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(54) Method of image formation.

(57) A method of forming an image is disclosed. The method comprises the step of providing a silver halide photographic light-sensitive material on a drum in a camera, imagewise exposing the material to light which has the wavelength of 460 to 600 nm and has not substantially the wavelength of 360 nm or less, and developing the exposed material. The material comprises a support and, provided thereon, a silver halide emulsion layer containing a sensitizing dye having an absorption maximum within the wavelength range of 450 to 580 nm and, provided on the surface of the support opposite to the emulsion layer, a backing coat layer comprising a hydrophilic colloid layer and having a specific resistance of from 1×10^9 to 1×10^{12} Ω at 25 °C and 20% RH. The material contains a hydrazine derivative or tetrazolium derivative and is oriented to curve to the backing coat layer side.

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FIELD OF THE INVENTION

The present invention relates to a method of image formation with excellent antistatic property using a silver halide photographic light-sensitive material, more specifically a method of image formation which is suitable for electrostatic adsorption cameras and offers good reproduction for dot to dot enlargement and dot to dot curtailment.

BACKGROUND OF THE INVENTION

Generally, plastic films are very liable to charge, and this nature often poses many limitations on their use. For example, polyethylene terephthalate is commonly used as a support for silver halide photographic light-sensitive materials, but it is liable to charge at low humidity such as in winter. In recent years, there have been trends for high-sensitivity photographic emulsions to be coated at high speed or for high-sensitivity light-sensitive materials to be exposed in automatic printer. In these situations, much weight should be placed on antistatic measures.

When a light-sensitive material becomes charged, discharge can cause static marks or adherence of dust and other foreign matters, which can cause pinholes and considerably deteriorates the quality; workability lowers because the deteriorated quality should be corrected. For this reason, antistatic agents are usually used in light-sensitive materials. There have recently been used fluorine-containing surfactants, cationic surfactants, amphoteric surfactants, surfactants or polymeric compounds containing a polyethylene oxide group, and polymers having a sulfonic acid group or phosphoric acid group in their molecular structure.

In addition, this antistatic layer is usually provided on the backing coat layer side.

In the film-making process for catalogues and large posters, it is a common practice to magnify or reduce photographic dot images, and image formation methods offering even wider latitude are required to improve dot gradation reproduction.

To meet this requirement, the conventional lithographic developing methods have been replaced by new developing processes which use a contrast improver such as a hydrazine compound or tetrazolium compound to ensure highly preservable, stable and very high contrast.

However, none of these methods are satisfactory from the viewpoint of dot to dot enlargement or dot to dot curtailment.

On the other hand, cameras such as C-880, produced by Dainippon Screen Manufacturing Co., Ltd., are effective in this situation. In this type of cameras the film backing coat layer is electrostatically adsorbed to the drum and rolled around the drum before exposure, and they, have a drawback that the film fails to be rolled around the drum (jamming) upon exposure when an antistatic layer is present on the backing coat layer side.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method of image formation using a silver halide photographic light-sensitive material which offers excellent reproduction for dot to dot enlargement and dot to dot curtailment, makes it possible to carry out exposure free of transportation failure even with electrostatic adsorption camera, and has excellent antistatic property.

The object described above is accomplished by a method of forming an image,comprising the step of, providing a silver halide photographic light-sensitive material on a drum in a camera, imagewise exposing the material to light which has the wavelength of 460 to 600 nm and has not substantially the wavelength of 360 nm or less, and developing the exposed material, said material comprising a support and provided thereon, a silver halide emulsion layer containing a sensitizing dye having an absorption maximum within the wavelength range of 450 to 580 nm and provided on the surface of the support opposite to the emulsion layer, a backing coat layer comprising a hydrophilic colloid layer and having a specific resistance of from 1×10^9 to $1 \times 10^{12}\Omega$ at 25°C and 20% RH, said material containing a hydrazine derivative or tetrazolium derivative and oriented to curve to the backing coat layer side to be capable of being wound round said drum easily with the backing coat layer cantacting said drum.

As stated above, for accomplishing the object of the present invention, it is effective to subject a light-sensitive material having an antistatic layer and containing a contrast improver to exposure through a UV-cutting filter. In the case of electrostatic adsorption cameras, there occurs a problem that the film fails to be rolled around the drum (jamming) upon exposure when the antistatic layer is present on the backing coat layer side. The inventors found that this problem can be solved by making a film curling on the backing coat layer side and limiting the surface specific resistance of the antistatic layer within the practically effective range according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, curling of the light-sensitive material in the backing coat layer side means that the light-sensitive material curls with the backing coat layer face sunk, including curls resulting from film rolling.

Some methids are available for curling the film toword the backing coat side. In the first method, curling can be adjusted by changing the amount of gelatin coated on each of the faces sandwiching the support; the film can be curled toward the backing coat side by increasing the amount of gelatin coated on the backing coat side relative to the amount of gelatin coated on the opposite side with respect to the support (silver halide emulsion layer side in the present invention).

The gelatin amount ratio, (total amount of gelatin on the silver halide emulsion layer side)/(total amount of gelatin on the backing coat side), is preferably less than 1.0. More preferably, the amount of gelatin coated on the backing coat side is 2.5 to 3.5 g/m^2.

In the second method, the film can be curled toward the backing coat side by changing the amount of polymer latex or matting agent added to the film.

In the third method, the film can be curled by keeping the film rolled with its backing coat side by a heat treatment at over 30 °C while keeping the film rolled with its backing coat surface facing indide.

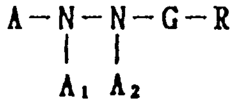
Two or more of these three methods may be used in combination.

In the present invention, imagewise exposure with 460 to 600 nm light which is substantially free from light whose wavelength is under 360 nm can be achieved by the use of a UV-cutting optical filter or by the use of the light-sensitive material containing a UV absorbent. It is preferable to use an optical filter which does not substantially transmit light having a wavelength of not more than 360 nm, like Refilter, produced by Konica Corporation. More specifically, the transmittance of the optical filter is preferably not more than 30%, more preferably not more than 10% of light having the wavelength of not more than 360 nm. For light having the wavelength of 460 to 600 nm, the optical filter's transmittance is preferably not less than 50%, more preferably not less than 80%.

Examples of light sources used for the method of image formation of the present invention include halogen lamps, xenon lamps and fluorescent lamps, with the effect of the invention enhanced when using a xenon light source.

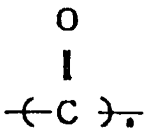
The hydrazine derivative for the present invention preferably has a structure represented by the following Formula H.

Formula H



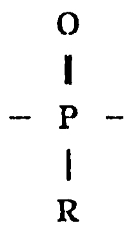
$$A-\underset{A_1}{\underset{|}{N}}-\underset{A_2}{\underset{|}{N}}-G-R$$

wherein A represents an aryl group or a heterocyclic group having at least one of a sulfur atom and an oxygen atom; G represents a



$$\left(\overset{O}{\overset{\|}{C}}\right).$$

group, a sulfonyl group, a sulfoxy group, a

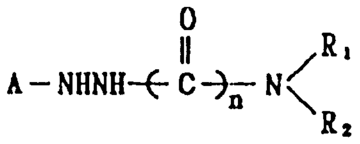


$$-\overset{\overset{\Large O}{\|}}{\underset{\underset{\Large R}{|}}{P}}-$$

group or a iminomethylene group; n represents an integer of 1 or 2; A_1 and A_2 independently represent a hydrogen atom or a substituted or unsubstituted alkylsulfonyl group or substituted or unsubstituted acyl group and at least one of them is a hydrogen group; R represents a hydrogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, a carbamoyl group, an oxycarbonyl group or -O-R_3 group (R_3 represents an alkyl group, an alkenyl group or a saturated heterocyclic group.

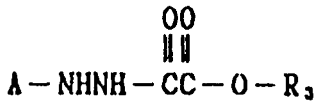
More preferably, the compound is represented by the following Formula A or B.

Formula A



$$A-NHNH\left(\overset{\overset{O}{\|}}{C}\right)_{n}N\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

Formula B



$$A-NHNH-\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}-O-R_3$$

wherein A represents an aryl group or a heterocyclic group having at least one of a sulfur atom and an oxygen atom; n represents an integer of 1 or 2. When n is 1, R_1 and R_2 independently represent a a hydrogen atom, an alkyl group, an alkenyl group, an alkinyl group, an aryl group, a heterocyclic group, a hydroxy group, an alkoxy group, an alkenyloxy group, an alkinyloxy group, an aryloxy group or a heterocyclic oxy group; R_1 and R_2 may cooperate with the nitrogen atom to form a ring. When n is 2, R_1 and R_2 independently represent a hydrogen atom, an alkyl group, an alkenyl group, an alkinyl group, an aryl group, a saturated or unsaturated heterocyclic group, a hydroxy group, an alkoxy group, an alkenyloxy group, an alkinyloxy group, an aryloxy group or a heterocyclic oxy group. Provided that n is 2, at least one of R_1 and R_2 represents an alkenyl group, an alkinyl group, a saturated heterocyclic group, a hydroxy group, an alkoxy group, an alkenyloxy group, an alkinyloxy group, an aryloxy group or a heterocyclic oxy group. R_3 represents an alkinyl group or a saturated heterocyclic group.

The compound represented by Formula A or B includes those wherein at least one of the H atoms in -NHNH- has been substituted by a substituent.

Details of A, R_1 and R_2 are the same as described in Japanese Patent Application No. 222638/1990.

The H atoms in -NHNH- in Formulas A and B, i.e., the hydrogen atoms of hydrazine may be substituted by a substituent such as a sulfonyl group (e.g., methanesulfonyl, toluenesulfonyl), an acyl group (e.g., acetyl, trifluoroacetyl, ethoxycarbonyl) or an oxalyl group (e.g., ethoxalyl, pyruvoyl); the compounds represented by Formulas A and B include such substituted compounds.

In the present invention, more preference is given to the compound of Formula A wherein n is 2, and the compound of Formula B.

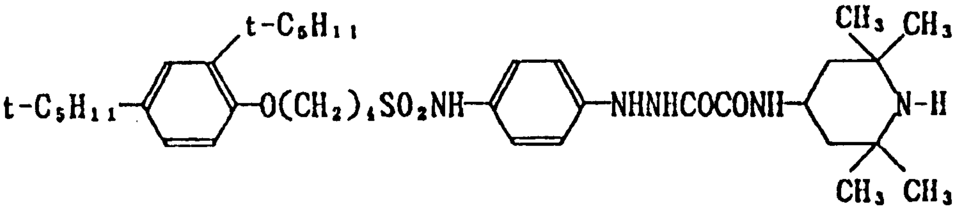
With respect to the compound of Formula A wherein n is 2, it is more preferable that R_1 and R_2 independently represent a hydrogen atom, an alkyl group, an alkenyl group, an alkinyl group, an aryl group, a saturated or unsaturated heterocyclic group, a hydroxy group or an alkoxy group and at least one of R_1

and R_2 represent an alkenyl group, an alkinyl group, a saturated heterocyclic group, a hydroxy group or an alkoxy group.

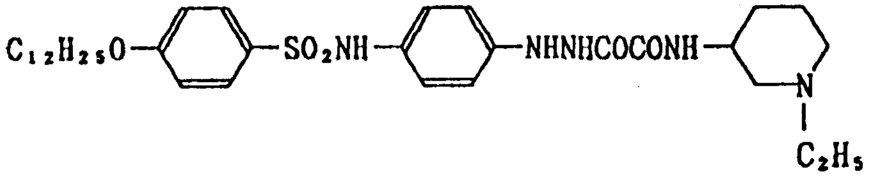
Typical examples of the compounds represented by Formulas A and B include Compounds H-1 through H-187 described in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 327402/1990, pp. 20-58, Compounds I-1 through I-45 described in Japanese Patent O.P.I. Publication No. 17054/1990, pp. 23-32, and the following compounds.

Exemplified compounds

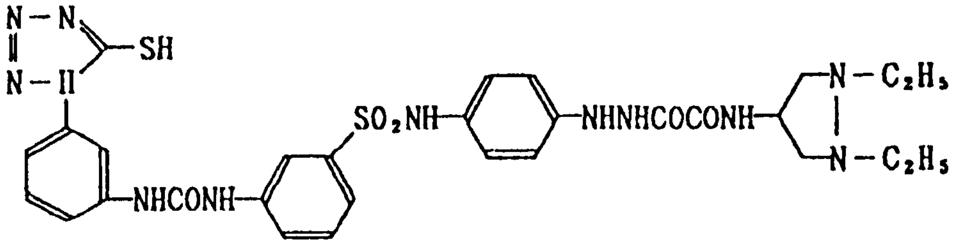
H - 1



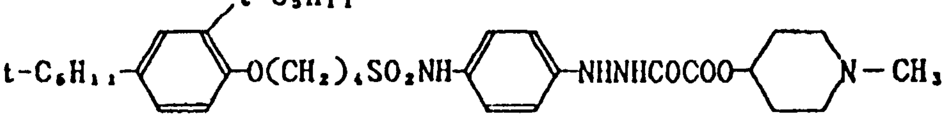
H - 2



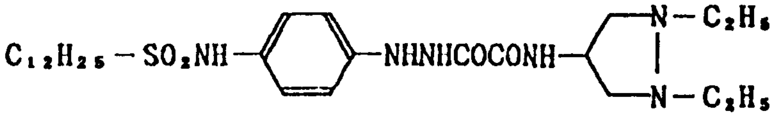
H - 3



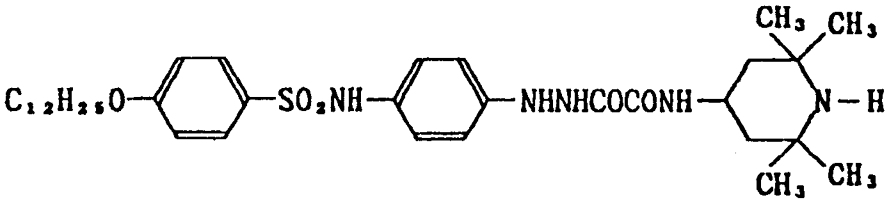
H - 4



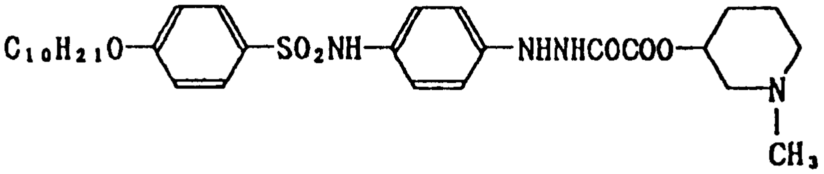
H - 5


C12H25 - SO2NH
NHNHCOCONH
N - C2H5
N - C2H5

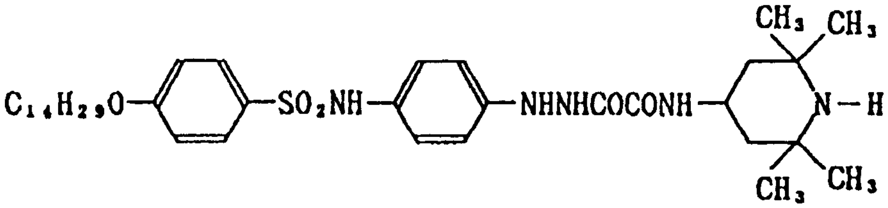
H - 6


C12H25O
SO2NH
NHNHCOCONH
CH3
CH3
N - H
CH3
CH3

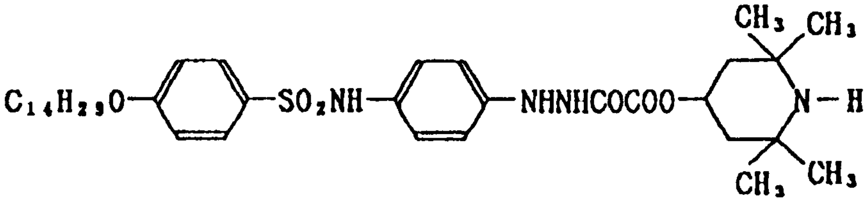
H - 7


C10H21O
SO2NH
NHNHCOCOO
N
CH3

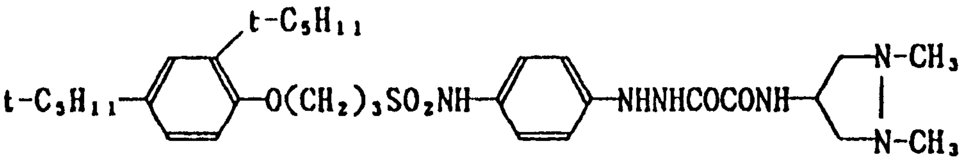
H － 8



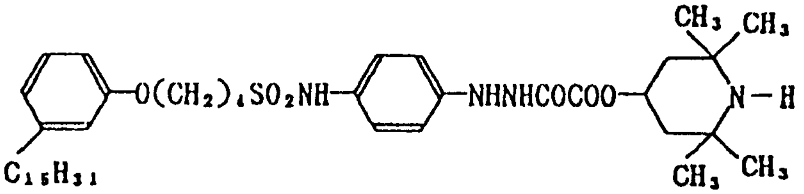
H － 9



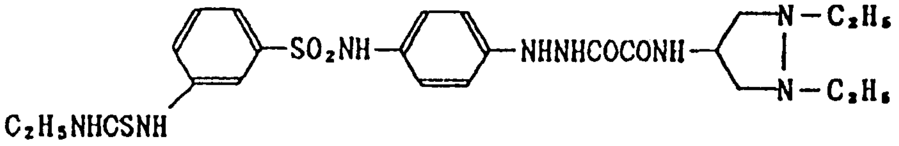
H － 10



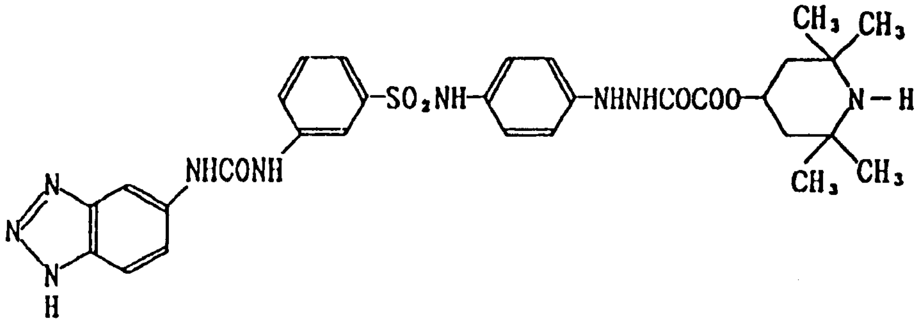
H - 11



H - 12



H - 13



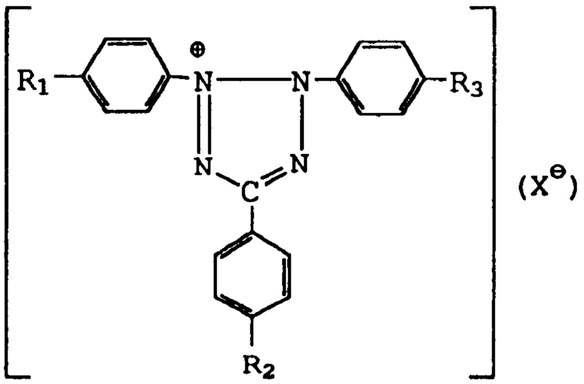
The tetrazolium compound used for the present invention is described below.

In addition, when hydrazine compounds are contained as hardeners, it is preferable that at least one of nucleustion-promoting compounds described on line 1 in page 68 to line 12 in page 144 of Japanese Patent Application 234203/1990 is contained in a silver halide emulsion layer and/or non-light-sensitive layer on the side of silver halide emulsion layer on the support. Practical examples of nucleustion-promoting compounds are as follows:

In addition to the above mentioned compounds, compounds I-1 - I-26 described in pp. 69 - 72 of Japanese Patent Application 234203/1990, compounds II-1 - II-29 described in pp. 73 - 78 of said Application, compounds III-1 - III-25 described in PP. 80 - 83, compounds IV-1 - IV-41 described in pp. 84 - 90 of said Application, compounds V-I-1 - V-I-27 described in pp. 92 - 96, compounds V-II-1 - V-II-30 described in pp. 98 - 103 of said Application, compounds V-III-1 - V-III-35 described in pp. 105 - 111 of said Application, compounds VI-I-1 - VI-I-44 described in pp. 113 - 121, VI-II-1 - VI-II-68 described in PP. 123 - 135 and compounds VI-III-1 - VI-III-35 described in PP. 137 - 143 of said Application are cited.

The tetrazolium compound can be represented by the following formula T:

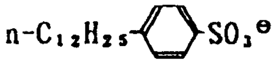
Formula T



In the present invention, the substituents R_1, R_2 and R_3 for the phenyl group of the triphenyltetrazolium compound represented by Formula T are preferably hydrogen atoms or groups whose Hammett's σ value (σP), which indicates the tendency toward electron attraction, has a negative or positive sign, with preference given to those having a negative value. Specific figures for Hammett's σ value in phenyl substitution are given in a large number of papers, including the report by C. Hansch et al. cited in the Journal of Medical Chemistry, 20, 304 (1977). Examples of preferable groups whose Hammett's value has a negative sign include the methyl group (σP = -0.17; the figures in parentheses below are σP values), an ethyl group (-0.15), a cyclopropyl group (-0.21), a n-propyl group (-0.13), an isopropyl group (-0.15), a cyclobutyl group (-0.15), a n-butyl group (-0.16), an isobutyl group (-0.20), a n-pentyl group (-0.15), a cyclohexyl group (-0.22), an amino group (-0.66), an acetylamino group (-0.15), a hydroxyl group (-0.37), a methoxy group (-0.27), an ethoxy group (-0.24), a propoxy group (-0.25), a butoxy group (-0.32) and a pentoxy group (-0.34). All these groups are useful as a substituent for the compound of Formula T for the present invention.

Examples of the compound of Formula T for the present invention are given below.

Table T

Compound No.	R_1'	R_2	R_3	$X^{\ominus}$
T-1	H	H	H	$C\ell^{\ominus}$
T-2	H	p-CH_3	p-CH_3	$C\ell^{\ominus}$
T-3	H	m-CH_3	m-CH_3	$C\ell^{\ominus}$
T-4	H	o-CH_3	o-CH_3	$C\ell^{\ominus}$
T-5	p-CH_3	p-CH_3	p-CH_3	$C\ell^{\ominus}$
T-6	H	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
T-7	H	m-OCH_3	m-OCH_3	$C\ell^{\ominus}$
T-8	H	o-OCH_3	o-OCH_3	$C\ell^{\ominus}$
T-9	p-OCH_3	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
T-10	H	p-C_2H_5	p-C_2H_5	$C\ell^{\ominus}$
T-11	H	m-C_2H_5	m-C_2H_5	$C\ell^{\ominus}$
T-12	H	p-C_3H_7	p-C_3H_7	$C\ell^{\ominus}$
T-13	H	p-OC_2H_5	p-OC_2H_5	$C\ell^{\ominus}$
T-14	H	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
T-15	H	p-OCH_3	p-OC_2H_5	$C\ell^{\ominus}$
T-16	H	p-OC_5H_{11}	p-OCH_3	$C\ell^{\ominus}$
T-17	H	p-OC_8H_{17}-n	p-OC_8H_{17}-n	$C\ell^{\ominus}$
T-18	H	p-$C_{12}H_{25}$-n	p-$C_{12}H_{25}$-n	$C\ell^{\ominus}$
T-19	H	p-$N(CH_3)_2$	p-$N(CH_3)_2$	$C\ell^{\ominus}$
T-20	H	p-NH_2	p-NH_2	$C\ell^{\ominus}$
T-21	H	p-OH	p-OH	$C\ell^{\ominus}$
T-22	H	m-OH	m-OH	$C\ell^{\ominus}$
T-23	H	p-$C\ell$	p-$C\ell$	$C\ell^{\ominus}$
T-24	H	m-$C\ell$	m-$C\ell$	$C\ell^{\ominus}$
T-25	p-CN	p-CH_3	p-CH_3	$C\ell^{\ominus}$
T-26	p-SH	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
T-27	H	p-OCH_3	p-OCH_3	

The tetrazolium compound for the present invention can easily be synthesized in accordance with the method described in Chemical Review, 55, 335-483, for instance.

The tetrazolium compound for the present invention is used preferably in the content range from about 1 mg to 10g, more preferably from about 10 mg to 2 g per mol of silver halide contained in the silver halide photographic light-sensitive material of the invention.

Although the tetrazolium compound for the present invention gives good results when used singly, one or more kinds thereof can be used in any ratio without deterioration of the desired properties.

It is a preferred mode of embodiment of the present invention to add the tetrazolium compound relating to the invention to a silver halide emulsion layer. It is another preferred mode of embodiment of the present invention to add the tetrazolium compound to the hydrophilic colloid layer adjacent directly to the silver halide emulsion layer, or the hydrophilic colloid layer adjacent thereto via an interlayer.

As a still another preferred mode of embodiment of the invention, the tetrazolium compound relating to the invention may be contained in the silver halide photographic light-sensitive material by dissolving it in an appropriate organic solvent such as methanol, ethanol or another alcohol, ether or ester and coating the solution directly on the outermost layer on the silver halide emulsion layer side of the silver halide photographic light-sensitive material by the overcoat method, for instance.

The light-sensitive material of the present invention preferably incorporates a sensitizing dye represented by the following Formula 1, 2, 3 or 4.

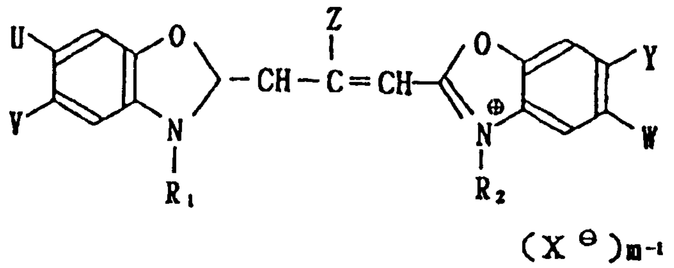
As sensitizing dyes having absorption maximum in the range from 450 to 580 nm, a cyanin dye, a merocyanine dye, a complex cyanine dye, a complex merocyanine dye, a holo polar cyanine dye, a hemicyanine dye, a styryl dye and a hemioxonol dye are included. Especially preferable dyes are a cyanine dye, a merocyanine dye and a dye belonging to a complex merocyanine dye. For these dyes, any nuclel conventionally used for cyanine dyes as basic heterocyclic ring nuclei can be used. Namely, a pyrroline nucleus, a oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus and a pyridine nucleus; nuclei to which an alicyclic hydrocarbon ring is united; nuclei to which an aromatic hydrocarbon ring is united including an indolinine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthothiazole nucleus a benzthiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus can be used. These nuclei may be substituted on a carbon atom.

For a merocyanine dye or a complex merocyanine dye, as a nucleus having a ketomethylene structure, heterocyclic ring nuclei having 5 to 6 members such as a pyrasoline-5-on nucleus, a thiohydantoin nucleus, a 2-thio-oxazolidine-2,4-dion nucleus, a thiazoline-2,4-dion nucleus, a rhodanine nucleus and a thiobarbituric acid nucleus can be used.

To be cocrete, those described in page 23 of Research Disclosure volume 176 RD-17643 (August issue in 1978) and U.S. Patents Nos. 4,425,425 and 4,425,426 can be used.

When they have absorption maximum in the area exceeding 580 nm, the safe light property on ortho is deteriorated remarkably and when they have absorption maximum not more than 450 nm, anticipated sensitivity cannot be obtained.

Formula 1

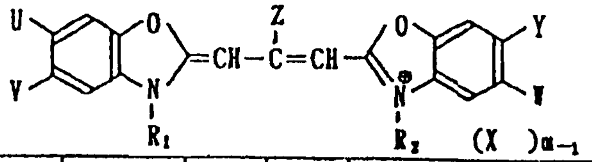


wherein R_1 and R_2 independently represent a substituted or unsubstituted alkyl group, and at least one of R_1 and R_2 is a sulfoalkyl group or a carboxyalkyl group. Z represents an alkyl group or an aralkyl group. U, V, W and Y independently represent a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted alkoxycarbonyl group, a carboxyl group or a hydroxyl group. X^- represents an acid anion. m represents 1 or 2; when an intramolecular salt is formed, m is 1.

Details of Formula 1 are the same as described in Japanese Patent Application No. 316778/1990, pp. 58-61.

Examples of the compound of Formula 1 for the present invention are given in Table 1 below.

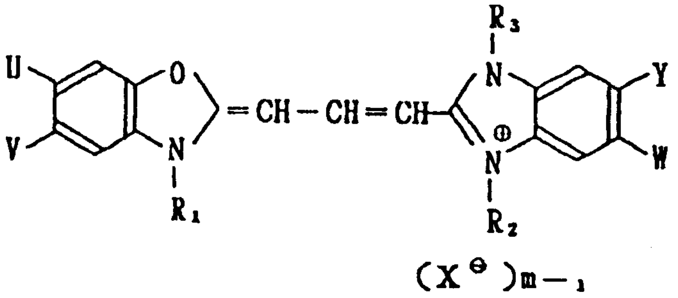
Table 1



[1]No.	V	W	U	Y	R_1	R_2	Z
1	$C\ell$	$C\ell$	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
2	$C\ell$	$C\ell$	H	H	$(CH_2)_4SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
3	$C\ell$	$C\ell$	CH_3	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
4	$C\ell$	$C\ell$	CH_3	CH_3	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
5	$C\ell$		H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
6	$C\ell$		CH_3	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
7	$C\ell$		CH_3	CH_3	$(CH_2)_3SO_3Na$	$(CH_2)_4SO_3$	C_2H_5
8	CH_3		CH_3	CH_3	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
9	OCH_3	OCH_3	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
10	OCH_3	OCH_3	H	H	$(CH_2)_3SO_3Na$	CH_2COO	CH_3
11			H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
12	CF_3	CF_3	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
13	CF_3		H	H	$(CH_2)_4SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
14		OCH_3	H	H	$(CH_2)_4SO_3Na$	$(CH_2)_3SO_3$	CH_3
15	OCH_3	$COCH_3$	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5
16	OCH_3		H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3$	C_2H_5

Formula 2 is described below.

Formula 2

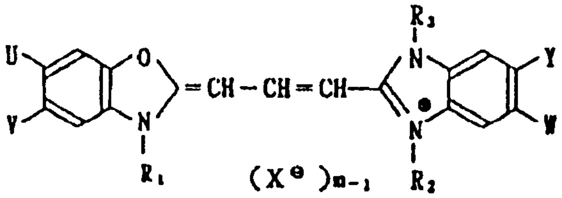


wherein R_1, R_2 and R_3 independently represent a substituted or unsubstituted alkyl group. U, V, W and Y independently represent a hydrogen atom, a halogen atom, a trifluoromethyl group, a cyano group, a carboxyl group, an alkoxy group, an alkoxycarbonyl group, a hydroxyl group, an acyloxy group, a hydroxyalkyl group, a hydroxyalkoxy group or a phenyl group. X^- represents an acid anion. m represents 1 or 2; when an intramolecular salt is formed, m is 1.

Details of the compound represented by Formula 2 are the same as described in Japanese Patent Application No. 316778/1990, pp. 63-64.

Examples of the compound of Formula 2 for the present invention are given in Table 2 below.

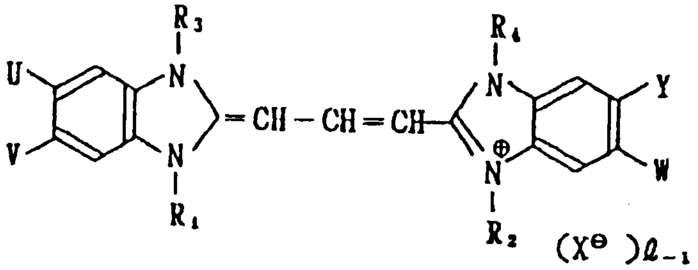
Table 2



(2)No.	V	W	U	Y	R_1	R_2	R_3	$X^{\ominus}$
1	H	$C\ell$	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	$I^{\ominus}$
2	H	$C\ell$	$C\ell$	$C\ell$	CH_3	CH_3	C_2H_5	$I^{\ominus}$
3	H	$C\ell$	H	$C\ell$	CH_3	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	
4	OH	$C\ell$	H	$C\ell$	C_2H_5	$(CH_2)_4SO_3^{\ominus}$	C_2H_5	
5	H	$C\ell$	H	$C\ell$	C_2H_5	$(CH_2)_4SO_3^{\ominus}$	$(CH_2)_3OH$	
6	H	$C\ell$	H	$C\ell$	C_2H_5	$(CH_2)_3SO_3^{\ominus}$	$CH_2CH_2OCH_2CH_2OH$	
7	$C\ell$	$C\ell$	H	$C\ell$	C_2H_5	$(CH_2)_3SO_3^{\ominus}$	$CH_2-\overset{OH}{CH}-CH_3$	
8	CF_3	$C\ell$	H	$C\ell$	C_2H_5	$(CH_2)_3SO_3^{\ominus}$	C_2H_4OH	
9	H	CN	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	
10	OCH_3	CN	H	H	$(CH_2)_2SO_3Na$	$(CH_2)_2SO_3^{\ominus}$	C_2H_5	
11	$COOCH_3$	CN	H	H	C_2H_5	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	
12	H	CF_3	H	H	C_2H_5	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	
13	H	$C\ell$	H	CH_3	$(CH_2)_2SO_3Na$	$(CH_2)_2COO^{\ominus}$	C_2H_5	
14		$C\ell$	H	H	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	C_2H_5	
15		$C\ell$	H	H	C_2H_5	C_2H_5	C_2H_5	$I^{\ominus}$
16		CF_3	H	H	C_2H_5	C_2H_5	C_2H_5	$I^{\ominus}$

Formula 3 is described below.

Formula 3



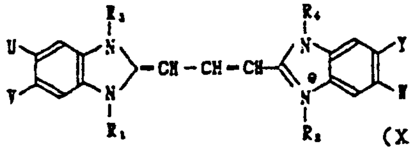
wherein R_1, R_2, R_3 and R_4 independently represent a substituted or unsubstituted alkyl group (see Table 2), U, V, W and Y independently represent a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted alkoxycarbonyl group, a carboxyl group, a hydroxyl group, a cyano group or a substituted or unsubstituted acyloxy group, and l represents 1 or 2, provided that when an intramolecular salt is formed, l is 1.

The anion represented by X^- has the same definition as X^- in Formula 1.

Details of the compound represented by Formula 3 are the same as described in Japanese Patent Application No. 316778/1990, pp. 66-67.

Examples of the compound of Formula 3 for the present invention are given in Table 3 below.

Table 3



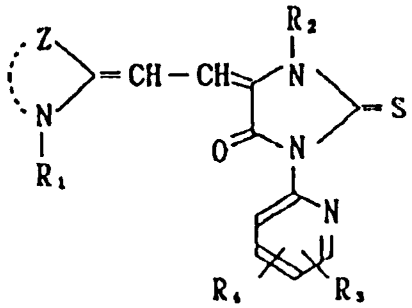
$(X^{\ominus})_{\ell-1}$

[3] No.	V	W	U	Y	R_1	R_2	R_3	R_4	$X^{\ominus}$
1	$COOC_2H$	$COOC_2H_5$	H	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-
2	CF_3	CF_3	H	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-
3	F	F	H	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-
4	CF_3	CF_3	Cℓ	Cℓ	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-
5	$SO_2N(CH_3)_2$	$SO_2N(CH_3)_2$	H	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-
6	Cℓ	Cℓ	H	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-
7	$CONH_2$	$CCNH_2$	H	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-
8	Cℓ	Cℓ	Cℓ	Cℓ	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	C_2H_5	
9	$COOC_2H_5$	$COOC_2H_5$	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	C_2H_5	
10	CN	CN	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	C_2H_5	
11	$SO_2N(CH_3)_2$	$SO_2N(CH_3)_2$	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	C_2H_5	
12	$COOC_2H_5$	$COOC_2H_5$	Cℓ	Cℓ	$(CH_2)_4SO_3Na$	$(CH_2)_4SO_3^{\ominus}$	C_2H_5	C_2H_5	
13	CN	CN	Cℓ	Cℓ	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3^{\ominus}$	C_2H_5	C_2H_5	
14	CO_2CH_3	CO_2CH_3	H	H	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3^{\ominus}$	CH_2CH_2CN	CH_2CH_2CN	
15	Cℓ	Cℓ	Cℓ	Cℓ	$(CH_2)_2CO_2C_2H_5$	C_2H_5	CH_3	CH_3	I^-
15	CH_3O	CH_3O	H	H	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I^-

The sensitizing dyes represented by Formulas 1 through 3 for the present invention are known compounds which can easily be synthesized by known methods, including the method described in a reference cited in "The Cyanine Dyes and Related Compounds", written by F. M. Homes, published by Interscience Publishers, New York (1964).

Formula 4 is described below.

Formula 4



wherein Z represents a group of atoms necessary to form an oxazole nucleus, benzoxazole nucleus or naphthoxazole nucleus.

R_1 represents a substituted or unsubstituted alkyl group.

R_2 represents an alkoxycarbonylalkyl group, a hydroxyalkyl group, a hydroxyalkoxyalkyl group, a carbamoylalkyl group, a hydroxyphenyl group, a hydroxyalkylphenyl group, a phenyl group, an alkoxyalkyl group or the substituent $(CH_2)_n$-A or $(CH_2)_n$-O-$(CH_2)_n$-A, wherein A represents a nitrile group, an alkylsulfonyl group, a sulfonamide group, an alkylsulfonylamino group or a lower alkoxy group; n represents an integer of 1 to 4.

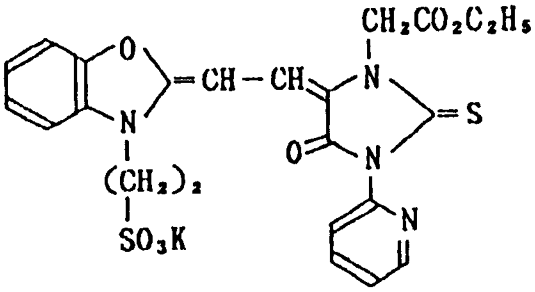
R_3 and R_4, whether identical or not, independently represent a hydrogen atom, an alkyl group, an alkoxy group, an alkylsulfonyl group, a sulfo group, a chlorine atom, a fluorine atom or a carboxyl group.

With respect to the compound of Formula 4, R_1 preferably represents a sulfo group or a linear or a branched C_{1-4} alkyl group substituted by a carboxyl group and/or a hydroxyl group. Examples of such groups for R_1 include a sulfoethyl group, a sulfopropyl group, a 3-sulfobutyl group, a 4-sulfobutyl group, a carboxymethyl group, a carboxyethyl group, a hydroxyethyl group and a 3-sulfo-2-hydroxypropyl group.

Details of the compound represented by Formula 4 are the same as described in Japanese Patent Application No. 151504/1989, pp. 7-14.

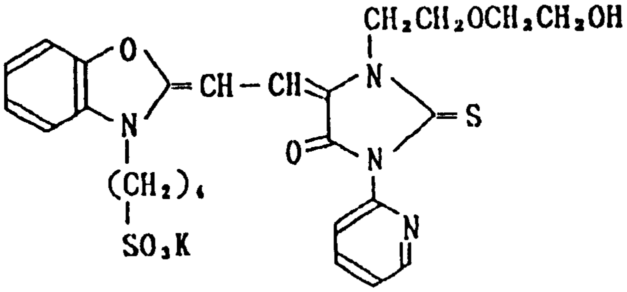
Typical examples of the compound of Formula 4 for the present invention include Compounds I-1 through I-37 described in Japanese Patent O.P.I. Publication No. 151504/1989, pp. 14-26, except for the following compounds. Typical examples are given below.

4 - 1



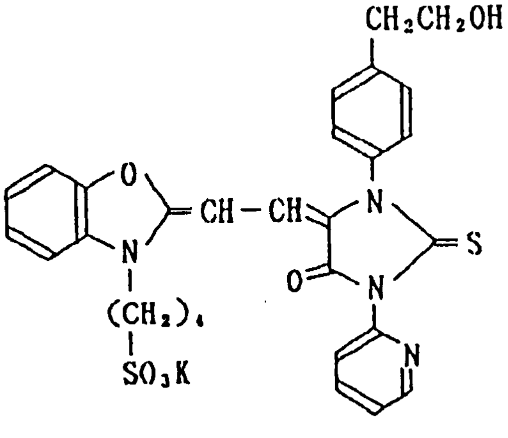
CH₂CO₂C₂H₅
O
N
CH
CH
N
S
O
N
(CH₂)₂
SO₃K
N

4 - 2



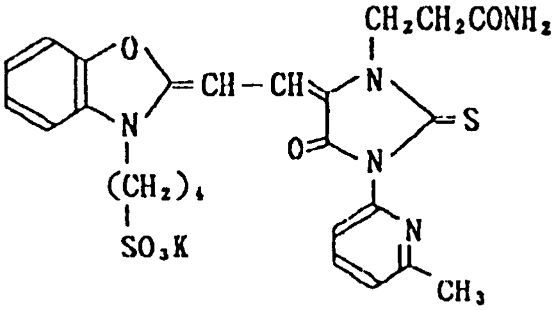
CH₂CH₂OCH₂CH₂OH
O
N
CH
CH
N
S
O
N
(CH₂)₄
SO₃K
N

4 - 3

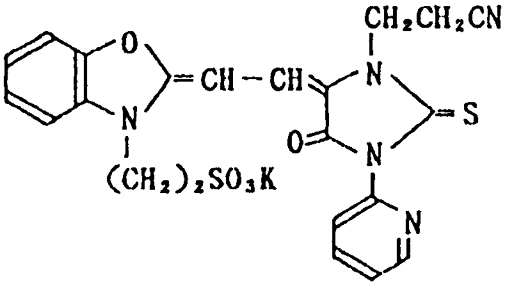


CH₂CH₂OH
O
N
CH
CH
N
S
O
N
(CH₂)₄
SO₃K
N

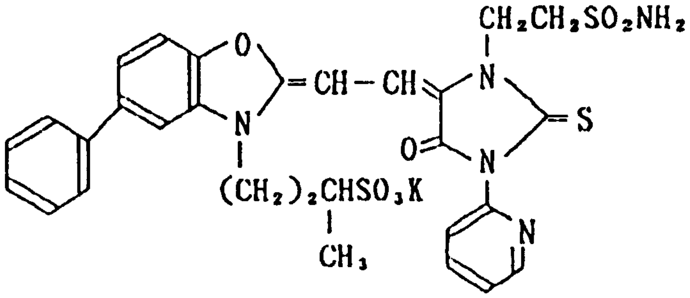
4 - 4


CH₂CH₂CONH₂
O
N
CH - CH
N
S
O
N
(CH₂)₄
SO₃K
N
CH₃

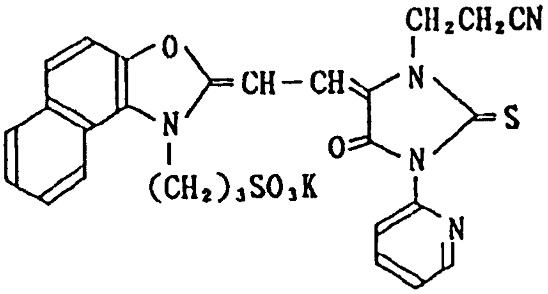
4 - 5


CH₂CH₂CN
O
N
CH - CH
N
S
O
N
(CH₂)₂SO₃K
N

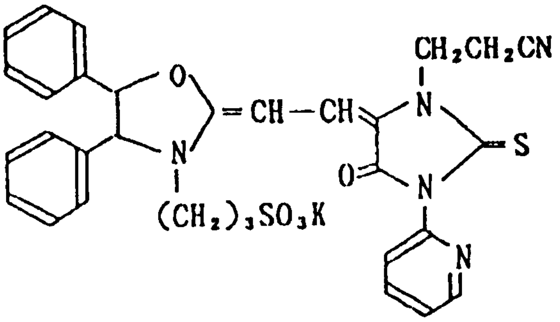
4 - 6


CH₂CH₂SO₂NH₂
O
N
CH - CH
N
S
O
N
(CH₂)₂CHSO₃K
CH₃
N

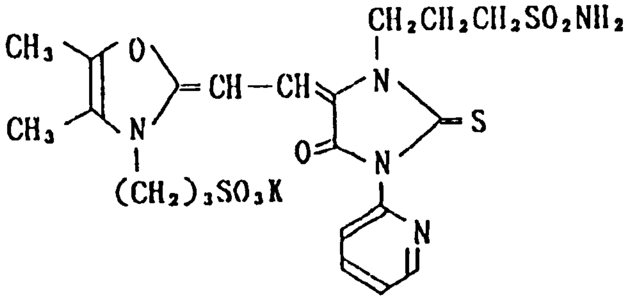
4 − 7



4 − 8



4 − 9



The compound of Formula 4 for the present invention can be synthesized in accordance with the methods of synthesis of dimethinemerocyanine described in Japanese Patent Examined Publication Nos. 549/1971, 18105/1971, 18106/1971, 18108/1971, 4085/1972 and 52574/1983 and US Patent Nos.2,839,403, 3,384,486, 3,625,698, 3,480,439 and 3,567,458.

Addition and dispersion of the merocyanine dyes represented by Formulas 1 through 4 for the present invention into silver halide emulsion can be achieved by known conventional methods, including the method described in Japanese Patent Examined Publication No. 44895/1974 and Japanese Patent O.P.I. Publication No. 11419/1975, wherein the dye is added in dispersion along with surfactant, the method described in Japanese Patent O.P.I. Publication Nos. 16624/1978, 102732/1978 and 102733/1978 and US Patent Nos. 3,469,987 and 3,676,147, wherein the dye is added in dispersion along with hydrophilic medium, and the method described in East German Patent No. 143,324, wherein the dye is added in solid solution. Also, the merocyanine dye may be added to the emulsion in dispersion in a water-soluble solvent, such as water, ethanol, methanol, acetone, n-propanol, fluorinated alcohol or pyridine or mixture thereof. Although addition may be at any time during the emulsion processing process, it is preferable to add the dye during or after chemical ripening. The amount of merocyanine dye added for the present invention is such that the silver halide emulsion is spectrally sensitized, for example, 1 mg t 2 g, preferably 10 mg to 1 g per mol of silver halide.

For the purpose of supersensitization, the merocyanine dye for the present invention may be used in combination in any ratio with other dyes disclosed in Japanese Patent Examined Publication Nos. 4933/1968, 4936/1968, 18107/1971, 1999/1971, 11114/1972, 1762/1973, 38408/1973, 38937/1981 and 52574/1983 and US Patent Nos. 2,519,001 and 3,745,014.

In the present invention, the surface specific resistance of the light-sensitive material is determined using Teraohm-meter (R-503 model), produced by Kawaguchi Denki, after moisture control at an ambient temperature of 25 ° C and an ambient humidity of 20% for 2 hours.

If the surface specific resistance of the light-sensitive material exceeds 1×10^{12} Ω, the light-sensitive material will be liable to electrify and undergo static marks as described above or pinholes due to adhesion of dust and othe foreign matters, which cosiderably deteriorate the quality.

If the surface specific resistance is lower than 1×10^{12} Ω, the above failure due to static marks or pinholes is reduced significantly. However, transportavility is considerably deteriorated in cameras of the type in which the film is electrostatically absorbed, rolled around a drum, exposed and transported, like C-880, a camera for film making process produced by Dainippon Screen Manufacturing Co., Ltd.

To obtain a backing coat layer having a surface specific resistance of from 1×10^{9} to 1×10^{12}Ω, a water-soluble electroconductive polymer or an ionic inorganic compound is added to a hydrophilic colloid layer which essentially comprises gelatin, or an electroconductive layer is formed between a support and a hydrophilic colloid layer which essentially comprises gelatin.

The ionic inorganic compound is preferably an alkali metal salt or alkaline earth metal salt, such as LiCl, NaCl, KNO_3, KBr or CaCl. The amount of its addition is preferably 10 to 1000 mg/m^2.

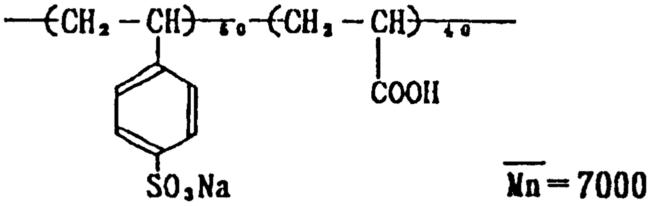
The electroconductive layer preferably comprises a metal oxide or a reaction product or a metal oxide reaction product a water-soluble electroconductive polymer, a hydrophobic latex, and or epoxy hardener.

The water-soluble electroconductive polymer has at least one electroconductive group selected from a sulfonic acid group, a sulfate group, a quaternary ammonium salt, a tertiary ammonium salt and a carboxyl group. The electroconductive group should be present at not less than 5% by weight per polymer molecule. The water-soluble electroconductive polymer may contain a hydroxyl group, an amino group, an epoxy group, an aziridine group, an active methine group, a sulfinic acid group, an aldehyde group and a vinylsulfone group.

The number-average molecular weight of the polymer is 3000 to 100000, preferably 3500 to 50000.

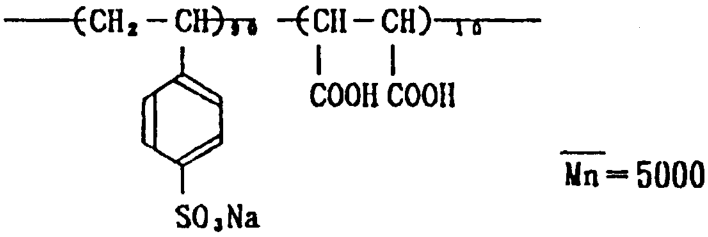
Examples of the water-soluble electroconductive polymer for the present invention are given below.

P - 1



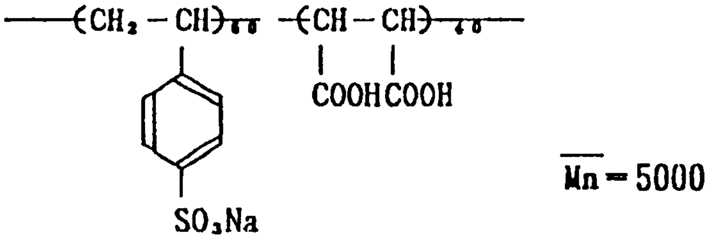
$\overline{Mn} = 7000$

P - 2



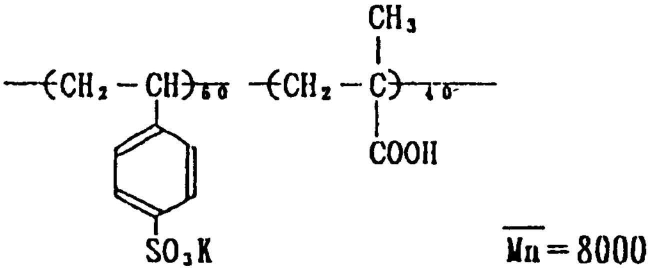
$\overline{Mn} = 5000$

P - 3



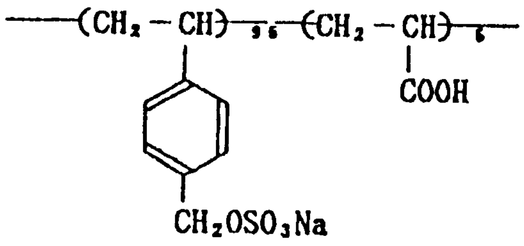
$\overline{Mn} = 5000$

P - 4



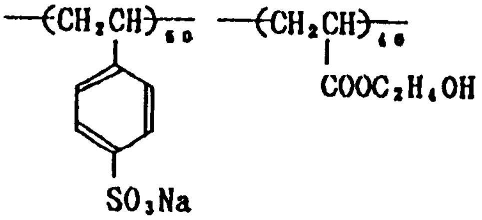
$\overline{Mn} = 8000$

P - 5



$\overline{Mn} \fallingdotseq 25000$

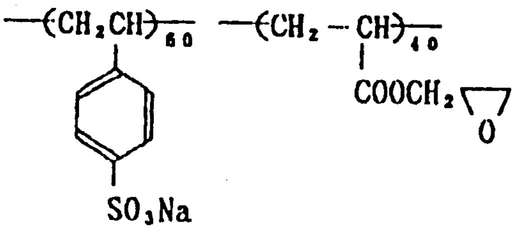
P - 6



x : y = 90 : 10

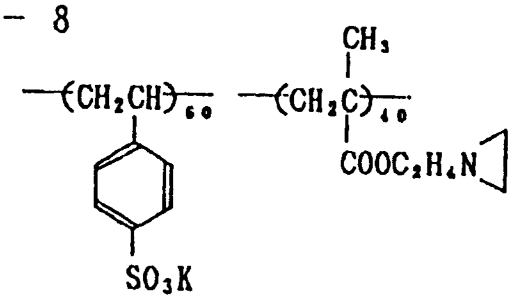
$\overline{Mn} - 7000$

P - 7



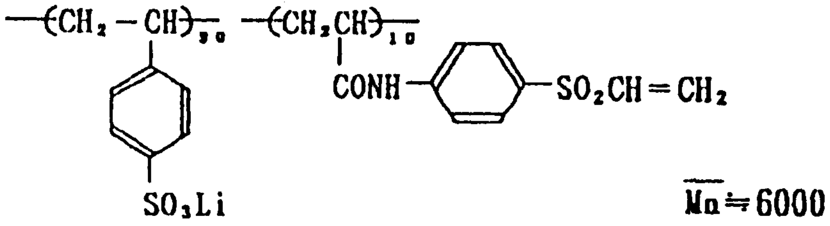
$\overline{Mn} = 5000$

P - 8

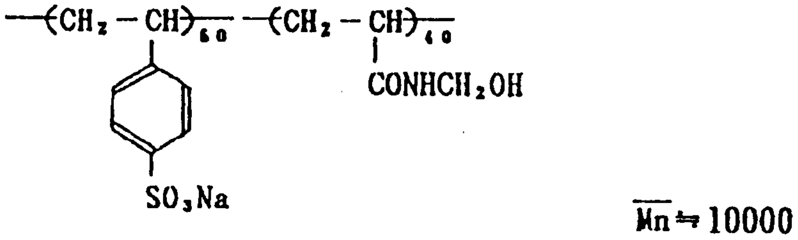


$\overline{Mn} - 8000$

P - 9



P - 10

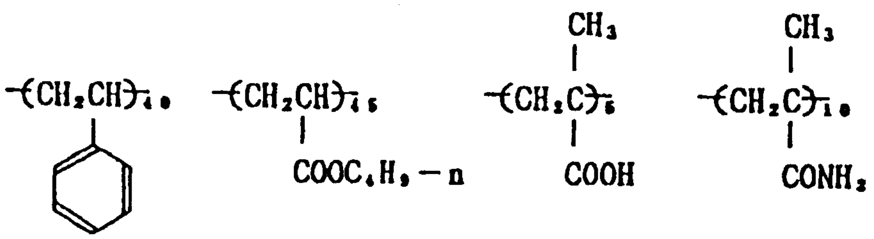


With respect to P-1 through P-10, $\overline{Mn}$ represents average molecular weight (average molecular weight means number-average molecular weight in the present specification) as determined by GPC and expressed as polyethylene glycol.

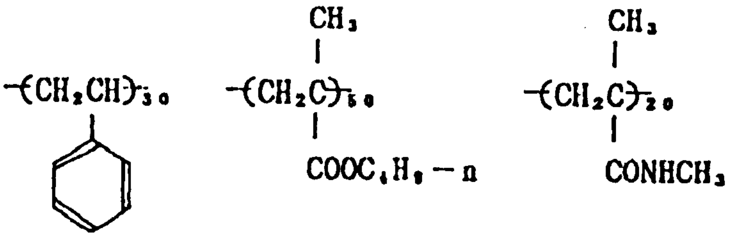
The hydrophobic polymer grains contained in the water-soluble electroconductive polymer layer comprise a latex which is substantially insoluble in water. The hydrophobic polymer is obtained by polymerizing any combination of monomers selected from styrene, styrene derivatives, alkyl acrylates, alkyl methacrylates, olefin derivatives, halogenated ethylene derivatives, vinyl ester derivatives and acrylonitrile, with preference given to those containing at least 30 mol%, more preferably not less than 50 mol% of styrene derivative, alkyl acrylate or alkyl methacrylate.

Examples of the latex for the present invention are given below.

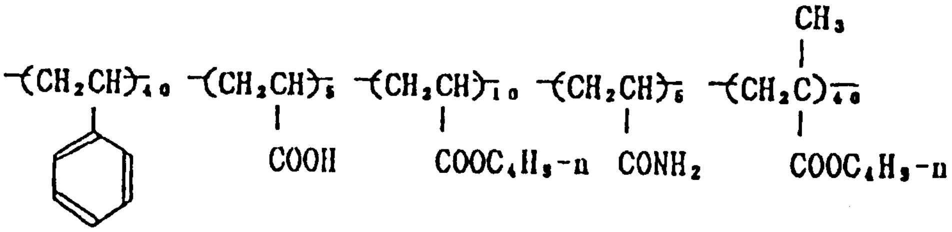
L - 1



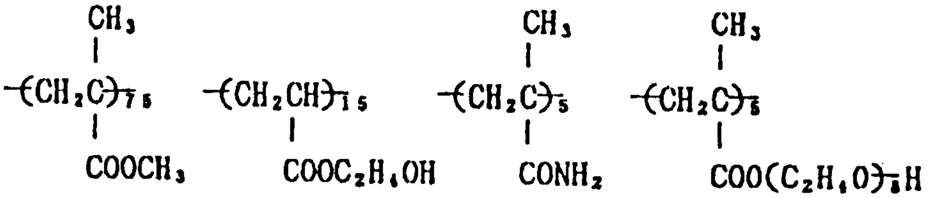
L - 2



L - 3

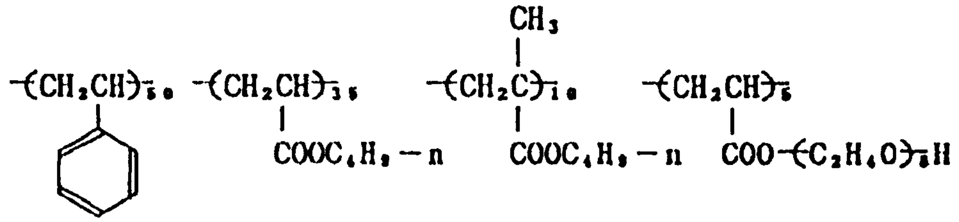


L - 4

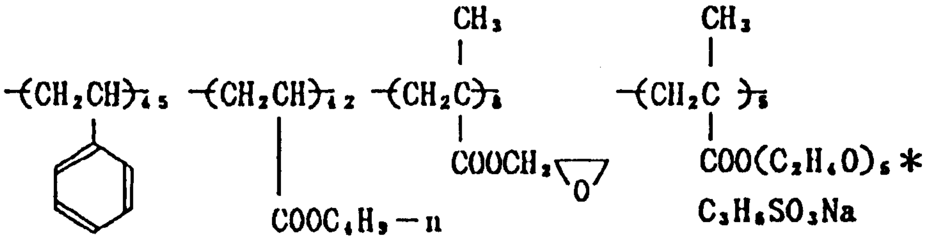


$$-\!\!(\mathrm{CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}})_{75}\;-\!\!(\mathrm{CH_2\underset{\underset{\displaystyle COOC_2H_4OH}{|}}{CH}})_{15}\;-\!\!(\mathrm{CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CONH_2}{|}}{C}}})_{5}\;-\!\!(\mathrm{CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COO(C_2H_4O)_8H}{|}}{C}}})_{5}$$

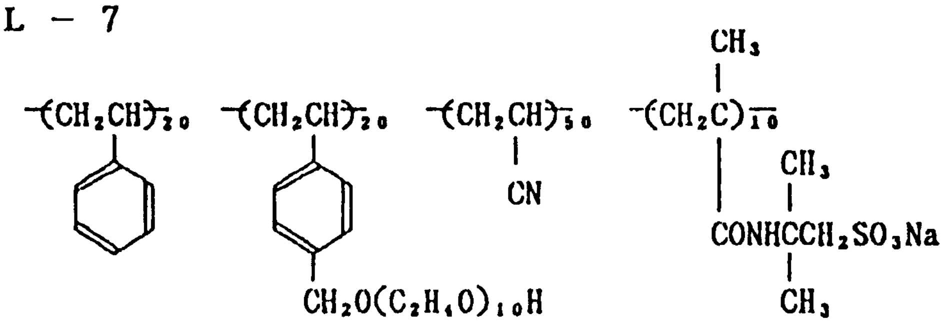
L − 5


CH₃
-(CH₂CH)₅₀
-(CH₂CH)₃₅
-(CH₂C)₁₀
-(CH₂CH)₅
COOC₄H₉ − n
COOC₄H₉ − n
COO-(C₂H₄O)₈H

L − 6


CH₃
CH₃
-(CH₂CH)₇₅
-(CH₂CH)₁₂
-(CH₂C)₈
-(CH₂C)₅
COOCH₂
O
COO(C₂H₄O)₆ *
C₃H₆SO₃Na
COOC₄H₉ − n

L − 7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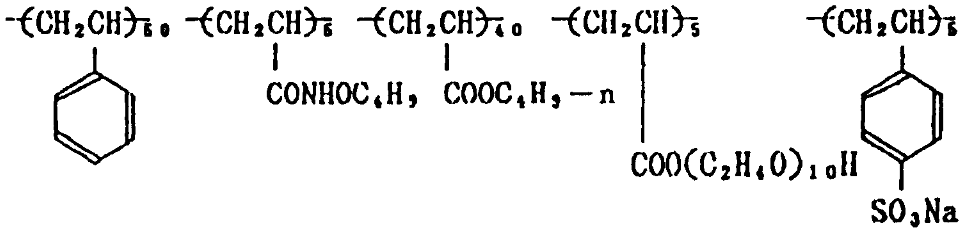
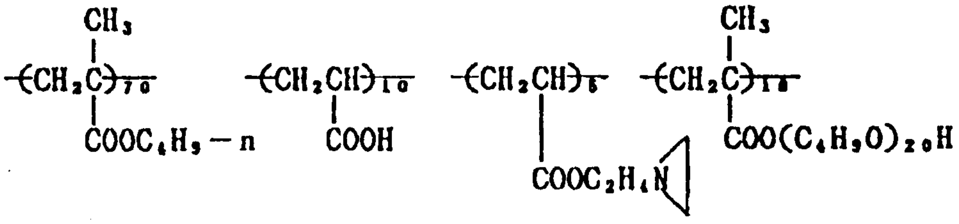
-(CH₂CH)₂₀
-(CH₂CH)₅₀
-(CH₂C)₁₀
CH₃
CN
CONHCCH₂SO₃Na
CH₂O(C₂H₄O)₁₀H
CH₃

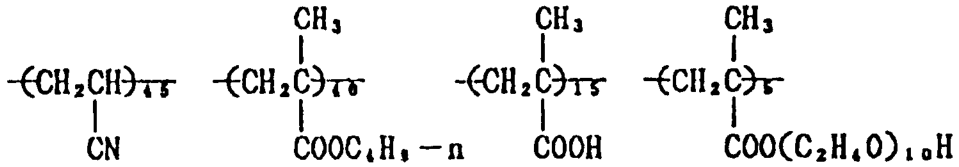
L − 8


-(CH₂CH)₆₀
-(CH₂CH)₅
-(CH₂CH)₂₀
-(CH₂CH)₅
-(CH₂CH)₅
CONHOC₄H₉
COOC₄H₉ − n
COO(C₂H₄O)₁₀H
SO₃Na

L - 9



L - 10



$$-(CH_2\underset{CN}{CH})_{45}-\ -(CH_2\underset{COOC_4H_9-n}{\overset{CH_3}{C}})_{40}-\ -(CH_2\underset{COOH}{\overset{CH_3}{C}})_{15}-\ -(CH_2\underset{COO(C_2H_4O)_{10}H}{\overset{CH_3}{C}})_{5}-$$

Any epoxy hardener can be used with no limitation, as long as it has an epoxy group. It can be used in combination with one or more other hardeners such as aldehyde hardeners and vinylsulfone hardeners.

The epoxy compound preferably contains a hydroxyl group or ether condensation linkage. In the present invention, epoxy equivalence is obtained by the following equation.

Epoxy equivalence = molecular weight/number of epoxy groups in one molecule. This value can also be obtained colorimetrically by the method described in "Shin Jikken Kagaku Koza, Vol. 13 (1), Yuki Kozo", p. 58, published by Maruzen.

The epoxy equivalence is preferably 50 to 300, more preferably 80 to 210. Epoxy equivalence values exceeding 300 result in insufficient hardening; coatability decreases as the amount increases. Insufficient hardening tends to lead to scratches. Epoxy equivalence values under 50 offer strong hardening but result in haze and residual color deterioration; no improvement is obtained even when the amount is reducing.

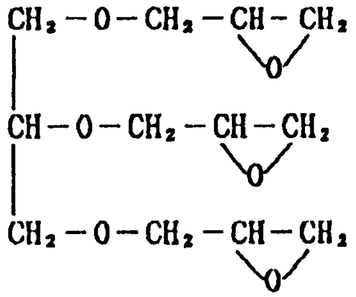
Examples of the epoxy compound for the present invention are given below.

Figures in parentheses are values for epoxy equivalence.

Epoxy equivalence

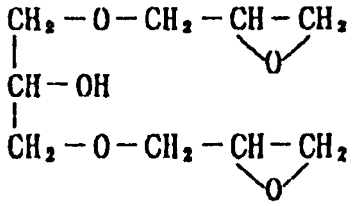
E - 1

(83.3)



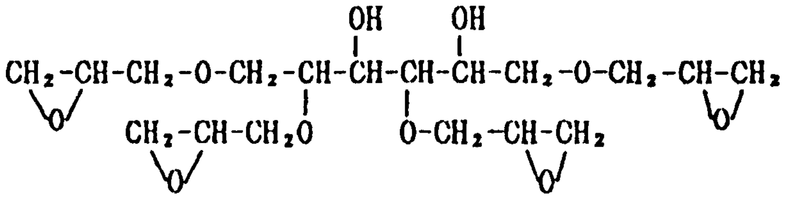
E - 2

(102)



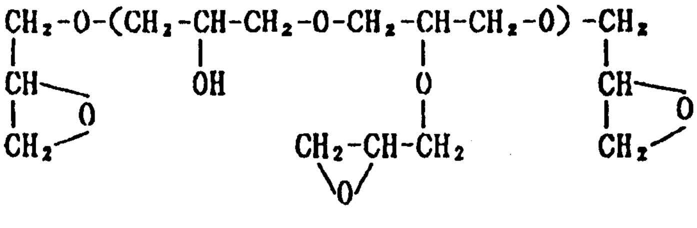
E - 3

(101.5)

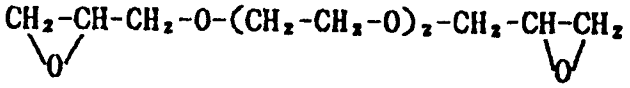


E - 4

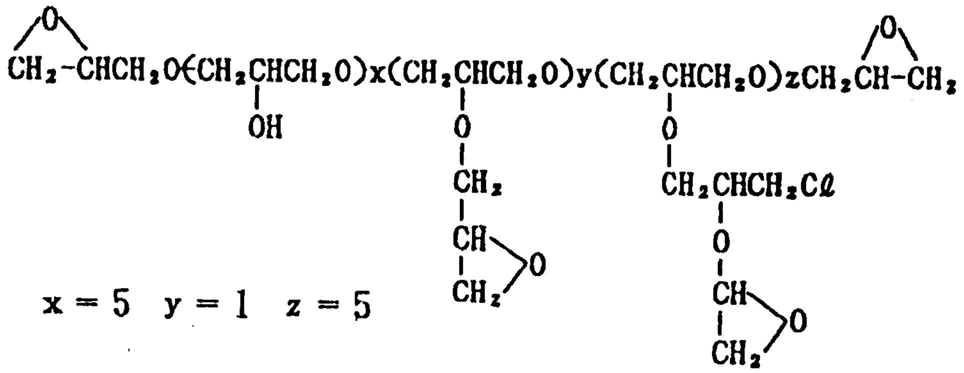
(148)



E - 5 (109)



E - 6 (196)



x = 5 y = 1 z = 5

The amount of epoxy hardener added is preferably 5 mg/m^2 to 1 g/m^2.

The epoxy hardener may be also added to any of an antistatic layer, subbing layer, emulsion layer, backing coat layer and protective layer. It is preferably added to the antistatic layer or the hydrophilic colloid layer on the antistatic layer side.

To the electroconductive layer described above, which comprises a reaction product of a water-soluble electroconductive polymer, a hydrophobic latex and an epoxy hardener, the description and compounds described in Japanese Patent Application No. 316788/1990, pp. 4-30, are applicable.

The metal oxide for the electroconductive layer may be indium oxide, tin oxide or a metal oxide doped with antimony atom, or any combination thereof.

Two types of indium oxide, namely indous oxide In_2O and indic oxide In_2O_3 are known, but it is preferable to use indic oxide for the present invention.

Two types of tin oxide, namely stannous oxide SnO and stannic oxide SnO_2 are known, but it is preferable to use stannic oxide for the present invention.

Examples of metal oxides doped with antimony atom include tin oxide and iridium oxide. To dope these metal oxides with antimony, a halide, alkoxy derivative or nitrate of tin or indium and a halide or nitrate of antimony and a halide, alkoxy derivative or nitrate of antimony are mixed, oxidized and burnt. These metal compounds are easily available from metal compound manufacturers such as Nippon Yttrium Co., Ltd. The doping antimony content is preferably 0.5 to 10% by weight of the weight of tin or indium. These inorganic compounds are added preferably in dispersion in a hydrophilic colloid such as gelatin or in a polymeric compound such as acrylic acid or maleic acid. The amount of their addition per binder is preferably 1 to 100% by weight.

The film surface pH of the electroconductive layer for the present invention is preferably not more than 8.0, more preferably 3.0 to 7.5. Too low film surface pH values are undesirable from the viewpoint of film stability.

Although the electroconductive layer for the present invention may be on the support side with respect to the light-sensitive layer or the opposite side or on both sides, preference is given to the opposite side.

In the present invention, the electroconductive layer is coated on a transparent support. Although any photographic transparent support can be used, it is preferable to use polyethylene terephthalate or cellulose triacetate as prepared to have a visible light transmittance of over 90%.

The silver halide emulsion for the present invention may comprise any silver halide in common use in silver halide emulsions, such as silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide and silver chloride.

The silver halide emulsion for the present invention permits the use of sensitizing methods and other various techniques and additives known to those skilled in the art.

For example, the silver halide photographic emulsion and backing coat layer for the present invention may contain various chemical sensitizers, toning agents, hardeners, surfactants, thickeners, plasticizers, lubricants, developing inhibitors, UV absorbents, anti-irradiation dyes, heavy metals and matting agents, by various methods. They may also contain a polymer latex.

Examples of supports which can be used for the silver halide photographic light-sensitive material of the present invention include cellulose acetate, cellulose nitrate, polyesters such as polyethylene terephthalate, polyolefins such as polyethylene, polystyrene, baryta paper, polyolefin-coated paper, glass and metals. These supports are undercoated as necessary.

The silver halide photographic light-sensitive material of the present invention can be developed by various known methods such as those in common use after exposure.

The black-and-white developer is an alkaline solution containing a developing agent such as hydroxybenzene, aminophenol or amino benzene, and may contain other sulfites, carbonates, bisulfites, bromides and iodides of alkali metal salts.

EXAMPLES

The present invention is hereinafter described in more detail by means of the following examples, but the invention is not by any means limited thereby.

Example 1

Preparation of support 1 having an electroconductive layer

Polyethylene terephthalate, which was subbed with styrene-containing hydrophobic latex after corona discharge at an energy level of 10W/(m^2•min), was again subjected to corona discharge at an energy level of 10W/(m^2•min). Then, an epoxy hardener (E) was added to an antistatic solution with the following composition, and after adjusting to a pH of 5.0 with sulfuric acid, it was coated using an air knife coater at a rate of 50 m/min to obtain the solution coating amount of 10 cc/m^2.

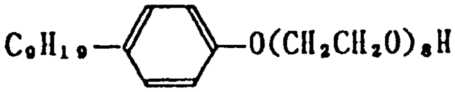
Water-soluble electroconductive polymer	P-3	60 g/l
Hydrophobic polymer grains	L-3	40 g/l
Ammonium sulfate		0.5 g/l
Polyethylene oxide compound (molecular weight 600)		6 g/l
Hardener	E-1	6 g/l
Hardener	E-6	6 g/l
Water was added to make a total quantity of 1 liter. E was added while coating.		

Under parallel flow drying conditions of a drying air temperature of 90 °C and an overall heat transfer coefficient of 25 Kcal/(m^2•hr• °C), drying was carried out for 30 seconds, followed by heat treatment at 140 °C for 90 seconds.

On this antistatic layer was gelatin coated and dried to be 2 g/m^2.

Preparation of support 2 having an electroconductive layer

A polyethylene terephthalate support, which was subbed with styrene-containing hydrophobic latex after corona discharge at an energy level of 10 W/(m^2•min), was again subjected to corona discharge at an energy level of 10 W/(m^2•min). Then, an antistatic solution with the following composition was coated.

Gelatin	35 mg/m^2
SnO_2/Sb(8/2) (grain size 0.3 µm)	250 mg/m^2
	5 mg/m^2

Then, the solution was dried at 90°C for 2 minutes and subjected to heat treatment at 140°C for 90 seconds. This electroconductive layer was coated on one face of the support.

Prepavation of support 3

On the polyethyleneterephthalate base were coated a sublayer as descrebed in Example 1 of Japanese Patent O.P.I. No. 19941/84.

Preparation of a silver halide photographic light-sensitive material

Preparation of an emulsion A

Using the following solutions A, B and C, a silver chlorobromide emulsion was prepared.

Solution A	
Ossein gelatin	17 g
Sodium polyisopropylene-polyethyleneoxydisuccinate in 10% aqueous solution of ethanol	5 ml
Distilled water	1280 ml

Solution B	
Silver nitrate	170 g
Distilled water	410 ml

Solution C	
Sodium chloride	45.0 g
Potassium bromide	27.4 g
Rhodium trichloride trihydrate	28 µg
Sodium polyisopropyleneoxydisuccinate in 10% ethanol solution	3 ml
Ossein gelatin	11 g
Distilled water	407 ml

After keeping Solution A at 40°C, sodium chloride was added to obtain an EAg value of 160 mV.

Next, using the mixer-stirrer described in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982, Solutions B and C were added by the double jet method.

Flow rate was gradually increased over a period of 80 minutes of entire addition time while keeping a constant EAg value.

EAg value was changed from 160 mV to 120 mV using a 3 ml/l aqueous solution of sodium chloride 5 minutes after initiation of addition, and whereafter this level was maintained until completion of mixing.

To keep a constant EAg value, a 3 mol/l aqueous solution of sodium chloride was used to regulate the EAg value.

Addition time (min)	Solution B (ml/min)	Solution C (ml/min)
0	1.13	1.11
10	1.13	1.11
20	2.03	1.99
30	3.17	3.11
40	4.57	4.48
50	6.22	6.10
60	8.13	7.97
70	10.29	10.01
80	12.74	12.49

To determine the EAg value, a metallic silver electrode and a double junction type saturated Ag/AgCl reference electrode were used (the electrode configuration used was the double junction disclosed in Japanese Patent O.P.I. Publication No. 197534/1982).

To add Solutions B and C, a flow rate variable roller tube constant flow pump was used

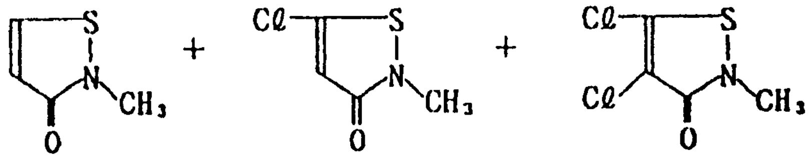
Through the course of addition, emulsion samples were taken and observed for the absence of newly formed grains in the emulsion system by electron microscopy.

During addition, a 3% aqueous solution of nitric acid was added to keep the pH of the system at constantly 3.0.

After completion of addition of Solutions B and C, the emulsion was subjected to Ostwald ripening for 10 minutes, after which it was desalted and washed with water by a conventional method. Then, 1 g of a mixture of the following compounds (Components A, B and C) and 600 ml of an aqueous solution of ossein gelatin (containing 30 g of ossein gelatin) were added and dispersed at 55 ° C for 30 minutes with stirring, followed by addition of water to make a total quantity of 750 ml.

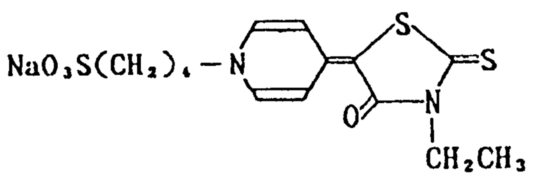
After gold-sulfur sensitization of Emulsion A, potassium bromide was added at 500 mg per mol of silver halide, followed by addition of the sensitizing dye 4-5 at 300 mg per mol of the silver halide contained in the emulsion. After keeping the emulsion standing for 10 minutes, the stabilizer 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added and Sensitizing Dye B was added at 100 mg per mol of the silver halide contained in the emulsion

Components A + B + C



〔A〕 : 〔B〕 : 〔C〕 = 46 : 50 : 4

Sensitizing dye B



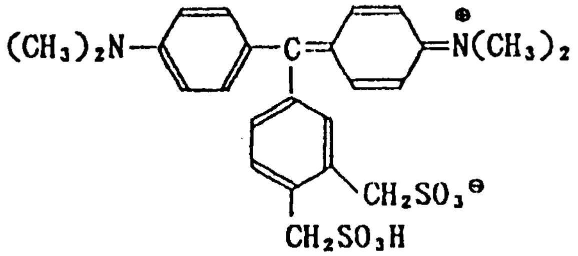
Next, the tetrazolium compound of Formula T was added at 700 mg per mol of silver halide as shown in Table 4, and 300 mg of sodium p-dodecylbenzenesulfonate, 2 g of styrene-maleic acid copolymer and 1.25

g/m^2 of styrenebutyl acrylate-acrylic acid copolymer latex (average grain size about 0.25 μm) were added. This mixture was coated on the supports 1 and 2 on the side having no electroconductive layer to obtain an Ag amount of 4.0 g/m^2 and a gelatin amount of 2.0 g/m^2. At the same time, bis-(2-ethylhexyl)sulfosuccinate, as an extender, at 10mg/m^2, and the following compounds C and D and 20 mg of glyoxal were coated to obtain a protective layer.

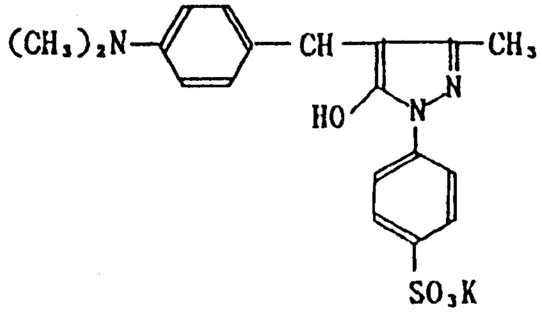
Compound C	
1-phenyl-3-pyrazolidone	80 mg/Ag 1 mol

Compound D	
5-nitroindazole	80 mg/Ag 1 mol

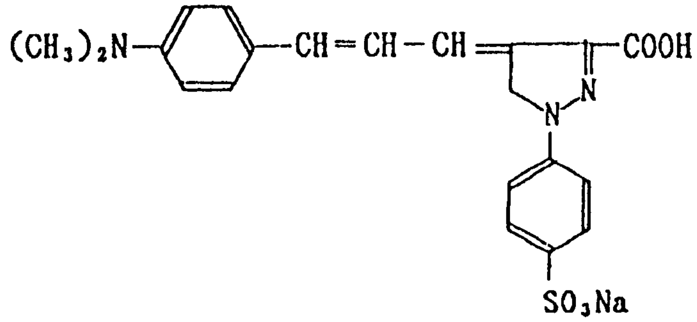
Backing coat layer composition



40mg/m²



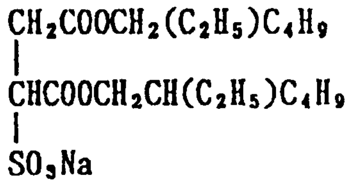
30mg/m²



30mg/m²

Gelatin	See Table 4
Surfactant: Saponin	0.1 g/m^2
Hardener: Glyoxal	0.01 g/m^2
Sodium dodecylbenzenesulfonate	0.01 g/m^2

Composition 4 (backing protective layer composition)

Gelatin	See Table 4
Matting agent: Polymethyl methacrylate with an average grain size of 3.0 to 5.0 µm	50 mg/m^2
Surfactant S-2:  $\mathrm{CH_2COOCH_2(C_2H_5)C_4H_9}$ – $\mathrm{CHCOOCH_2CH(C_2H_5)C_4H_9}$ – $\mathrm{SO_3Na}$	10 mg/m^2
Hardener: Glyoxal	25 mg/m^2

A backing coat layer and a backing protective layer were coated to be in the amount described above of the component.

Table 4 (1/2)

Sample No.	Support	Amount of gelatin (g/m^2)		Curling mm	T-Salt	Filter used	Remark
		BC layer	BC protective layer				
1	1	1.5	0.5	6	T-3	-	Comparative
2	1	2.0	1.0	2	T-3	F-1	Comparative
3	1	2.5	0.5	0	T-3	F-3	Comparative
4	1	2.5	1.0	-4	T-3	-	Comparative
5	1	2.5	1.0	-4	T-3	F-1	Inventive
6	1	3.0	0.5	-4	T-3	F-2	Inventive
7	1	3.0	1.0	-10	T-3	F-3	Inventive
8	1	2.5	0.5	0	T-8	F-1	Comparative
9	1	2.5	1.0	-4	T-8	F-1	Inventive
10	1	2.5	1.0	-4	T-8	F-4	Inventive
11	1	2.5	1.5	-10	T-8	F-3	Inventive
12	1	1.5	0.5	6	T-11	F-1	Comparative
13	1	2.0	1.0	2	T-11	F-2	Comparative
14	1	2.5	0.5	0	T-11	F-3	Comparative
15	1	2.5	1.0	-4	T-11	-	Comparative
16	1	2.5	1.0	-4	T-11	F-1	Inventive
17	1	2.5	1.0	-4	T-11	F-3	Inventive
18	1	3.0	0.5	-4	T-11	F-1	Inventive
19	1	3.0	1.0	-10	T-11	F-4	Inventive
20	1	2.5	1.5	-10	T-11	F-3	Inventive
21	2	1.5	0.5	6	T-3	F-1	Comparative
22	2	2.5	1.0	-4	T-3	F-2	Inventive

Table 4 (2/2)

Sample No.	Support	Amount of gelatin (g/m^2)		Curling mm	T-Salt	Filter used	Remark
		BC layer	BC protective layer				
23	2	3.0	1.0	-10	T-3	F-3	Inventive
24	2	1.5	0.5	6	T-8	F-2	Comparative
25	2	2.5	1.0	-4	T-8	F-3	Inventive
26	2	3.0	1.0	-10	T-8	F-1	Inventive
27	2	2.5	1.0	-4	T-11	-	Comparative
28	2	2.5	1.0	-4	T-11	F-1	Inventive
29	2	3.0	1.0	-10	T-11	F-2	Inventive
30	2	2.5	1.5	-10	T-11	F-3	Inventive
31	3	3.0	1.0	-10	T-8	F-1	Comparative
32	3	2.5	1.0	-4	T-11	F-3	Comparative
33	3	1.5	0.5	6	T-11	F-1	Comparative
34	3	2.0	1.0	2	T-11	F-1	Comparative

The surface specific resistance on the backing coat layer side was $1 \times 10^{11}\Omega$ for support 1, $4 \times 10^{11}\Omega$ for support 2 and $4 \times 10^{12}\Omega$ for support 3.

The samples obtained were evaluated as follows. Testing methods

1. Evaluation of dot to dot enlargement image quality

(1) Preparation of original

Using a scanner SG808 (II), produced by Dainippon Screen Manufacturing Co., Ltd., and a light-sensitive material RSD II for dedicated use, produced by Konica Corporation, a dotted transmission image of human figure and a step wedge with a varied dot percent were prepared.

The screen line number was 150 lines/inch.

(2) Picture taking

Exposure was carried out under a dot magnification of 120% using the fine zoom C-880F, produced by Dainippon Screen Manufacturing Co., Ltd., The sample was subjected to exposure through the original so that the portion on the sample corresponding to the 95% portion of the original step wedge had a dot percent of 5%. The filter for the present invention was placed between the original and the light source. The filters F1 through F4 used are illustrated in Figure 1.

(3) After adjustment of dot percent on the smaller dot side (high light portion) by regulating the amount of exposure as in (2) above, the gradation reproducibility (unlikeliness of dot separation) in the shadow portion in each sample was evaluated according to the descending order of Grades 5 through 1. Grades 1 and 2 cannot be put to practical use. Grades 3, 4 and 5 can be put to practical use.

2. Evaluation of sensitivity (dot to dot enlargement sensitivity)

Exposure time was obtained so that 95% portion of the dot to dot enlargement original step wedge became 5% on the sample, and was expressed as percent value relative to 100 of the sensitivity obtained in Test No.1.

3. Determination of curling

To determine the degree of curling, a 10 mm × 50 cm film sample was cut out from a 508 mm × 61 m roll after each sample was kept for 4 hours under the condition of 25 ° C and 20% RH, it was suspended so that its longer side was in the vertical direction, and the distance between the lowermost end of the sample and the vertical line was measured. When this distance is zero, the sample has no curling. A shift to the emulsion side means emulsion side curling, while a shift to the backing side means BC side curling. Here, for convenience, emulsion side curling is represented by + and BC side curling by -.

4. Evaluation of transportability

A roll of film with a size of 508 mm width × 61 m length was loaded on C880F, Fine Zoom produced by Dainippon Screen Manufacturing Co., Ltd., and transportability was evaluated for a distance of 30 cm.

Evaluation was made after 100 cycles of testing. The evaluation criteria are as follows.

A: No transportation failure.
B: Other cases.

5. Evaluation of pinholes

After moisture control at an ambient temperature of 25 ° C and an ambient relative humidity of 20% for 2 hours, each obtained sample was charged using a rubber roller and brought into cantact with the emulsion face side charged with cigarette ash. Then, after the cigarette ash was gently brushed down, exposure was conduced using the Fine Zoom C-880F, produced by Dainippon Screen Manufacturing Co., Ltd., and a 10% dot original, under such conditions that a 90% dot area was obtained.

After development, each film was visually observed using a × 10 manifying glass and evaluated in five grades. The evaluation criteria included "5" for no pinholes, "3" for the presence of pinholes but no commercial problem, and "1" for the worst level with many pinholes. The results are shown in Table 6.

6. Development

The exposed samples were processed with the following developer and fixer in an automatic developing machine.

The results are shown in Table 5. Processing conditions

Procedure	Temperature	Time
Development	28°C	30 seconds
Fixation	28°C	About 20 seconds
Washing	Normal temperature	About 20 seconds
Drying	50°C	15 seconds

Developer

Composition A	
Pure water (ion exchange water)	150 ml
Disodium ethylenediaminetetraacetate	2 g
Diethylene glycol	50 g
Potassium sulfite (55% W/V aqueous solution)	100 ml
Potassium carbonate	50 g
Hydroquinone	15 g
5-methylbenzotriazole	200 mg
1-phenyl-5-mercaptotetrazole	30 mg
Potassium bromide	4.5 g
Potassium hydroxide was added to obtain a pH of 10.4.	

Composition B	
Pure water (ion exchange water)	3 ml
Diethylene glycol	50 g
Disodium ethylenediaminetetraacetate	25 mg
Acetic acid (90% aqueous solution)	0.3 ml
5-nitroindazole	110 mg
1-phenyl-3-pyrazolidone	700 mg
Compositions A and B were dissolved in 500 ml of water in this order and was diluted to 1 liter for use as a developer.	

Fixer

Composition A	
Ammonium thiosulfate (72.5% W/V aqueous solution)	240 ml
Sodium sulfite	17 g
Sodium acetate trihydrate	6.5 g
Boric acid	6 g
Sodium citrate dihydrate	2 g
Acetic acid (90% W/W aqueous solution)	13.6 ml

Composition B	
Pure water (ion exchange water)	17 ml
Sulfuric acid (50% W/W aqueous solution)	4.7 g
Aluminum sulfate (8.1% Al_2O_3 W/W aqueous solution)	26.5 g
Compositions A and B were dissolved in 500 ml of water in this order and were diluted to 1 liter for use as a fixer. This fixer had a pH of about 4.3.	

Table 5

Sample No.	Dot to dot enlargement		Transportability	Pinhole
	Sensitivity	Reproducibility		
1	100	2	B	4
2	95	4	B	4
3	85	5	B	5
4	100	2	A	5
5	95	4	A	5
6	93	5	A	5
7	90	5	A	5
8	95	4	B	5
9	93	4	A	5
10	85	5	A	5
11	90	5	A	5
12	115	4	B	4
13	110	5	B	4
14	105	5	B	4
15	118	2	A	5
16	115	4	A	5
17	110	5	A	5
18	115	4	A	5
19	100	5	A	5
20	105	5	A	5
21	95	4	B	4
22	90	5	A	4
23	88	5	A	4
24	92	5	B	3
25	90	5	A	4
26	95	4	A	4
27	120	2	A	4
28	115	4	A	4
29	110	5	A	4
30	107	5	A	4
31	95	5	A	1
32	110	5	A	2
33	115	4	B	1
34	115	5	A	1

From the results shown in Table 5, it is evident that the samples according to the present invention have good transportability, good antistatic performance and excellent dot to dot enlargement property.

Example 2

Samples were prepared and evaluated in the same manner as in Example 1 except that the following emulsions were used instead.

(Formula of developing solution 2)

Sodium ethylenediaminetetraacetate	1 g
Sodium sulfate	60 g
Boric acid	40 g
Hydorquinone	35 g
Sodium hydroxide	8 g
Sodium bromide	3 g
5-methylbenzotriazole	0.2 g
2-mercaptobenzothiazole	0.1 g
2-mercaptobenzothiazole-5-sulfonic acid	0.2 g
1-phenyl-4,4-dimethyl-3-pyrazolidone	0.2 g
Add water to make 1 l. pH was adjusted to 10.8 with sodium hydroxide.	

(Formula of fixer 2)

Composition A	
Ammonium thiosulfate	240 ml
Sodium sulfate	17 g
Sodium acetate trihydrate	6.5 g
Boric acid	6.0 g
Sodium citrate dihydrate	2.0 g

Composition B	
Pure water (ion-exchange water)	17 ml
Sulfuric acid (an aqueous solution with 50%w/v)	4.7 g
Aluminum sulfate (an aqueous solution having 8.1 %w/v in terms of Al_2O_3)	26.5 g

For preparing the fixing solution, the above-mentioned components A and B were dissolved into water of 500 ml to make 1 l in all to be used. The pH of this fixer was adjusted to 4.8 with acetic acid.

Emulsions

An aqueous solution of silver nitrate and an aqueous solution of potassium bromide and potassium iodide were mixed by the double jet method while keeping a pAg of 7.9 under the presence of ammonia to yield a monodispersed silver iodobromide emulsion B comprising cubic grains with an average grain size of 0.2 µm (silver iodide content of 1 mol%, silver bromide content of 99 mol%).

Separately, an aqueous solution of silver nitrate and an aqueous solution of potassium bromide were mixed by the double jet method while keeping a pAg of 7.9 under the presence of ammonia to yield a monodispersed silver iodobromide emulsion C comprising cubic grains with an average grain size of 0.35 µm.

Emulsion B was subjected to sulfur sensitization with sodium thiosulfate.

Emulsions B and C were each spectrally sensitized by the addition of the sensitizing dye 1-4 of 6×10^{-4} mol and 4.5×10^{-4} mol, respectively, per mol of silver along with 0.4 mol% of potassium iodide per mol of silver.

Also to the emulsions was the stabilizer 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene added.

Emulsions B and C thus treated were mixed to have a silver halide ratio of 6 to 4 by weight. To the resulting emulsion was added 1200 g of the hydrazine compound [H] shown in Table 6 per mol of silver.

Also added were the surfactant, alkylbenzenesulfonate and the hardener, vinylsulfone hardener. After adjusting to a pH of 5.8, each emulsion was coated on the support so that the amount of silver coated was 3.6 g/m^2 and the amount of gelatin coated was 2 g/m^2. Also, a protective layer was formed thereon so that the amount of gelatin coated was 0.75 g/m^2.

The samples thus obtained were evaluated in the same manner as in Example 1. The results are shown in Table 7.

Table 6 (1/2)

Sample No.	Support	Amount of gelatin (g/m2)		Curling mm	Hydrazine comopound	Filter used	Remark
		BC layer	BC protective layer				
1	1	1.5	0.5	6	H-3	-	Comparative
2	1	2.0	1.0	2	H-3	F-1	Comparative
3	1	2.5	0.5	0	H-3	F-3	Comparative
4	1	2.5	1.0	-4	H-3	-	Comparative
5	1	2.5	1.0	-4	H-3	F-1	Inventive
6	1	3.0	0.5	-4	H-3	F-2	Inventive
7	1	3.0	1.0	-10	H-3	F-3	Inventive
8	1	2.5	0.5	0	H-6	F-1	Comparative
9	1	2.5	1.0	-4	H-6	F-1	Inventive
10	1	2.5	1.0	-4	H-6	F-4	Inventive
11	1	2.5	1.5	-10	H-6	F-3	Inventive
12	1	1.5	0.5	6	H-1	F-1	Comparative
13	1	2.0	1.0	2	H-1	F-2	Comparative
14	1	2.5	0.5	0	H-1	F-3	Comparative
15	1	2.5	1.0	-4	H-1	-	Comparative
16	1	2.5	1.0	-4	H-1	F-1	Inventive
17	1	2.5	1.0	-4	H-1	F-3	Inventive
18	1	3.0	0.5	-4	H-1	F-1	Inventive

Table 6 (2/2)

Sample No.	Support	Amount of gelatin (g/m2)		Curling mm	Hydrazine comopound	Filter used	Remark
		BC layer	BC protective layer				
19	1	3.0	1.0	-10	H-1	F-4	Inventive
20	1	2.5	1.5	-10	H-1	F-3	Inventive
21	2	1.5	0.5	6	H-3	F-1	Comparative
22	2	2.5	1.0	-4	H-3	F-2	Inventive
23	2	3.0	1.0	-10	H-3	F-3	Inventive
24	2	1.5	0.5	6	H-6	F-2	Comparative
25	2	2.5	1.0	-4	H-6	F-3	Inventive
26	2	3.0	1.0	-10	H-6	F-1	Inventive
27	2	2.5	1.0	-4	H-1	-	Comparative
28	2	2.5	1.0	-4	H-1	F-1	Inventive
29	2	3.0	1.0	-10	H-1	F-2	Inventive
30	2	2.5	1.5	-10	H-1	F-3	Inventive
31	3	3.0	1.0	-10	H-6	F-1	Comparative
32	3	2.5	1.0	-4	H-1	F-3	Comparative
33	3	1.5	0.5	6	H-1	F-1	Comparative
34	3	2.0	1.0	2	H-1	F-1	Comparative

Table 7

Sample No.	Dot to dot enlargement		Transportability	Pinhole
	Sensitivity	Reproducibility		
1	100	2	B	4
2	95	3	B	3
3	85	4	B	4
4	100	2	A	4
5	93	3	A	4
6	90	4	A	5
7	87	5	A	5
8	92	3	B	4
9	90	4	A	4
10	85	4	A	5
11	87	4	A	4
12	110	3	B	3
13	105	4	B	3
14	115	5	B	3
15	110	1	A	4
16	105	3	A	4
17	110	4	A	4
18	110	4	A	5
19	100	5	A	5
20	100	4	A	4
21	92	4	B	3
22	88	4	A	4
23	84	4	A	4
24	90	5	B	3
25	88	5	A	3
26	93	4	A	3
27	115	2	A	3
28	110	4	A	4
29	105	4	A	4
30	105	4	A	3
31	92	4	A	1
32	105	4	A	1
33	110	4	B	1
34	110	4	A	1

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graph showing the absorption spectra of the filters for the present invention, in which the symbols F1, F2, F3 and F4 each denote a filter.

Claims

1. A method of forming an image, comprising the step of, providing a silver halide photographic light-sensitive material on a drum in a camera,
imagewise exposing the material to light which has the wavelength of 460 to 600 nm and has not substantially the wavelength of 360 nm or less, and
developing the exposed material,
said material comprising a support and, provided thereon, a silver halide emulsion layer containing a sensitizing dye having an absorption maximum within the wavelength range of 450 to 580 nm and, provided on the surface of the support opposite to the emulsion layer, a backing coat layer comprising a hydrophilic colloid layer and having a specific resistance of from 1×10^{9} to $1 \times 10^{12}\Omega$ at 25 °C and 20% RH, said material containing a hydrazine derivative or tetrazolium derivative and oriented to curve to the backing coat layer side.

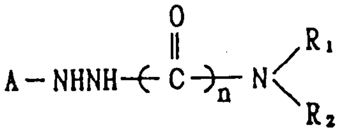
2. The method of claim 1, wherein said exposing is carried out using a filter which does not transmit light of the wavelength of not more than 360 nm.

3. The method of claim 2, wherein transmittance of said filter is not less than 50 % at the wavelength of 460 to 600 nm and is not more than 30 % at the wavelength of not more than 360 nm.

4. The method of claim 2, wherein transmittance of said filter is not less than 80 % at the wavelength of 460 to 600 nm and is not more than 10 % at the wavelength of not more than 360 nm.

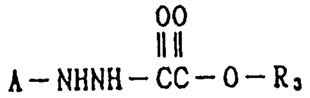
5. The method of claim 1, wherein said hydrazine derivative includes a compound represented by the following formula A or B:

formula A



$$\mathrm{A-NHNH}\!\left(\overset{O}{\overset{\|}{C}}\right)_{n}\!\mathrm{N}\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

formula B

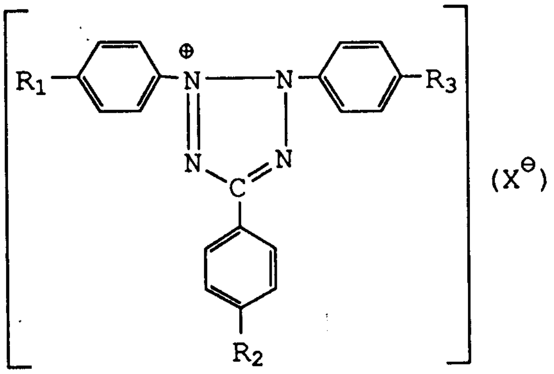


$$\mathrm{A-NHNH-}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\mathrm{-O-R_3}$$

wherein A represents an aryl group or a heterocyclic ring containing a sulfur atom or an oxygen atom; n is an integer of 1 or 2, provided that when n is 1, R_1 and R_2 each represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic ring, a hydroxy group, an alkoxy group, an alkenyloxy group, an alkynyloxy group, an aryloxy group, a heterocyclicoxy group, provided R_1 and R_2 may combine with each other together with a nitrogen atom to form a ring, and when n is 2, R_1 and R_2 each represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic ring, a hydroxy group, an alkoxy group, an alkenyloxy group, an alkynyloxy group, an aryloxy group, a heterocyclicoxy group, provided at least one of R_1 and R_2 represents an alkenyl group, an alkynyl group, a saturated heterocyclic ring, a hydroxy group, an alkoxy group, an alkenyloxy group, an alkynyloxy group, an aryloxy group,or a heterocyclicoxy group; and R_3 represents an alkinyl group or a saturated heterocyclic ring.

6. The method of claim 1, wherein said tetrazolium derivative includes a compound represented by the following formula T:

formula T



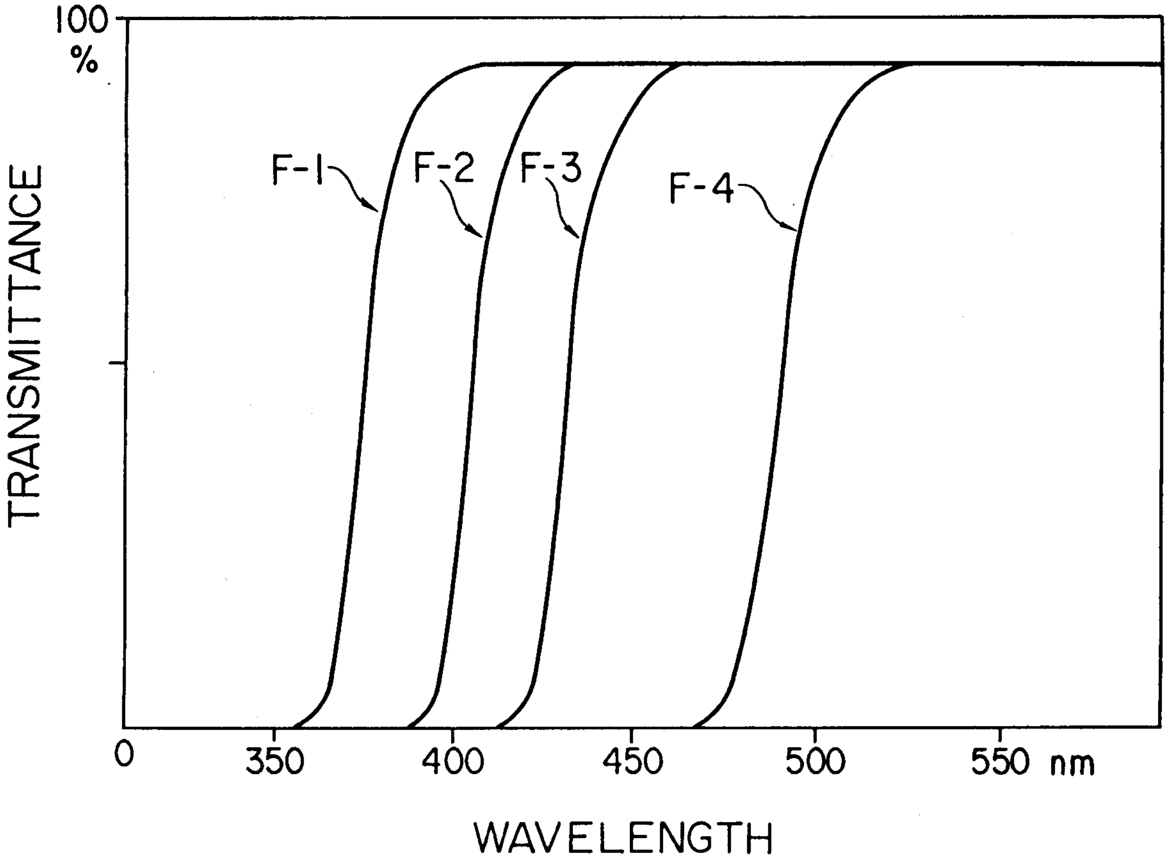
wherein R_1, R_2 and R_3 each represent a hydrogen atom or a substituent giving a positive or negative σ value, and X is an anion.

7. The method of claim 1, wherein the hydrophilic colloid layer contains gelatin and a water soluble electroconductive polymer or an ionic inorganic compound.

8. The method of claim 1, wherein an electroconductive layer is further provided between the support and the hydrophilic colloid layer.

9. The method of claim 8, wherein said electroconductive layer comprises a metal oxide or a reaction product of a water-soluble electroconductive polymer, a hydrophobic latex and an epoxy hardener.

FIG. 1


100 %
TRANSMITTANCE
F-1
F-2
F-3
F-4
0
350
400
450
500
550 nm
WAVELENGTH