulose, diacetylcellulose and triacetylcellulose, sugars such as dextran, agar, sodium alginate and starch derivatives, and synthetic polymers such as poly(vinyl alcohol), poly(vinyl acetate), poly(acrylic acid ester), poly(methacrylic acid ester), polystyrene, polyacrylamide, poly(N-vinylpyrrolidone), polyester, poly(vinyl chloride) and poly(acrylic acid).

Gelatin (for example, lime treated gelatin, acid treated gelatin, enzymatically degraded gelatin, phthalated gelatin, acetylated gelatin), acetylcellulose, diacetylcellulose, triacetylcellulose, poly(vinyl acetate), poly(vinyl alcohol), poly(butyl acrylate), polyacrylamide and dextran, for example, are especially desirable as binders.

A high by-volume content of the electrically conductive material in the electrically conductive layer is desirable for making more effective use of the electrically conductive metal oxide or electrically conductive polymer compound which is used in the present invention and for reducing the resistance of the electrically conductive layer, but a minimum binder content of about 5% is required for providing the layer with adequate strength and so the content, by volume, of the electrically conductive metal oxide or electrically conductive polymer compound is preferably within the range from 5 to 95%.

The amount of electrically conductive metal oxide or electrically conductive polymer compound used in the present invention is preferably from 0.05 to 20 grams, and most desirably from 0.1 to 10 grams, per square meter of photographic material. The surface resistivity of the electrically conductive layer in the present invention in an atmosphere of 25% RH at 25°C is not more than 10^{12} Ω, and most desirably not more than 10^{11} Ω. Good anti-static properties are obtained in this way.

At least one electrically conductive layer which contains an electrically conductive metal oxide or electrically conductive polymeric compound which can be used in the present invention is preferably established as a structural layer of the photosensitive material in the present invention. For example, in may form a surface protective layer, a backing layer, an intermediate layer or an under-layer, and two or more such layers may be established, as desired.

A further improvement can be made in respect of the anti-static properties in the present invention by using fluorine containing surfactants conjointly with the above mentioned electrically conductive substances.

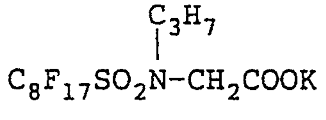
Surfactants which have a fluoroaryl group, a fluoroalkenyl group or a fluoroalkyl group which has at least 4 carbon atoms, and which have, as an ionic group, an anionic group (sulfonic acid (or salt), sulfuric acid (or salt), carboxylic acid (or salt), phosphoric acid (or salt)), a cationic group (amine salt, ammonium salt, aromatic amine salt, sulfonium salt, phosphonium salt), a betaine group (carboxyamine salt, carboxyammonium salt, sulfoamine salt, sulfoammonium salt, phosphoammonium salt), or a non-ionic group (substituted or unsubstituted polyoxyalkylene group, polyglyceryl group or sorbitan residual group) are preferred as the fluorine containing surfactants which can be used in the present invention.

These fluorine containing surfactants have been disclosed, for example, in JP-A-49-10722, British Patent 1,330,356, U.S. Patents 4,335,201 and 4,347,308, British Patent 1,417,915, JP-A-55-149938, JP-A-58-196544 and British Patent 1,439,402.

Actual examples of these surfactants are indicated below.

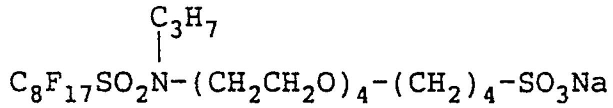
F-1 $C_8F_{17}SO_3K$

F-2



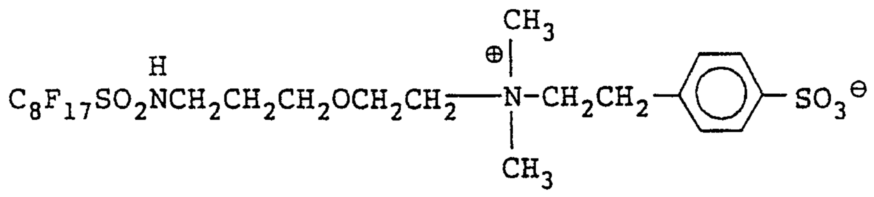
$$C_8F_{17}SO_2\overset{\overset{C_3H_7}{|}}{N}-CH_2COOK$$

F-3



$$C_8F_{17}SO_2\overset{\overset{C_3H_7}{|}}{N}-(CH_2CH_2O)_4-(CH_2)_4-SO_3Na$$

F-4



No limitation is imposed upon the layer to which the fluorine containing surfactant is added, provided that it is added to at least one layer of the photographic material, and it can be added, for example, to a surface protecting layer, an emulsion layer, an intermediate layer, an under-layer or a backing layer. The fluorine containing surfactant is preferably added to a surface protecting layer, and its inclusion in the protective layer on either the emulsion layer side or the backing layer side, or in the protective layers on both sides, is especially desirable.

In those cases where the surface protecting layer is comprised of two or more layers, the fluorine containing surfactant may be used in both of these layers, or it can be used as an overcoat over the surface protecting layer.

The amount of fluorine containing surfactant used in the present invention is from 0.0001 to 1 gram, preferably from 0.0002 to 0.25 gram, and most desirably from 0.0003 to 0.1 gram, per square meter of photographic material.

Furthermore, two or more types of fluorine based surfactant can be used in the form of a mixture in the present invention.

Other anti-static agents can be used conjointly in the layer which contains the fluorine containing surfactant or in another separate layer, and it is possible to obtain a more desirable anti-static effect in this way.

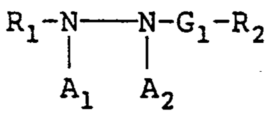
Various known methods of coating, for example dip coating, roller coating, curtain coating and extrusion coating, can be used for coating the photographic emulsion layers and other hydrophilic colloid layers. Multi-layers may be coated simultaneously using the methods disclosed, for example, in U.S. 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 and black and white photosensitive materials, but it is preferably applied to black and white photographic materials, and it can be applied to various films for plate making purposes such as lith films and scanner films, to X-ray films for direct and indirect medical and industrial purposes, black and white camera films for photographic purposes, and microfilms for COM and general purposes, and its application to various photographic plate making films is especially desirable.

When applied to various photographic plate making films, the present invention is preferably applied to silver halide photographic materials which provide a high contrast image.

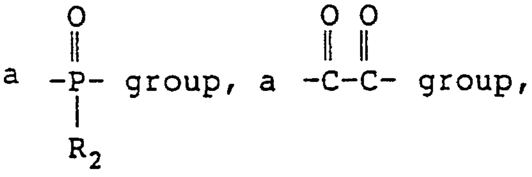
The hydrazine derivatives represented by general (I) below or tetrazolium compounds can be incorporated in the emulsion layer in order to provide a high contrast image.

The hydrazine derivatives which can be used in the present invention are preferably compounds which can be represented by the general formula (I) indicated below.



$$R_1-\underset{A_1}{\underset{|}{N}}-\underset{A_2}{\underset{|}{N}}-G_1-R_2 \qquad (I)$$

In this formula, R_1 represents an aliphatic group or an aromatic group, R_2 represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, a hydrazino group, a carbamoyl group or an oxycarbonyl group, G_1 represents a carbonyl group, a sulfonyl group, a sulfoxy group,



$$\text{a } -\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R_2}{|}}{P}}- \text{ group, a } -\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}- \text{ group,}$$

a thiocarbonyl group or an iminomethylene group, and A_1 and A_2 both represent hydrogen atoms, or one represents a hydrogen atom and the other represents a substituted or unsubstituted alkylsulfonyl group, a substituted or unsubstituted arylsulfonyl group, or a substituted or unsubstituted acyl group.

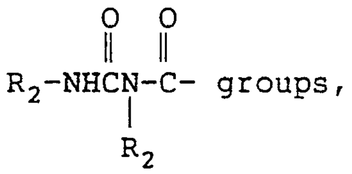
The aliphatic groups represented by R_1 in general formula (I) preferably have from 1 to 30 carbon atoms, and they are most desirably linear chain, branched or cyclic alkyl groups which have from 1 to 20 carbon atoms. Here, the branched alkyl groups may be cyclized in such a way that a saturated heterocyclic ring containing one or more hetero atoms is formed. Furthermore, the alkyl group may have substituent groups, for example aryl, alkoxy, sulfoxy, sulfonamido or carboxamido groups.

The aromatic groups represented by R_1 in general formula (I) are single ring or double ring aryl groups or unsaturated heterocyclic groups. Here, the unsaturated heterocyclic groups may be condensed with single ring or a double ring aryl group to form heteroaryl groups.

For example, R_1 may be a benzene ring, a naphthalene ring, a pyridine ring, a pyrimidine ring, an imidazole ring, a pyrazole ring, a quinoline ring, an isoquinoline ring, a benzimidazole ring, a thiazole ring or a benzothiazole ring, and of these, those which contain a benzene ring are preferred.

Aryl groups are especially desirable for R_1.

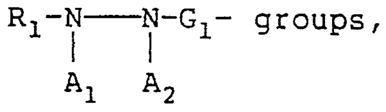
The aryl groups or unsaturated heterocyclic groups represented by R_1 may be substituted, and typical substituent groups include, for example, alkyl groups, aralkyl groups, alkenyl groups, alkynyl groups, alkoxy groups, aryl groups, substituted amino groups, acylamino groups, sulfonylamino groups, ureido groups, urethane groups, aryloxy groups, sulfamoyl groups, carbamoyl groups, alkylthio groups, arylthio groups, sulfonyl groups, sulfinyl groups, hydroxy groups, halogen atoms, cyano groups, sulfo groups, alkyloxycarbonyl groups, aryloxycarbonyl groups, acyl groups, alkoxycarbonyl groups, acyloxy groups, carbonamido groups, sulfonamido groups, carboxyl groups, phosphoric acid amido groups, diacylamino groups, imido groups and



$$R_2\text{-NH}\overset{\displaystyle O}{\overset{\|}{C}}\underset{\displaystyle R_2}{\underset{|}{N}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}\ \text{groups,}$$

and the preferred substituent groups are, for example, linear chain, branched or cyclic alkyl groups (which preferably have from 1 to 20 carbon atoms), aralkyl groups (preferably single ring or double ring groups of which the alkyl part has from 1 to 3 carbon atoms), alkoxy groups (which preferably have from 1 to 20 carbon atoms), substituted amino groups (preferably amino groups substituted with alkyl groups which have from 1 to 20 carbon atoms), acylamino groups (which preferably have from 2 to 30 carbon atoms), sulfonamido groups (which preferably have from 1 to 30 carbon atoms), ureido groups (which preferably have from 1 to 30 carbon atoms) and phosphoric acid amido groups (which preferably have from 1 to 30 carbon atoms).

The alkyl groups represented by R_2 in general formula (I) are preferably alkyl groups which have from 1 to 4 carbon atoms, and these may be substituted, for example, with halogen atoms, cyano groups, carboxyl groups, sulfo groups, alkoxy groups, phenyl groups, acyl groups, alkoxycarbonyl groups, aryloxycarbonyl groups, carbamoyl groups, alkylsulfo groups, arylsulfo groups, sulfamoyl groups, nitro groups, heteroaromatic groups and



$$R_1\text{-}\underset{\displaystyle A_1}{\underset{|}{N}}\text{——}\underset{\displaystyle A_2}{\underset{|}{N}}\text{-}G_1\text{-}\ \text{groups,}$$

and these groups may also be substituted groups.

The aryl groups are preferably single ring or double ring aryl groups, for example groups which contain a benzene ring. These aryl groups may be substituted, for example, with the same substituent groups as described above in connection with the alkyl groups.

The alkoxy groups preferably have from 1 to 8 carbon atoms, and they may be substituted, for example, with halogen atoms and aryl groups.

The aryloxy groups preferably have a single ring and this may be substituted, for example, with halogen atoms.

The amino groups are preferably unsubstituted amino groups, or alkylamino groups which have from 1 to 10 carbon atoms, or arylamino groups, and they may be substituted, for example, with alkyl groups, halogen atoms, cyano groups, nitro groups and carboxyl groups.

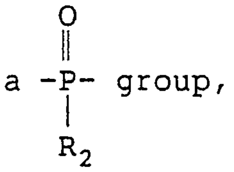
The carbamoyl groups are preferably unsubstituted carbamoyl groups or aryl carbamoyl groups or alkylcarbamoyl groups which have from 1 to 10 carbon atoms, and they may be substituted, for example, with alkyl groups, halogen atoms, cyano groups and carboxyl groups.

The oxycarbonyl groups are preferably aryloxycarbonyl groups or alkoxycarbonyl groups which have from 1 to 10 carbon atoms, and they may be substituted, for example, with one or more alkyl groups, halogen atoms, cyano groups and nitro groups.

In those cases where G_1 is a carbonyl group, the preferred groups among those which can be represented by R_2 are, for example, hydrogen atom, alkyl groups (for example, methyl, trifluoromethyl, 3-hydroxypropyl, 3-methanesulfonamidopropyl, phenylsulfonylmethyl), aralkyl groups (for example, o-hydroxybenzyl) and aryl groups (for example, phenyl, 3,5-dichlorophenyl, o-methanesulfonamidophenyl, 4-methanesulfonylphenyl), and the hydrogen atom is especially desirable.

Furthermore, in those cases where G_1 is a sulfonyl group, R_2 is preferably an alkyl group (for example, methyl), an aralkyl group (for example, o-hydroxyphenylmethyl), an aryl group (for example, phenyl), or a substituted amino group (for example, dimethylamino).

In those cases where G_1 is a sulfoxy group, R_2 is preferably a cyanobenzyl group or a methylthiobenzyl group, and in those cases where G_1 is



$$\text{a } -\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R_2}{|}}{P}}- \text{ group,}$$

R_2 is preferably a methoxy, ethoxy, butoxy, phenoxy or phenyl group, and most desirably a phenoxy group.

In those cases where G_1 represents an N-substituted or unsubstituted iminomethylene group, R_2 is preferably a methyl, ethyl, or substituted or unsubstituted phenyl group.

The substituent groups listed in connection with R_1 are appropriate as substituent groups for R_2.

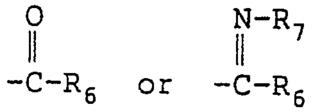
G_1 in general formula (I) is most desirably a carbonyl group.

Furthermore, R_2 may be a group such that the G_1-R_2 part is cleaved from the rest of the molecule and a cyclization reaction occurs, forming a ring structure which contains the atoms of the -G_1-R_2 part, and in practice this may be represented by the general formula (a).

-R_3-Z_1 (a)

In this formula, Z_1 is a group which makes a nucleophilic attack on G_1 and cleaves the G_1-R_3-Z_1 part from the rest of the molecule and R_3 is a group derived by removing one hydrogen atom from R_2, and Z_1 can make a nucleophilic attack on G_1 and form a ring structure with G_1, R_3 and Z_1.

More precisely, Z_1 is a group which, when the reaction intermediate R_1-N=N-G_1-R_3-Z_1 has been formed by the oxidation of the hydrazine compound of general formula (I) for example, readily undergoes a nucleophilic reaction with G_1 and causes the R_1-N=N group to be cleaved from G_1, and in practice it may be a functional group which reacts directly with G_1, such as OH, SH or NHR_4 (where R_4 is a hydrogen atom, an alkyl group, an aryl group, -COR_5 or -SO_2R_5, where R_5 represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group for example), or COOH for example, (the OH, SH, NHR_4, -COOH groups in the case may be temporarily protected in such a way that these groups are formed by hydrolysis with an alkali for example), or a functional group which can react with G_1 as a result of the reaction of a nucleophile such as a hydroxide ion or a sulfite ion such as

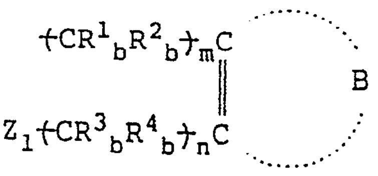


$$-\overset{\overset{\displaystyle O}{\|}}{C}-R_6 \quad \text{or} \quad -\overset{\overset{\displaystyle N-R_7}{\|}}{C}-R_6$$

(where R_6 and R_7 represent hydrogen atoms, alkyl groups, alkenyl groups, aryl groups or heterocyclic groups).

Furthermore, the ring formed by G_1, R_3 and Z_1 is preferably a five or six membered ring.

Those of the groups represented by general formula (a) which can be represented by the general formulae (b) and (c) are preferred.

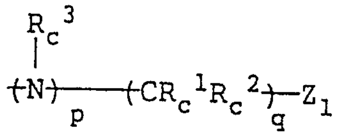


(b)

In this formula, R^1_b - R^4_b represent, for example, hydrogen atoms, alkyl groups (which preferably have from 1 to 12 carbon atoms), alkenyl groups (which preferably have from 2 to 12 carbon atoms) or aryl groups (which preferably have from 6 to 12 carbon atoms), and they may be the same or different. B represents the atoms which are required to complete a five or six membered ring which may have substituent groups, m and n represent 0 or 1, and (m + n) has a value of 1 or 2.

Examples of five or six membered rings formed by B include the cyclohexene ring, the cyclopentene ring, the benzene ring, the naphthalene ring, the pyridine ring and the quinoline ring.

Z^1 has the same significance as in general formula (a).



$$-(\overset{\overset{R_c^3}{|}}{N})_p-(CR_c^1R_c^2)_q-Z_1$$

(c)

In this formula, R_c^1 and R_c^2 represent, for example, hydrogen atoms, alkyl groups, alkenyl groups, aryl groups or halogen atoms, and they may be the same or different.

R_c^3 represents a hydrogen atom, an alkyl group, an alkenyl group or an aryl group.

Moreover, p represents 0 or 1, and q represents 1, 2, 3 or 4.

R_c^1, R_c^2 and R_c^3 may be joined together to form a ring provided that the structure permits an intramolecular nucleophilic attack by Z_1 on G_1.

R_c^1 and R_c^2 are preferably hydrogen atoms, halogen atoms or alkyl groups, and R_c^3 is preferably an alkyl group or an aryl group.

Moreover, q preferably has a value of from 1 to 3, and when q is 1, p is 1 or 2; when q is 2, p is 0 or 1; and when q is 3, p is 0 or 1. Moreover, when q is 2 or 3 the then R_c^1 and R_c^2 may be the same or different. Z_1 has the same significance as in general formula (a).

A_1 and A_2 represent hydrogen atoms, alkylsulfonyl groups which have not more than 20 carbon atoms, arylsulfonyl groups (preferably phenylsulfonyl groups or substituted phenylsulfonyl groups in which the sum of the Hammett substituent constants is at least -0.5), acyl groups which have not more than 20 carbon atoms (preferably benzoyl groups or substituted benzoyl groups in which the sum of the Hammett substituent constants is at least -0.5, or linear chain, branched or cyclic unsubstituted or substituted aliphatic acyl groups (which have halogen atoms, ether groups, sulfonamido groups, carbonamido groups, hydroxyl groups, carboxyl groups or sulfonic acid groups as substituent groups).

A_1 and A_2 are most desirably hydrogen atoms.

The groups represented by R_1 or R_2 in general formula (I) may have incorporated within them ballast groups or polymers as normally used in immobile photographically useful additives such as couplers. Ballast groups are groups which are comparatively inert in the photographic sense which have at least eight carbon atoms, and they can be selected, for example, from among the alkyl groups, alkoxy groups, phenyl groups, alkylphenyl groups, phenoxy groups and alkylphenoxy groups. Furthermore, those disclosed, for example, in JP-A-1-100530 can be cited as polymers.

R_1 or R_2 in general formula (I) may have incorporated within it a group which is adsorbed strongly on silver halide grain surfaces. Examples of such absorbing groups include the thiourea groups, heterocyclic thioamido groups, mercaptoheterocyclic groups and triazole groups disclosed, for example, in U.S. Patents 4,385,108 and 4,459,347, JP-A-59-195233, JP-A-59-200231, JP-A-59-201045, JP-A-59-201046, JP-A-59-201047, JP-A-59-201048, JP-A-59-201049, JP-A-61-170733, JP-A-61-270744, JP-A-62-948, JP-A-63-234244, JP-A-63-234246 and Japanese Patent Application No. 62-67501.

The amount of hydrazine derivative added in the present invention is preferably from 1 x 10^{-6} mol to 5 x 10^{-2} mol, and most desirably from 1 x 10^{-5} mol to 2 x 10^{-2} mol, per mol of silver halide.

Actual examples of the tetrazolium compounds which can be used in the present invention are indicated below, but the compounds which can be used in the invention are certainly not limited to these examples.

(1) 2-(Benzothiazol-2-yl)-3-phenyl-5-dodecyl-2H-tetrazolium bromide
(2) 2,3-Diphenyl-5-(4-tert-octyloxyphenyl)-2H-tetrazolium chloride
(3) 2,3,5-triphenyl-2H-tetrazolium
(4) 2,3,5-tri(p-carboxyethylphenyl)-2H-tetrazolium
(5) 2-(benzothiazol-2-yl)-3-phenyl-5-(o-chlorophenyl)-2H-tetrazolium
(6) 2,3-Diphenyl-2H-tetrazolium
(7) 2,3-Diphenyl-5-methyl-2H-tetrazolium)
(8) 3-(p-Hydroxyphenyl)-5-methyl-2-phenyl-2H-tetrazolium
(9) 2,3-Diphenyl-5-ethyl-2H-tetrazolium
(10) 2,3-Diphenyl-5-n-hexyl-2H-tetrazolium
(11) 5-Cyano-2,3-diphenyl-2H-tetrazolium
(12) 2-(Benzothiazol-2-yl)-5-phenyl-3-(4-tolyl)-2H-tetrazolium
(13) 2-(Benzothiazol-2-yl)-5-(4-chlorophenyl)-3-(4-nitrophenyl)-2H-tetrazolium
(14) 5-Ethoxycarbonyl-2,3-di(3-nitrophenyl)-2H-tetrazolium
(15) 5-Acetyl-2,3-di(p-ethoxyphenyl)-2H-tetrazolium
(16) 2,5-Diphenyl-3-(p-tolyl)-2H-tetrazolium
(17) 2,5-Diphenyl-3-(p-iodophenyl)-2H-tetrazolium
(18) 2,3-Diphenyl-5-(p-diphenyl)-2H-tetrazolium
(19) 5-(p-Bromophenyl)-2-phenyl-3-(2,4,6-trichlorophenyl)-2H-tetrazolium
(20) 3-(p-Hydroxyphenyl)-5-(p-nitrophenyl)-2-phenyl-2H-tetrazolium
(21) 5-(3,4-Dimethoxyphenyl)-3-(2-ethoxyphenyl)-2-(4-methoxyphenyl)-2H-tetrazolium
(22) 5-(4-Cyanophenyl)-2,3-diphenyl-2H-tetrazolium
(23) 2,3-Di(4-methoxyphenyl)-5-nitro-2H-naphtho(1,2-d)-1,2,3-triazolium

The non-diffusible compounds obtained by reacting the diffusible compounds among the above mentioned illustrative compounds with an anion can be used in those cases where the tetrazolium compounds used in the present invention are to be used as non-diffusible compounds.

The tetrazolium compounds which can be used in the present invention can be used individually, or a plurality of these compounds can be used conjointly.

The tetrazolium compounds which can be used in the present invention are preferably used in amounts ranging from 1 x 10^{-3} to 5 X 10^{-2} mol per mol of silver halide.

Various means of exposure can be used with photosensitive materials of the present invention. Any light source which emits radiation with a band width corresponding to the sensitive wavelengths of the photosensitive material can be used for the exposing light source or write-in light source. Natural light (sunlight), incandescent electric lamps, sealed halogen lamps, mercury lamps, fluorescent lamps or flash lamps such as strobes and burning metal flash bulbs, for example, can be used in general. Gas, dye solution or semiconductor lasers which emit light in wavelength regions from the ultraviolet region through to the infrared region, light emitting diodes, and plasma light sources can also be used as light sources for recording purposes. Furthermore, exposing devices such as a fluorescent screen with which light is released from phosphors which have been excited by an electron beam (CRT, fluorescent sensitized paper for example) or in which a beam like or surface type light source is combined with a micro-shutter array such as a liquid crystal display (LCD) or a lead titanium zirconate doped with lanthanum (PLZT) device, for example, can also be used. The spectral distribution of the light which is used to make an exposure can be adjusted, as required, using color filters.

The photographic processing of a photosensitive material of the present invention can be carried out using any of the known methods and known processing baths such as those disclosed, for example, on pages 28 - 30 of Research Disclosure 176 (RD-17643). This photographic processing may be of the type with which a silver image is formed (black and white photographic processing) or of the type in which a dye image is formed (color photographic processing), depending on the intended purpose. The processing temperature is generally selected between 20° C and 50° C.

The known developing agents can be included in the developer which is used in the case of black and white photographic processing. Thus, dihydroxybenzenes (for example hydroquinone), 3-pyrazolidones (for example, 1-phenyl-3-pyrazolidone) and aminophenols (for example, N-methyl-p-aminophenol) can be used individually or in combinations as developing agents. Known preservatives, alkali agents, pH buffers and anti-foggants, for example, are also generally included in the developer, and dissolution promotors, toners, development accelerators (for example, quaternary salts, hydrazine, benzyl alcohol), surfactants, anti-foaming agents, hard water softening agents, film hardening agents (for example, glutaraldehyde) and thickening agents, for example, may be included, as required.

The compounds disclosed, for example, in JP-A-53-77616, JP-A-54-37732, JP-A-53-137133, JP-A-60-140340 and JP-A-60-14959, and various compounds which contain N or S atoms, are effective as development accelerators or accelerators for nuclear infectious development which are suitable for use in the present invention.

The amino compounds disclosed in Japanese Patent Application No. 1-294185 can be used for the developers which are used in the present invention.

Furthermore, the development rate can be increased and the processing time can be shortened in practice by adding amines to the developer as disclosed in U.S. Patent 4,269,929.

Moreover, pH buffers such as the alkali metal sulfites, carbonates, borates and phosphates, development inhibitors and anti-foggants such as bromide, iodide and the organic anti-foggants (of which the nitroindazoles or benzotriazoles are especially desirable) can also be included in the developer. Furthermore, hard water softening agents, dissolution promotors, toners, development accelerators, surfactants (the aforementioned polyalkylene oxides are especially desirable), anti-foaming agents, film hardening agents and agents for preventing silver contamination of the film (for example, 2-mercaptobenzimidazole sulfonic acids) may be included, as required.

The use of thiosulfate and thiocyanate is desirable in the fixer, and water soluble aluminum salts, acetic acid and dibasic acids (for example tartaric acid, citric acid) or salts of these acids may be included, as required.

Sodium thiosulfate and ammonium thiosulfate can be used for the thiosulfate, but ammonium thiosulfate is especially desirable from the viewpoint of the fixing rate. The amount of fixing agent used can be varied appropriately, but is generally from about 0.1 mol/liter to about 5 mol/liter.

Water soluble aluminum salts and chromium salts as acid film hardening agents and ethylenediamine tetraacetic acid complexes with trivalent iron compounds as oxidizing agents can be included in the fixer in the present invention. The preferred compounds are water soluble aluminum salts, for example, aluminum chloride, aluminum sulfate and potassium alum. The amount added is preferably from 0.01 to 0.2 mol/liter, and most desirably from 0.03 to 0.08 mol/liter.

Tartaric acid or derivatives thereof, or citric acid or derivatives thereof, can be used individually as the aforementioned dibasic acid, or two or more such compounds can be used conjointly. These compounds are effective when included in amounts of at least 0.005 mol per liter of fixer, and they are especially effective in amounts of from 0.01 mol/liter to 0.03 mol/liter.

In practical terms, use can be made of tartaric acid, potassium tartrate, sodium tartrate, potassium hydrogen tartrate, sodium hydrogen tartrate, potassium sodium tartrate, ammonium tartrate, ammonium potassium tartrate, aluminum potassium tartrate, antimonyl potassium tartrate, antimonyl sodium tartrate, lithium hydrogen tartrate, lithium tartrate, magnesium hydrogen tartrate, boron potassium tartrate, and lithium potassium tartrate for example.

Examples of citric acid and derivatives thereof which are effective in the present invention include citric acid, sodium citrate, potassium citrate, lithium citrate and ammonium citrate.

Preservatives (for example, sulfite, bisulfite), pH buffers (for example, acetic acid, boric acid), pH adjusting agents (for example, sulfuric acid) and chelating agents (as mentioned earlier) can be included, as required, in the fixer. Here, the pH buffer is used in amounts of the order of from 10 to 40 grams/liter, and preferably in amounts of from 18 to 25 grams/liter, in view of the high pH value of the developer.

The fixing temperature and time are, as in the case of the developer, from about 20°C to about 50°C, and not more than 20 seconds, and preferably from 3 to 15 seconds.

A photographic material which has been developed and fixed in accordance with the method of the present invention is washed with water and dried. Water washing is carried out so as to remove more or less completely the silver salts which have been dissolved by fixing, and a time of from 5 seconds to 20 seconds at from about 20°C to about 50°C is preferred. Drying is carried out at from about 40°C to about 100°C and the drying time is varied appropriately according to the ambient conditions, but it is usually from about 5 seconds to about 20 seconds.

Roller transport type automatic development machines have been disclosed, for example, in U.S. Patents 3,025,779 and 3,545,971, and in this present specification these are referred to simply as roller transport type processors. A roller transport type processor involves the four processes of development, fixation, washing with water and drying, and although the method of the present invention does not exclude other processes (for example a stop proces), the use of these four processes is most desirable.

The method of development of the present invention is especially suitable for rapid processing in which an automatic processor is used. The automatic processor may be of the roller transport type, the belt transport type or some other type. The processing time is not more than 60 seconds, and preferably not more than 45 seconds, dry to dry, in accordance with the present invention.

The compounds disclosed in JP-A-56-24347 as agents for preventing the occurrence of silver contamination can be used in a developer of the present invention. The compounds disclosed in JP-A-61-267759 as dissolution promotors which are added to a developer can be used. Moreover, the compounds disclosed in JP-A-62-186256 and the compounds disclosed in JP-A-60-93433 as pH buffers which are used in developers can be used.

ILLUSTRATIVE EXAMPLES

EXAMPLE 1

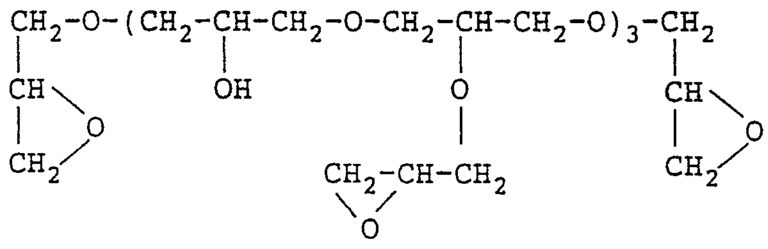
The first under-layer of formulation (1) and the second under-layer of formulation (2) indicated below were coated sequentially onto both sides of a biaxially extended poly(ethylene terephthalate) support of thickness 100 μ.

Formulation (1) First Under-layer

An aqueous dispersion of a 90/8/1/1 by weight vinylidene chloride/methyl methacrylate/ acrylonitrile/methacrylic acid copolymer	15	parts by weight
2,4-Dichloro-6-hydroxy-s-triazine	0.25	part by weight
Fine polystyrene particles (average particle size 3 μm)	0.05	part by weight
Compound (a)	0.20	part by weight
Water to make up to	100	parts by weight

Moreover, 10 wt% of KOH was added and the coating liquid which had been adjusted to pH 6 was coated in such a way as to provide a dry film thickness of 0.9 μ on drying at a temperature of 180° C for 2 minutes.

Compound (a)

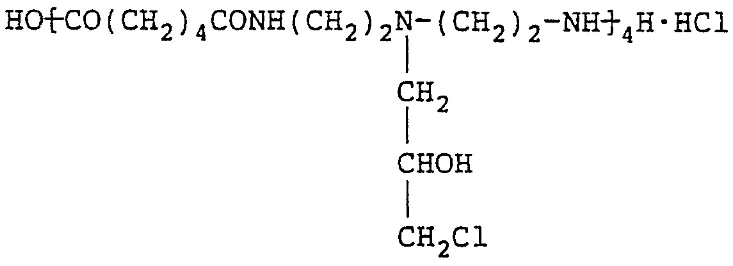


Formulation (2) Second Under-layer

Gelatin	1 part by weight
Methylcellulose	0.05 part by weight
Compound (b)	0.02 part by weight
$C_{12}H_{25}O(CH_2CH_2O)_{10}H$	0.03 part by weight
Compound (c)	3.5×10^{-3} part by weight
Acetic acid	0.2 part by weight
Water to make up to	100 parts by weight

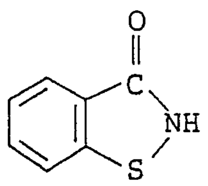
This coating liquid was coated in such a way as to provide a gelatin weight of 0.16 g/m^2 on drying for 2 minutes at a temperature of 170°C

Compound (b)



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

Compound (c)



The electrically conductive layer and the backing layer of formulations (3) and (4) indicated below were coated on one side of the support obtained in this way.

Formulation (3) Electrically Conductive Layer

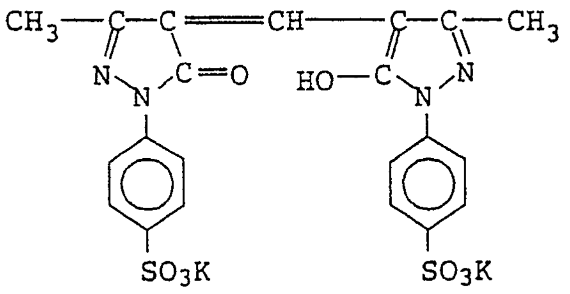
SnO_2/Sb (9/1 by weight) (average particle size 0.25 μ)	300 mg/m^2
Gelatin	170 mg/m^2
Compound (c)	7 mg/m^2
Sodium dodecylbenzenesulfonate	10 mg/m^2
Sodium dihexyl-α-sulfosuccinate	40 mg/m^2
Poly(sodium styrenesulfonate)	9 mg/m^2

Formulation (4) Backing Layer

Gelatin	1.8 g/m^2
Compound (d)	300 mg/m^2
Compound (e)	50 mg/m^2
Compound (f)	50 mg/m^2
Compound (c)	6 mg/m^2
Sodium dodecylbenzenesulfonate	50 mg/m^2
Sodium dibenzyl-α-sulfosuccinate	10 mg/m^2
1,2-Bis(vinylsulfonylacetamido)ethane	100 mg/m^2
Ethyl acrylate latex (average particle size 0.05 μ)	300 mg/m^2
Lithium perfluorooctanesulfonate	7 mg/m^2
Fine silicon dioxide particles (average particle size 4 μ, fine pore diameter 170 Å, surface area 300 m^2/g)	35 mg/m^2

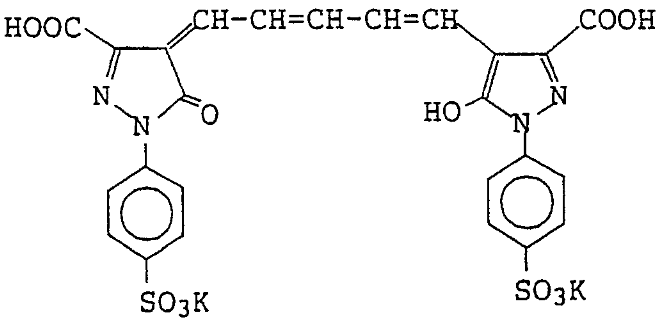
Moreover, the coating described below was carried out on the opposite side of the support.

Compound (d) (peak absorption wavelength; 420 nm)



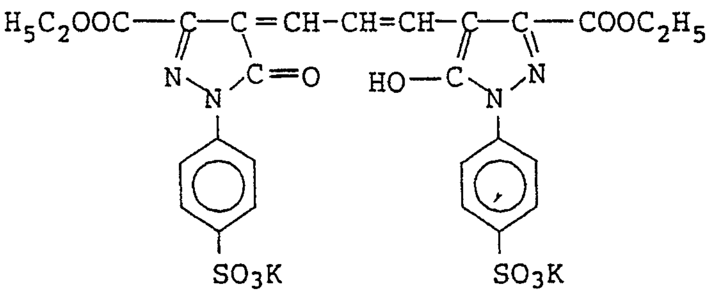
300 g/m^2

Compound (e) (peak absorption wavelength; 630 nm)



50 mg/m^2

Compound (f) (peak absorption wavelength; 550 nm)



50 g/m^2

Emulsion A was prepared in accordance with the method outlined below using liquids I and II indicated below.

Liquid I: Water 600 ml, gelatin 18 grams, pH 3.0

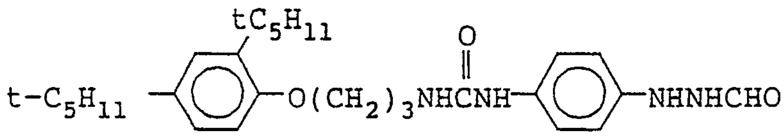
Liquid II: $AgNO_3$ 200 grams, water 800 ml

1) Emulsion A (Br 1 mol%, grain size 0.20 µ, Rh 1.0 × 10^{-5} mol/mol•Ag)

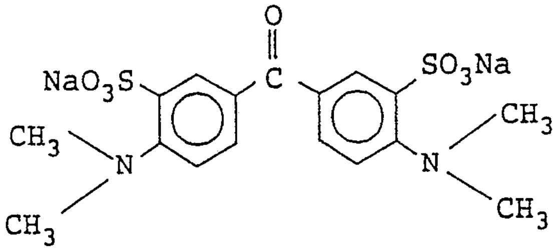
Liquid III_A: KBr 1.4 grams, NaCl 76 grams, $(NH_4)_3RhCl_6$ 4 mg, Water 800 ml

Liquids II and III were mixed simultaneously with liquid I which was being maintained at 40° C, the addition being made while maintaining a fixed rate of addition over a period of 20 minutes. After the removal of the soluble salts in the usual way well known in the industry, gelatin was added to the emulsion and 2-methyl-4-hydroxy-1,3,3a,7-tetraazaindene was added as a stabilizer without chemical ripening. The average grain size of this emulsion was 0.20 μ, the recovery of emulsion was 1 kg and the gelatin content was 60 grams. The hydrazine compound indicated below was added to this emulsion in an amount of 4 x 10^{-4} mol/mol•Ag and an emulsion was obtained.

Hydrazine Compound (Hz)

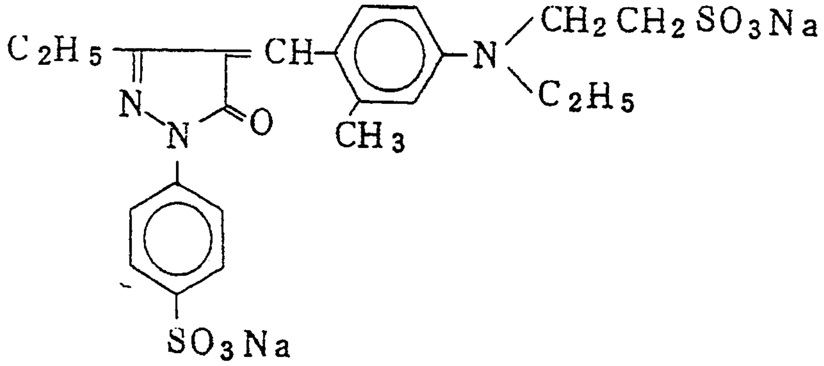


Ultraviolet Absorber (UV Absorber)



The ultraviolet absorber indicated above was added in an amount of 100 mg/m^2, after which a poly(ethyl acrylate) latex was added in an amount as solid fraction of 30 wt% with respect to the gelatin, 1,3-vinylsulfonyl-2-propanol was added as a film hardening agent and the emulsion (having a maximum sensitivity wavelength of 360 nm) was coated on the poly(ethylene terephthalate) film in such a way as to provide 2.5 g/m^2 of silver and 1.18 g/m^2 of gelatin, and a protective layer to which the yellow dye indicated below had been added in an amount of 120 mg/m^2 to improve safe-light safety was coated over this layer in such a way as to provide a coated weight of 0.9 g/m^2 of gelatin. The material so obtained was Sample 1-1.

Yellow Dye



Samples 1-2 to 1-4 were prepared by omitting the compounds (d), (e) and (f) from the backing layer formulation (4) and adding a solid dispersion of dye as shown in Table 1 to just formulation (2) for the second under-layer on the emulsion side. The dyes were milled together with a surfactant in a ball mill and solid dispersions in water were used. The gelatin coated weights of the second under-layer on the emulsion side are also shown in Table 1.

Moreover, Samples 1-5 and 1-6 were prepared by setting the compound (d) content in the backing layer formulation (4) to 100 mg/m^2 and leaving compounds (e) and (f) was they were, with the second-under layer on the emulsion side as shown in Table 1 in the same way.

TABLE 1

Sample Number	Dye in the Second Under-layer	Amount of Dye in Formulation (2)	Coated Weight of Gelatin in Second Under-layer	Backing Layer Dye
1-1 (Comparison)	None	None	0.16 g/m^2	Yes
1-2 (Comparison)	None	None	0.16 g/m^2	No
1-3 (Comparison)	Compound III-1	0.8 part by wt. (0.8)*	0.16 g/m^2	No
1-4 (Comparison)	Compound III-1 Compound III-3	0.8 part by wt. (0.8)* 0.4 part by wt. (0.4)*	0.16 g/m^2	No
1-5 (Invention)	Compound III-1	0.3 part by wt. (0.3)*	0.28 g/m^2	Yes
1-6 (Invention)	Compound VII-4	0.3 part by wt. (0.3)*	0.28 g/m^2	Yes

*: The figures in brackets show the ratio by weight of solid dispersed dye/hydrophilic colloid.

Samples 1-5 and 1-6 of the present invention were such that the reverse side was easily discriminated in a light room since it had a different color, as in the case of comparative Sample 1-1.

Conversely, with comparative examples 1-2 1-3 there was no great difference in the color of the reverse side and it could not be discriminated.

Next, samples 1-1 to 1-6 were exposed in an original construction comprised of:

a) A transparent or semi-transparent paste-up base
b) A line original
c) A transparent or semi-transparent past-up base
d) A screen dot original
e) The photosensitive material for reversal purposes.

The exposures were made using a P-607 ultra high pressure mercury lamp ORC-CHM-100 made by the Dainippon Screen Co. with the exposure being controlled by the use of neutral density filters (ND filters) in such a way that each sample had the same exposure time, and then the samples were processed for 12 seconds at 38°C in an FG-310PTS automatic processor made by the Fuji Photo Film Co., Ltd. using the developer A indicated below (with a dry to dry time of about 50 seconds) and a missing letter image quality evaluation was carried out. GR-FI was used for the fixer.

A missing letter image quality of 5 was very good in that when given the appropriate exposure so that a screen dot area of 50% formed a screen dot area of 50% on the sensitive material for reversal purpose the image quality reproduced letters of width 30 µm. On the other hand, a missing letter image quality of 1 was not good in that when a similar appropriate exposure was such that only letters of width at least 150 µm could be reproduced, and grades of 4 to 2 were established on the evaluation scale between the grades of 5 and 1. A grade of 3 or above is a practical level.

Developer A

Hydroquinone	45.0 grams
N-Methyl-p-aminophenol hemi-sulfate	0.8 gram
Sodium hydroxide	18.0 grams
Potassium hydroxide	55.0 grams
5-Sulfosalicylic acid	45.0 grams
Boric acid	25.0 grams
Potassium sulfite	110.0 grams
Ethylenediamine tetra-acetic acid, disodium salt	1.0 gram
Potassium bromide	6.0 grams
5-methylbenzotriazole	0.6 gram
n-Butyl-diethanolamine	15.0 grams
Water to make up to	1 liter
	(pH = 11.6)

As shown in Table 2, the results show that the coated samples of the present invention could be subjected to rapid processing in less than 60 seconds and could provide excellent missing letter performance.

TABLE 2

Sample No.		Missing Letter Image Quality	Scratch Strength
1-1	(Comparison)	2.5	140 grams
1-2	(Comparison)	1	147 grams
1-3	(Comparison)	3.5	82 grams
1-4	(Comparison)	3.5	65 grams
1-5	(Invention)	3.5	119 grams
1-6	(Invention)	3.5	124 grams

Next, samples 1-1 to 1-6 were immersed in the aforementioned developer and scratched after 20 seconds with a loaded sapphire needle of diameter 0.4 mm to determine the scratch strength. The liquid temperature was 38° C.

The samples of the present invention did have a reduced film strength but even so they were tolerable, and the film strength was much lower with samples 1-3 and 1-4 which had a high dye/gelatin ratio.

As outlined above, it is clear on looking at the samples of the present invention that they had good missing letter image quality, that the reverse side could be discriminated and that there was no catastrophic loss of film strength.

EXAMPLE 2

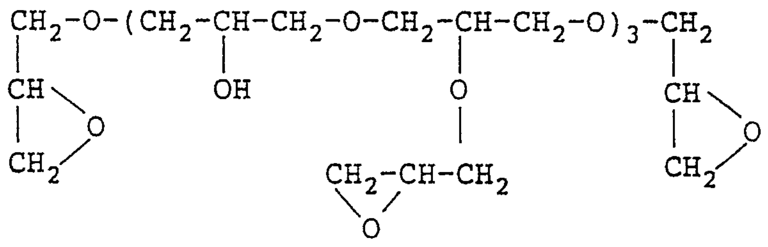
The first under-layer of formulation (1) and the second under-layer of formulation (2) indicated below were coated sequentially onto both sides of a biaxially extended poly(ethylene terephthalate) support of thickness 100 μ.

Formulation (1) First Under-layer

An aqueous dispersion of a 90/8/1/1 by weight vinylidene chloride/methyl methacrylate/acrylonitrile/methacrylic acid copolymer	15 parts by weight
2,4-Dichloro-6-hydroxy-s-triazine	0.25 part by weight
Fine polystyrene particles (average particle size 3 μ)	0.05 part by weight
Compound (a)	0.20 part by weight
Water to make up to	100 parts by weight

Moreover, 10 wt% of KOH was added and the coating liquid which had been adjusted to pH 6 was coated in such a way as to provide a dry film thickness of 0.9 μ on drying at a temperature of 180° C for 2 minutes.

Compound (a)

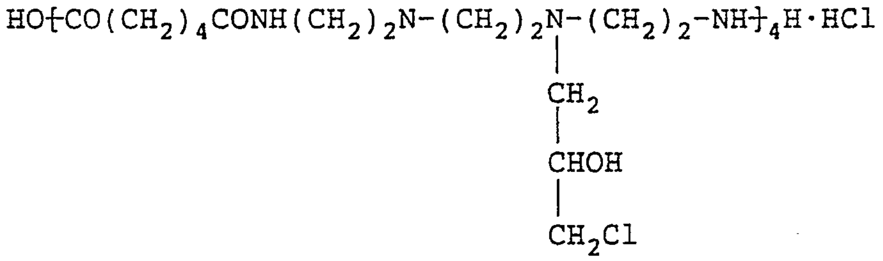


Formulation (2) Second Under-layer

Gelatin	1 part by weight
Methylcellulose	0.05 part by weight
Compound (b)	0.02 part by weight
$C_{12}H_{25}O(CH_2CH_2O)_{10}H$	0.03 part by weight
Compound (c)	3.5×10^{-3} part by weight
Acetic acid	0.2 part by weight
Water to make up to	100 parts by weight

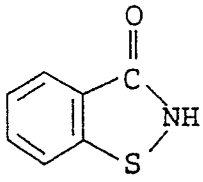
This coating liquid was coated in such a way as to provide a gelatin weight of 0.10 g/m^2 on drying for 2 minutes at a temperature of 170° C

Compound (b)



$$HO\!\left[CO(CH_2)_4CONH(CH_2)_2N-(CH_2)_2\underset{\begin{array}{c}|\\CH_2\\|\\CHOH\\|\\CH_2Cl\end{array}}{N}-(CH_2)_2-NH\right]_4H\cdot HCl$$

Compound (c)



The electrically conductive layer and the backing layer of formulations (3) and (4) indicated below were coated on one side of the support obtained in this way.

Formulation (3) Electrically Conductive Layer

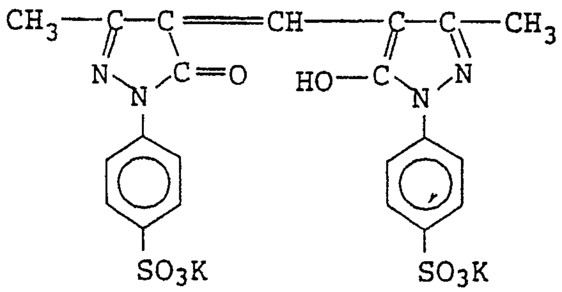
SnO_2/Sb (9/1 by weight) (average particle size 0.25 μ)	300 mg/m^2
Gelatin	170 mg/m^2
Compound (c)	7 mg/m^2
Sodium dodecylbenzenesulfonate	10 mg/m^2
Sodium dihexyl-α-sulfosuccinate	40 mg/m^2
Poly(sodium styrenesulfonate)	9 mg/m^2

Formulation (4) Backing Layer

Gelatin	1.7 g/m^2
Compound (d)	100 mg/m^2
Compound (e)	100 mg/m^2
Compound (f)	100 mg/m^2
Compound (c)	6 mg/m^2
Sodium dodecylbenzenesulfonate	41 mg/m^2
Sodium dibenzyl-α-sulfosuccinate	9 mg/m^2
1,2-Bis(vinylsulfonylacetamido)ethane	90 mg/m^2
Ethyl acrylate latex (average particle size 0.05 μ)	300 mg/m^2
Lithium fluorooctanesulfonate	6 mg/m^2
Fine silicon dioxide particles (average particle size 4 μ, fine pore diameter 170 Å, surface area 300 m^2/g)	35 mg/m^2

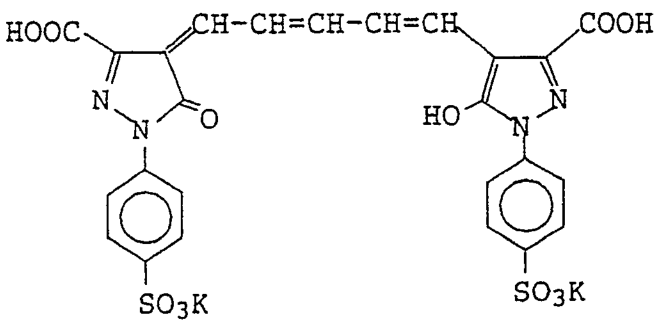
Moreover, the coating described below was carried out on the opposite side of the support.

Compound (d)



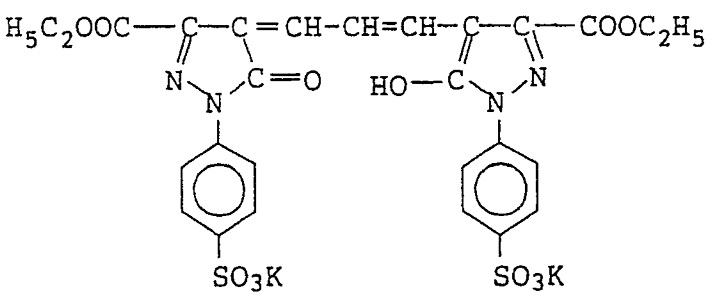
100 g/m^2

Compound (e)



100 mg/m^2

Compound (f)



100 g/m^2

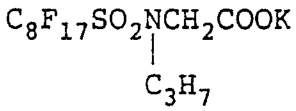
Preparation of the Emulsion

An aqueous solution of silver nitrate and a mixed aqueous solution of potassium iodide and potassium bromide which contained K_3IrCl_6 and $(NH_4)_3RhCl_6$ were added over a period of 15 minutes to an aqueous gelatin solution which contained 1,8-dihydroxy-3,6-dithiaoctane which was being vigorously stirred at 52° C, the addition being controlled in such a way that the pAg value was 7.7, and a mono-disperse cubic silver iodobromide of average grain size 0.21 μ which contained 0.5 mol% silver iodide and which ultimately contained 10^{-7} mol of K_3IrCl_6 and $(NH_4)_3RhCl_6$ respectively per mol of silver halide was obtained. This silver iodobromide emulsion was taken as a core and, using a similar precipitation environment to that used on the first occasion, an aqueous solution of potassium bromide and aqueous solution of silver nitrate were added with control such that the pAg value of the solution was 7.4, and a mono-disperse cubic core/shell silver iodobromide emulsion (average silver iodide content 0.5 mol%) of average grain size 0.28 μ was obtained. After washing with water and removing the soluble salts, 3 mg of sodium thiosulfate and 4 mg of chloroauric acid were added per mol of silver to this emulsion and chemical sensitization was carried out by heating to 65° C for 70 minutes, and 30 mg of a 1% solution of 4-hydroxy-6-methyl-1,3,3a,7-tetra-azaindene was added.

Using this emulsion, 20 mg per mol of silver halide of both 3-ethyl-2-(3-ethyl-benzothiazolinylidene-methylidene)-5-(3-ethyl-4-methyl-thiazolinylideneethylidene-rhodanine iodide and 4,4'-bis(di-naphthoxy-pyrimidylamino(stilbene-2,2-disulfonicacid, di-sodium salt, were added as spectrally sensitizing dyes, and 50 mg per mol of silver of 1-phenyl-5-mercaptotetrazole as added as an anti-foggant, polyethylene glycol was added in an amount of 25% with respect to the gelatin binder as a plasticizer, and 110 mg/m^2 of 2-bis-(vinylsulfonylacetamido)ethane was added as a film hardening agent, and the emulsion (having a maximum sensitivity wavelength of 645 nm) was coated onto the aforementioned support in such a way as to provide 3.2 g/m^2 of silver. The coated weight of gelatin was 1.8 g/m^2.

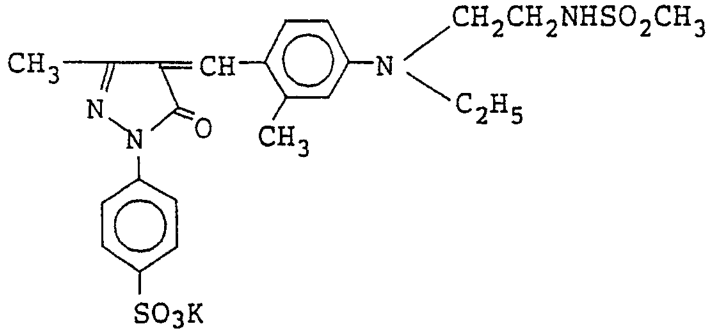
A layer containing 0.9 g/m^2 of gelatin, 180 mg/m^2 of compound (g) indicated below, 60 g/m^2 of poly-(methyl methacrylate) of particle size 3 - 4 μ as matting agent, 150 mg/m^2 of hydroquinone as an anti-foggant, and sodium dodecybenzenesulfonate and the fluorine containing surfactant indicated by the structural formula (h) below as coating promotors was coated at the same time over this layer as a protective layer, and Sample 2-1 was obtained.

(h)



$$C_8F_{17}SO_2\underset{\underset{C_3H_7}{|}}{N}CH_2COOK$$

(g)



<u>Comparative Sample 2-2</u>

Next, Sample 2-2 was obtained by omitting the dye compound (e) from the backing layer of sample 2-1 and establishing between the second under-layer on the emulsion side and the emulsion layer an anti-halation layer containing 100 mg/m^2 of a solid dispersed dye for which compound III-3 had been dispersed in a ball mill, 0.9 g/m^2 of gelatin and 40 mg/m^2 of 2-bis(vinylsulfonylacetamido)ethane as a film hardening agent, and to which a small amount of thickener had been added.

<u>Comparative Sample 2-3</u>

Sample 2-3 was obtained by omitting the dye compounds (e) and (f) from the backing layer of Sample 2-1 and establishing between the second under-layer on the emulsion side and the emulsion layer of a dye layer which contained 100 mg/m^2 of compound III-3 and 120 mg/m^2 of compound III-2, both of which had been dispersed in a ball mill, 0.5 g/m^2 of gelatin and 20 mg/m^2 of 2-bis(vinylsulfonylacetamido)ethane as a film hardening agent and to which a small amount of thickener had been added.

TABLE 3

Sample Number	Anti-halation Layer Dye	Anti-halation Layer Gelatin	Anti-halation Layer Dye/Gelatin Ratio	Total Gelatin Layer Side	Remarks
2-1 (Comparison)	None	0	-	2.8 g/m^2	
2-2 (Comparison)	III-3 100 mg/m^2	0.9 g/m^2	0.111	3.7	
2-3 (Comparison)	III-3 100 mg/m^2	0.5 g/m^2	0.440	3.3	
	III-2 120 mg/m^2				
2-4 (Invention)	III-3 100 mg/m^2	0.5 g/m^2	0.200	2.9	
2-5 (Invention)	I-33 100 mg/m^2	0.5 g/m^2	0.200	2.9	
2-6 (Invention)	I-37 100 mg/m^2	0.5 g/m^2	0.200	2.9	
2-7 (Comparison)	III-3 100 mg/m^2	0.5 g/m^2	0.200	2.9	No backing layer dye

Sample 2-4

Sample 2-4 was obtained by omitting the dye compound (e) from the backing layer of Sample 2-1, establishing between the second under-layer on the emulsion side and the emulsion layer an anti-halation layer which contained 100 mg/m^2 of compound III-3 which had been dispersed in the same way as before and 0.5 g/m^2 of gelatin and to which a small amount of thickener had been added, and reducing the gelatin content of the protective layer to 0.5 g/m^2.

Samples 2-5 and 2-6

Samples 2-5 and 2-6 were prepared in the same way as Sample 2-4 but changing the dyes as shown in Table 3.

Comparative Sample 2-7

Sample 2-7 was prepared by omitting the compounds (d) and (f) from the backing layer of sample 2-4 and removing the water soluble dyes.

The samples obtained in this way were evaluated by being subjected to a wedge exposure using He-Ne laser light which had a peak emission at 633 nm, developed for 10 seconds at 38° C, fixed, water washed and dried in an FG-310PTS processor made by the Fuji Photo Film Co., Ltd. using LD-745 developer and LF-308 fixer made by Fuji Photo Film Co., Ltd. The dry to dry processing time time was about 40 seconds, but Comparative Sample 2-2 did not dry properly and was not really suitable for rapid processing.

The image clarity was rather poor with Sample 2-1, but otherwise good image quality was obtained with no great difference to be seen between Samples 2-2 to 2-7.

Furthermore, each sample was developed in the same way after being left to stand for 3 minutes at a distance of 1 meter below a green safe-light (with a Fuji No. 4 safe-light filter) with a 20 watt electric lamp to evaluate safe-light safety, and a high fog density was observed only with Sample 2-7 which did not contain water soluble dye.

Next, Samples 2-1 to 2-7 were immersed in the same developer and scratched under load with a sapphire needle of diameter 0.4 mm after 20 seconds to evaluate film strength.

The results obtained are shown in table 4. Of the comparative samples, Sample 2-3 which had a high dye/gelatin ratio showed a marked reduction in film strength.

As outlined above, the samples of the present invention were very suitable for rapid processing, provided excellent image quality and had excellent film properties, and they were also excellent in terms of their handlability.

TABLE 4

Sample		Drying Properties	Film Strength
2-1	Comparison	good	177 grams
2-2	Comparison	poor	162
2-3	Comparison	good	93
2-4	Invention	good	150
2-5	Invention	good	146
2-6	Invention	good	149
2-7	Comparison	good	145

EXAMPLE 3

Samples 2-1 to 2-4 from Example 2 were exposed in the same way as in Example 2 and then they were developed for 10 seconds at 38° C in an FG-710 NH processor made by the Fuji Photo Film Co., Ltd. using the same developer and fixer as used in Example 2. The dry to dry processing time was about 30 seconds. Drying failure occurred with Samples 2-2 and 2-3, but Samples 2-1 and 2-4 were dried and were clearly suitable for rapid processing.

EXAMPLE 4

Sample 4-1

A similar backing layer to that used in Sample 2-1 except that 50 mg/m^2 of compound (e) was included was coated after coating a similar electrically conductive layer to that used in Sample 2-1 on the back of a support on which under-layers had been established in the same way as with Sample 2-1. Moreover, an anti-halation layer containing 60 mg/m^2 of III-3 and 0.35 g/m^2 of gelatin and to which a small amount of thickener had been added, and an emulsion layer (having the same composition as that of Sample 2-1) with 90% of the coated weights in Sample 2-1 were established. A protective layer consisting of 0.4 g/m^2 of gelatin, 100 mg/m^2 of compound III-2 which had been dispersed in a ball mill as described in International Patent Laid Open 88/04794, 60 mg/m^2 of poly(methyl methacrylate) matting agent of particle size 3 - 4 μ and 50 mg/m^2 of hydroquinone, and to which sodium dodecylbenzenesulfonate and compound (h) had been added as surfactants, was coated over this layer to provide Sample 4-1.

Sample 4-2

An anti-halation layer consisting of 100 mg/m^2 of III-3 solid dispersed dye and 0.98 g/m^2 of gelatin was coated onto a support on which under-layers had been established in the same way as for Sample 2-1, an emulsion layer the same as that used for Sample 2-1 except that gelatin was added to provide a gelatin content of 2.08 g/m^2 was coated over this layer and then a protective layer consisting of 0.48 g/m^2 of gelatin, 130 mg/m^2 of III-2 solid dispersed dye, 60 mg/m^2 of poly(methyl methacrylate) matting agent of particle size 3 - 4 μ and 150 mg/m^2 of hydroquinone, and to which coating promotor had been added, was coated over the top and Sample 4-2 was obtained.

Sample 4-2 was a comparative sample prepared as described in the illustrative examples of U.S. Patent 4,904,565.

On exposing and processing in the same way as in Example 3, Sample 4-1 was dried but Sample 4-2 was not dried and it could not be used for rapid processing.

Furthermore, on leaving Samples 4-1 and 4-2 to stand under an atmosphere at 25° C, 20% RH, Sample 4-1 remained flat but Sample 4-2 exhibited considerable curl in the emulsion surface and there were problems with handling.

Photographic materials which provide good clear image quality, which are suitable for rapid processing without adverse effect on film strength, and which have excellent handling properties in respect of safe-light safety and curl and dimensional changes can be obtained by means of the present invention.

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 comprising a transparent support, having thereon at least one silver halide emulsion layer, at least one hydrophilic colloid layer which contains at least one type of solid dispersed dye between said support and said silver halide emulsion layer and at least one hydrophilic colloid layer which contains at least one type of water soluble dye on the opposite side of the support to the side having said silver halide emulsion layer, wherein the coated weight of the hydrophilic colloid in the hydrophilic colloid layer which contains said solid dispersed dye is not more than 0.50 g/m^2 and the ratio by weight of the solid dispersed dye/hydrophilic colloid is not more than 0.4.

2. A method of forming an image, comprising imagewise exposing a silver halide photographic material of claim 1 and subjecting said exposed silver halide photographic material to aqueous development, wherein the dry to dry processing time is not more than 60 seconds.

3. A silver halide photographic material as in claim 1, wherein the total coated weight of hydrophilic colloid on the silver halide emulsion layer side of the silver halide photographic material is not more than 3.0 g/m^2.

4. A silver halide photographic material as in claim 1, wherein the peak absorption wavelength of the water soluble dye which is included in the hydrophilic colloid layer on the opposite side of the support to the silver halide emulsion layer in the silver halide photographic material is at least 10 nm removed from the wavelength of maximum sensitivity of said silver halide emulsion layer.

5. A silver halide photographic material as in claim 1, wherein the total coated weight of hydrophilic colloid on the opposite side of the support to the side having the silver halide emulsion layer in the silver halide photographic material is from 0.5 g/m^2 to 2.5 g/m^2.

6. A silver halide photographic material as in claim 1, wherein said silver halide photographic material is capable of providing a high contrast image.

7. A silver halide photographic material as in claim 1, wherein the amount of hydrophilic colloid coated in the solid dispersed dye layer is in the range of from 0.05 g/m^2 to 0.50 g/m^2.

8. A silver halide photographic material as in claim 1, wherein the amount of hydrophilic colloid coated in the solid dispersed dye layer is in the range of from 0.10 g/m^2 to 0.50 g/m^2.

9. A silver halide photographic material as in claim 1, wherein the proportion by weight of dye to hydrophilic colloid in the solid dispersed dye layer is not more than 0.3.

10. A method of forming an image, comprising imagewise exposing a silver halide photographic material of claim 1 and subjecting said exposed silver halide photographic material to aqueous development, wherein the dry to dry processing time is from 3 to 10 seconds.

11. A silver halide photographic material as in claim 1, wherein said silver halide photographic material is a black and white silver halide photographic material.