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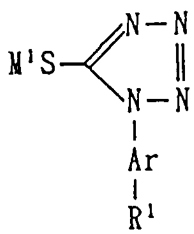
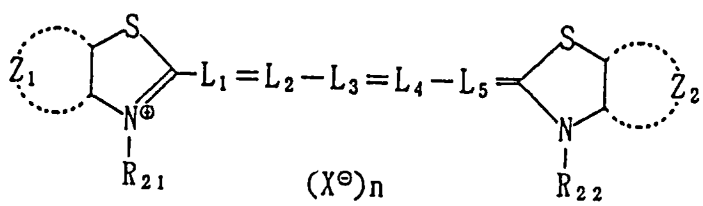
(54) **Silver halide photographic material.**

(57) The improved silver halide photographic material contains both a compound represented by the following general formula [I] and a compound represented by the following general formula [II] and it features high sensitivity experiencing less fog :



[I]



[II]

Jouve, 18, rue Saint-Denis, 75001 PARIS

BACKGROUND OF THE INVENTION

This invention relates to a silver halide photographic material, more particularly, to a silver halide photographic material that experiences less fog and which has high sensitivity.

Using specified sensitizing dyes to expand the wavelength range of intrinsic sensitivity of a silver halide emulsion, thereby making it sensitive to light in the visible range of spectrum where it has no native sensitivity is a well known technique. Sensitizing dyes used in a red-sensitive emulsion to achieve this purpose are required to satisfy various requirements such as providing adequate sensitivity and causing no stain by remaining in the processed photographic material. Certain kinds of pentamethinecyanine dyes have been known as sensitizers whose characteristics are believed to be good enough to meet those requirements. In fact, however, they are not completely satisfactory in terms of sensitivity and stain resistance and the current practice employed is to use the sensitizers in small amounts at the sacrifice of sensitivity.

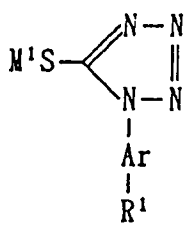
Using restrainers to reduce the fog occurring in silver halides is a well known technique. Among various restrainers used today, mercaptotetrazole derivatives are particularly known to be effective since they are capable of substantial reduction in fog. Two important requirements of effective restrainers are that they should not cause great desensitization other than the decrease in fog and that they should not adversely affect other layers. Mercaptotetrazole derivatives are effective in reducing the fog but, at the same time, they often reduce the sensitivity.

If conventional pentamethine sensitizers are used in combination with conventional restrainers, fog is reduced but, on the other hand, desensitization occurs, making it impossible to provide adequate sensitivity. Sensitivity drop is particularly noticeable when using emulsions that are substantially composed of silver chloride and which are most commonly used in modern photography because of their adaptability for high-speed processing. Furthermore, the decrease in fog has turned out not to be as great as expected, thus making it necessary to accomplish further improvements in this respect.

SUMMARY OF THE INVENTION

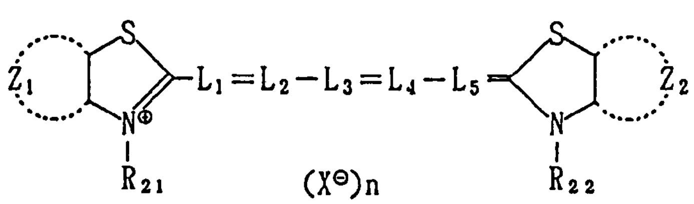
An object, therefore, of the present invention is to provide a silver halide photographic material that experiences less fog and which has high sensitivity.

This object of the present invention can be accomplished by a silver halide photographic material containing both a compound represented by the following general formula [I] and a compound represented by the following general formula [II]:



[I]

where Ar is an aromatic group; M^1 is a hydrogen atom, an alkali metal atom, an alkaline earth metal atom or an ammonium group; and R^1 is OR^2, $NR^3SO_2R^4$ or $COOM^2$ (where R^2 is a hydrocarbon group having 2 or more carbon atoms; R^3 is a hydrogen atom or a hydrocarbon group; R^4 is a hydrocarbon group; and M^2 is the same as M^1);



[II]

where Z_1 and Z_2 each represent the atomic group necessary to form an aromatic ring; R_{21} and R_{22} are each an alkyl group or an aryl group; L_1, L_2, L_3, L_4 and L_5 are each a methine group; $X^{\ominus}$ is an anion; n represents the integer necessary for neutralization of the charges in the molecule, provided that the total number of carbons in R_{21} and R_{22} and in the substituents on Z_1 and Z_2 is at least 6.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail.

First, the compound represented by the general formula [I] is described below. In the general formula [I], Ar represents an aromatic group such as phenyl, naphthyl or pyridyl. These aromatic groups may have substituents. It is particularly preferred for Ar to be a phenyl group since the advantage of the present invention is remarkable in that case.

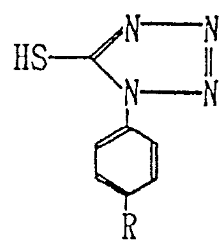
In the general formula [I], R^1 denotes OR^2, $NR^3SO_2R^4$ or $COOM^2$, where R^2 represents a hydrocarbon group having 2 or more carbon atoms, as exemplified by an alkyl group such as ethyl, hexyl or dodecyl, or an aryl group such as phenyl, p-t-butylphenyl, m-methoxyphenyl or o-methoxyphenyl. It is particularly preferred for R^2 to be an alkyl group since the advantage of the present invention is remarkable in that case. Preferably, R^1 is $NR^3SO_2R^4$ or OR^2; more preferably, R^1 is $NR^3SO_2R^4$.

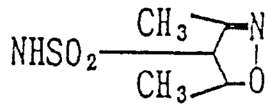
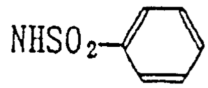
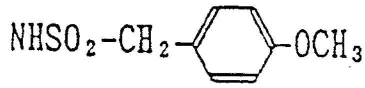
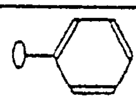
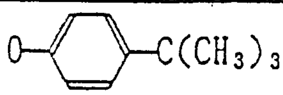
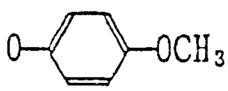
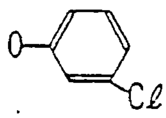
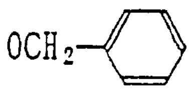
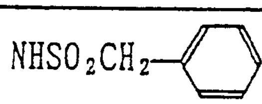
With further reference to the general formula [I], R^3 represents a hydrogen atom or a hydrocarbon group; examples of the hydrocarbon group include a methyl group, as well as the groups identical to those represented by R^2. It is particularly preferred for R^3 to be a hydrogen atom since the advantage of the present invention is remarkable in that case.

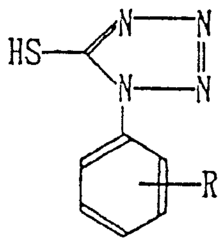
With further reference to the general formula [I], R^4 represents a hydrocarbon group and may be exemplified by hydrocarbon groups identical to those represented by R^3. It is particularly preferred for R^4 to be an alkyl group since the advantage of the present invention is remarkable in that case.

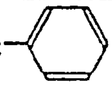
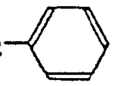
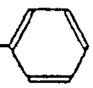
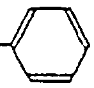
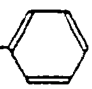
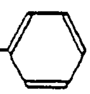
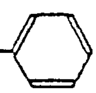
In connection with the general formula [I], M^1 and M^2 each represent a hydrogen atom, an alkali metal atom, an alkaline earth metal or an ammonium group, and exemplary metal atoms include sodium, lithium, potassium, calcium, etc. In case of a metal atom having divalency or higher valency, an anion is bonded to neutralize the electric charges. It is particularly preferred for M^1 to be a hydrogen atom since the advantage of the present invention is remarkable in that case.

Compounds represented by the general formula [I] are shown specifically below. Needless to say, the present invention is in no way limited to the examples given below.

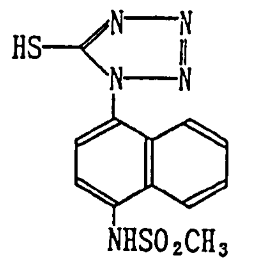


No.	R	No.	R
I-1	OCH_2CH_3	I-17	$NHSO_2CH_2CF_3$
I-2	$O(CH_2)_3CH_3$	I-18	$NHSO_2(CH_2)_3Cl$
I-3	$O(CH_2)_5CH_3$	I-19	
I-4	$O(CH_2)_7CH_3$	I-20	
I-5	$O(CH_2)_{11}CH_3$	I-21	
I-6		I-22	$NHSO_2CH_2CH=CH_2$
I-7		I-23	$NHSO_2CH_2C\equiv CH$
I-8		I-24	$NHSO_2N(CH_3)_2$
I-9		I-25	$NHSO_2(CH_2)_7CH_3$
I-10		I-26	COOH
I-11	$OCH_2CH=CH_2$		
I-12	$OCH_2C\equiv CH$		
I-13	$NHSO_2CH_3$		
I-14	$NHSO_2(CH_2)_3CH_3$		
I-15	$NHSO_2CH(CH_3)_2$		
I-16			

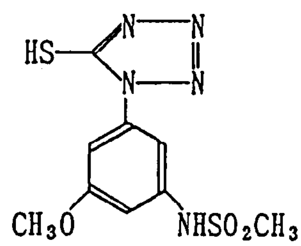


No.	R	No.	R
I -27	o-OCH_2CH_3	I -43	m-$NHSO_2CH_2$- 
I -28	o-$O(CH_2)_3CH_3$	I -44	m-$NHSO_2$- 
I -29	o-O- 	I -45	m-$NHSO_2N(CH_3)_2$
I -30	o-OCH_2- 	I -46	m-$NHSO_2(CH_2)_7CH_3$
I -31	o-$OCH_2CH{=}CH_2$	I -47	m-COOH
I -32	m-OCH_2CH_3	I -48	m-COONa
I -33	m-$O(CH_2)_5CH_3$		
I -34	m-O- 		
I -35	m-OCH_2- 		
I -36	o-$NHSO_2CH_3$		
I -37	o-$NHSO_2(CH_2)_2CH_3$		
I -38	o-$NHSO_2CH_2$- 		
I -39	o-$NHSO_2CH_2CH{=}CH_2$		
I -40	m-$NHSO_2CH_3$		
I -41	m-$NHSO_2(CH_2)_3CH_3$		
I -42	m-$NHSO_2CH(CH_3)_2$		

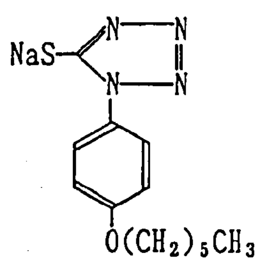
I-49



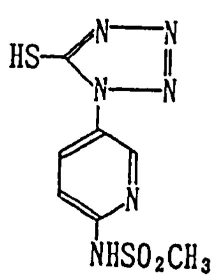
I-50



I-51



I-52



The compounds listed above can be synthesized with reference made to J. Chem. Soc., 49, 1748 (1927), J. Org. Chem., 39, 2469 (1965), Japanese Patent Laid-Open Publication (kokai) SHO No. 50-89034, Ann. Chim., 44 - 3, 1954, Japanese Patent Publication (kokoku) SHO No. 40-28496, Chem. Ber., 20, 231 (1887), and USP 3,259,976.

In the next place, the compound represented by the general formula [II] is described below.

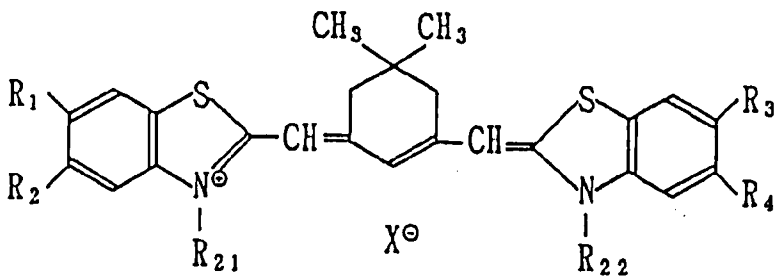
In the general formula [II], Z_1 and Z_2 each represent the atomic group necessary to form an aromatic ring such as a benzene ring or a naphthalene ring. These aromatic rings may have substituents. The aromatic ring formed by each of Z^1 and Z^2 is preferably a benzene ring.

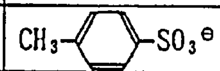
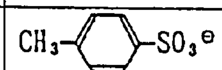
In the general formula [II], R_{21} and R_{22} each represent an alkyl group such as methyl, ethyl, propyl, pentyl, methoxyethyl, ethoxyethyl, 3-chloropropyl, 3-sulfopropyl, 4-sulfobutyl, carboxymethyl or benzyl. From the viewpoint of sensitivity, each of R_{21} and R_{22} is preferably an alkyl or alkoxyalkyl group.

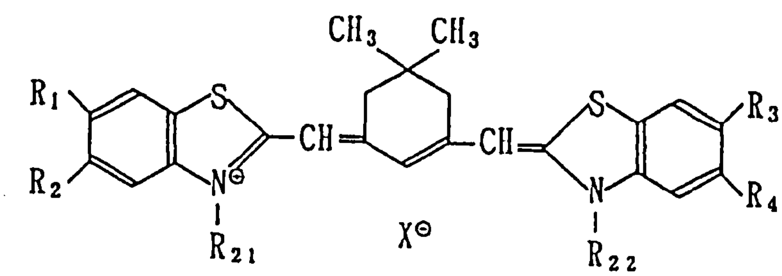
In the general formula [II], L_1, L_2, L_3, L_4 and L_5 each represent a methine group and may be exemplified by -CH=, -C(CH_3)= or -C(Cl)=. If desired, L_1, L_2, L_3, L_4, L_5, R_{21} and R_{22} may, in possible combinations, bind with themselves to form rings. It is preferred for L_1, L_3 and L_5 to be -CH=, and L_2 and L_4, taken together, may preferably form a dimethylcyclohexene ring.

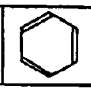
In the general formula [II], $X^{\ominus}$ represents an anion, and X represents a bromine atom, a chlorine atom, an iodine atom, or p-toluenesulfonic acid; n represents the integer necessary for neutralization of the charges in the molecule, provided that the total number of carbons in R_{21} and R_{22} and in the substituents on Z_1 and Z_2 is at least 6.

Compounds represented by the general formula [II] are shown specifically below. Needless to say, the present invention is in no way limited to the examples given below.

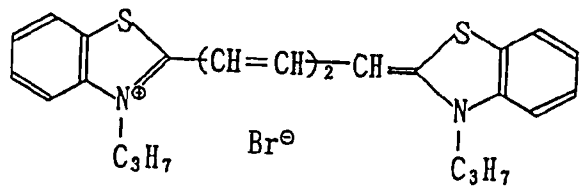


No.	R_1	R_2	R_3	R_4	R_{21}	R_{22}	$X^{\ominus}$
2−1	H	H	H	H	C_3H_7	C_3H_7	$Br^{\ominus}$
2−2	H	OCH_3	H	H	〃	〃	〃
2−3	CH_3	H	H	H	〃	〃	〃
2−4	CH_3	H	CH_3	H	C_2H_5	C_2H_5	〃
2−5	H	Cℓ	H	Cℓ	C_3H_7	C_3H_7	
2−6	H	H	H	H	$C_2H_4OCH_3$	〃	$Br^{\ominus}$
2−7	H	H	H	H	$C_2H_4OC_2H_5$	C_3H_7	〃
2−8	CH_3	H	H	H	〃	C_2H_5	〃
2−9	CH_3	H	CH_3	H	〃	〃	〃
2−10	〃	〃	〃	〃	$C_2H_4OCH_3$	〃	〃
2−11	〃	〃	〃	〃	C_5H_{11}	C_2H_5	〃
2−12	CH_3	CH_3	H	H	C_2H_5	〃	
2−13	H	H	H	H	$(CH_2)_3SO_3^{\ominus}$	C_3H_7	—
2−14	CH_3	H	CH_3	H	〃	C_2H_5	—
2−15	H	H	H	H	〃	$(CH_2)_3SO_3Na$	—
2−16	CH_3	H	CH_3	H	〃	〃	—



No.	R_1	R_2	R_3	R_4	R_{21}	R_{22}	$X^{\ominus}$
2−17	Cℓ	H	H	H	C_3H_7	C_3H_7	$Br^{\ominus}$
2−18	H	Br	H	H	〃	〃	〃
2−19	$-OCH_2CH_2O-$		H	H	C_2H_5	C_2H_5	〃
2−20	H		H	H	〃	〃	〃

2 - 21



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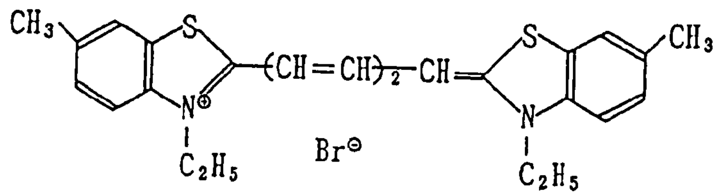

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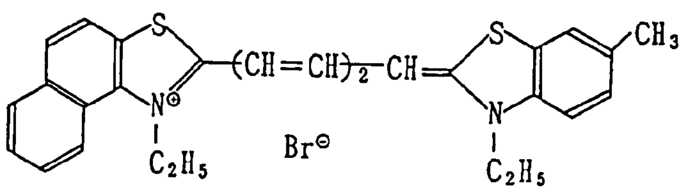
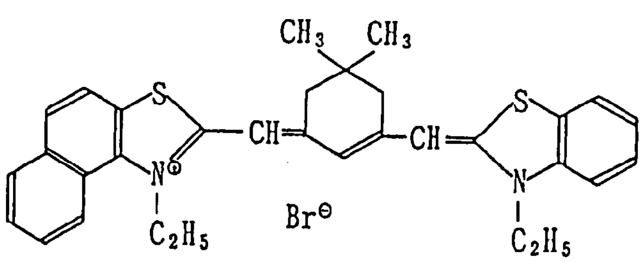


2 - 24



In order to have the restrainer of the present invention incorporated in silver halide emulsion layers, one may first dissolve the restrainer either in water or in an organic solvent (e.g. methanol or ethanol) that is freely miscible with water before adding it to silver halide emulsion layers. The restrainers of the present invention may be used either alone or in combination with themselves or with other fog restrainers outside the scope of the present invention.

The restrainer of the present invention may be added at any time either before or during the formation of silver halide grains, or sometime between the end of formation of silver halide grains and the start of chemical ripening, or during or after the end of chemical ripening, or between the end of chemical ripening and the start of emulsion coating. Preferably, the restrainer is added during or after the end of chemical ripening or sometime between the end of chemical ripening and the start of emulsion coating. The entire portion of the restrainer may be added at a time or it may be added in several portions.

The restrainer of the present invention may be added at the site of preparing silver halide emulsions or it may be added directly to the coating solutions of silver halide emulsions. If desired, the restrainer may be added to the coating solution for an adjacent non-light-sensitive hydrophilic colloidal layer, so that the restrainer is eventually incorporated into silver halide emulsion layers of interest through diffusion that occurs when two or more photographic layers are coated in superposition.

While there is no particular limitation on the amount in which the restrainer is to be added, it is typically added in amounts ranging from 1×10^{-6} to 1×10^{-1} mole, preferably from 1×10^{-5} to 1×10^{-2} mole, per mole of silver halide.

The silver halide grains to be used in the present invention may be coarse or fine and the distribution of their size may be narrow or broad.

The silver halide grains may be normal crystals or twinned crystals, with the ratio between [100] and [111] faces being adjusted to any value. The silver halide grains may have a uniform crystalline structure throughout from the interior to the surface; alternatively, the grains may have a lamellarstructure in which the crystalline structure differs between the interior and the surface. The silver halides of interest may be of a type that forms latent image predominantly on the surface or they may be of a type that forms latent image within the grains.

The silver halide grains can be prepared by any known methods that are commonly employed in the art.

The silver halide emulsions to be used in the present invention may be of any species that are selected from among a silver chloride emulsion, a silver chlorobromide emulsion, a silver chloroiodobromide emulsion, etc. While any species of silver halide emulsions may be used without particular limitation, the preferred silver halide emulsion is preferably one that contains silver halide grains of high chloride content.

The term "silver halide grains of high chloride content" means those silver halide grains which have a chloride content of at least 90 mol%. With silver halide grains of high chloride content, the AgBr content is preferably up to 10 mol% and the AgI content is preferably up to 0.5 mol%. A more preferred silver halide composition is silver chlorobromide having a AgBr content of 0.1 - 2 mol%.

The silver halide grains of high chloride content need not always be used independently but they may be used in admixture with other silver halide grains of a different composition, for example, silver halide grains having a AgCl content of 10 mol% or less.

In a silver halide emulsion layer containing silver halide grains of high chloride content, said silver halide grains of high chloride content preferably account for at least 60 wt%, more preferably at least 80 wt%, of all silver halide grains present in the emulsion layer under consideration.

The silver halide grains of high chloride content may have a uniform composition throughout from the interior to the surface of the grains; alternatively, the grains may have different compositions between the interior and the surface. If the interior of the grains has a different composition than their surface, the compositional change may be continuous or discontinuous.

The particle size of silver halide grains of high chloride content is not limited in any particular way but, considering other aspects of photographic performance such as adaptability for rapid access (high-speed processing) and sensitivity, the particle size is preferably in the range of 0.2 - 1.6 μm, more preferably in the range of 0.25 - 1.2 μm. Particle size measurements can be accomplished by various methods commonly used in the art. Typical methods are described in R.P. Loveland, "Methods of Particle Size Analysis" in ASTM Symposium on Light Microscopy, pp. 94 - 122, 1955, and in C.E. Kenneth Mees and T.H. James, "The Theory of the Photographic Process", Third Edition, Chapter 2, Macmillant Publishing Co., Inc., 1966.

Particle size measurements can be achieved using either the projected area of particles or the diameter of an equivalent circle. If the particles of interest have a uniform shape, the particle size distribution can be expressed fairly correctly in terms of either the diameter of an equivalent circle or the projected area.

The distribution of the particle size of silver halide grains with high chloride content may be polydispersed or monodispersed. Preferably, the silver halide grains under consideration are monodispersed, with the coefficient of variation (C.V.) in the particle size distribution of silver halide grains being no more than 0.22, more preferably 0.15 or less.

The silver halide grains to be used in emulsions in accordance with the present invention may be prepared by any suitable method such as an acid process, a neutral process or an ammoniacal process. The grains of interest may be allowed to grow at a time; alternatively, seed grains may first be prepared and then allowed to grow. The method of preparing seed grains may be the same as or different from the method of allowing the prepared seed grains to grow.

Soluble silver salts may be reacted with soluble halide salts by any of the methods such as normal precipitation, reverse precipitation, double-Jet precipitation and combinations of two or more of these processes. The reaction product yielded by double-jet precipitation is preferred. A modification of the double-jet method is the pAg-controlled double jet method described in Japanese Patent Laid-Open Publication (kokoku) SHO No. 54-48521.

If necessary, solvents for silver halide such as thioether may be used. Furthermore, nitrogen-containing heterocyclic compounds or compounds such as sensitizing dyes may be added either during or after the end of the formation of silver halide grains.

The silver halide grains to be used in the present invention may have any geometry. A preferred example is cubes having {100} faces as crystal surfaces. Also useful are those grains which have many sides, as exemplified by octahedral, tetradecahedral and dodecahedral grains. If desired, grains having twinned faces may additionally be used.

The silver halide grains to be used in the present invention may have a single geometry; alternatively, grains of various geometries may be mixed together.

In the process of grain formation and/or growth, metal ions are added to the silver halide grains under consideration by using cadmium salts, zinc salts, lead salts, thallium salts, iridium salts or complex salts thereof, or rhodium salts or complex salts thereof, or iron salts or complex salts thereof, so that the thus added metal ions can be incorporated in the interior and/or surface of the grains. Alternatively, by holding the silver halide grains in a suitable reducing atmosphere, nuclei for reduction sensitization can be imparted to the interior and/or surface of the grains.

The emulsion containing the silver halide grains to be used in the present invention (which emulsion is hereunder referred to as the "emulsion of the present invention") may be freed of unwanted soluble salts after the end of the growth of the silver halide grains or it may have those soluble salts contained as such. If the salts are to be removed, the methods described in Research Disclosure No. 17643 may be employed.

The silver halide grains to be contained in the emulsion of the present invention are preferably of such a type that a latent image is formed predominantly on the surface but they may be of another type that forms a latent image predominantly within the grains.

Chalcogen sensitizers may be used in the present invention. The term "chalcogen sensitizers" is the generic name for sulfur sensitizers, selenium sensitizers and tellurium sensitizers, and among these, sulfur and selenium sensitizers are preferred. Exemplary sulfur sensitizers include thiosulfates, allyl thiocarbazide, thiourea, allyl isothiocyanate, cystine, p-toluenethiosulfonate and rhodanine. Other sulfur sensitizers that can be used are described in USP 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, 3,656,955, West German Patent Laid-Open Publication (OLS) 1,422,869, and Japanese Patent Laid-Open Publication (kokai) SHO Nos. 56-24937, 55-45016, etc. The amount in which the sulfur sensitizers are added can vary over a substantial range depending upon various conditions such as pH, temperature and the size of silver halide grains. To give a guide figure, the sulfur sensitizers are preferably added in amounts of from about 10^{-7} to about 10^{-1} mole per mole of silver halide.

The emulsion of the present invention may be sensitized by reduction sensitization using a reductive material or noble metal sensitization in which a noble metal compound is also used.

The silver halide emulsion is to be used in the present invention may be optically sensitized to light in a desired wavelength range using dyes that are known as sensitizers in the photographic industry.

Gelatin is advantageously used as a binder (or protective colloid) in the silver halide photographic material of the present invention. Other binders that can be used are hydrophilic colloids such as gelatin derivatives, gelatin having other polymers grafted to make graft polymers, proteins, saccharide derivatives, cellulosic derivatives, and synthetic hydrophilic homo- and copolymers.

The silver halide photographic material of the present invention having the composition described above may typically be used as a color negative or positive film or as a color paper. The advantage of the present invention is particularly marked if the silver halide photographic material is used as a color paper for direct viewing.

When the silver halide photographic material of the present invention is to be used as a full-color photographic material, yellow couplers, magenta couplers and cyan couplers are used. There are no particular limitations on the yellow, magenta and cyan couplers that can be used and any known types of couplers may be used.

Exemplary yellow couplers that can be used include benzoyl acetanilide based couplers and pivaloyl acetanilide based couplers. Exemplary magenta couplers that can be used include 5-pyrazolone based couplers, pyrazolobenzimidazole based couplers, pyrazoloazole based couplers and open-chain acyl acetonitrile base couplers. Among these, 5-pyrazolone based magenta couplers and pyrazolotriazole based magenta couplers are particularly preferred. Exemplary cyan couplers that can be used include naphtholic couplers, phenolic couplers and imidazolic couplers.

The silver halide photographic material of the present invention may further contain, as appropriate, various additives including a hardener, an anti-irradiation agent, an anti-stain agent, an image stabilizer, a plasticizer, a latex, a surfactant, a matting agent, a lubricant and an antistat.

To form image, the silver halide photographic material of the present invention may be subjected to color development and subsequent processing in the manner known in the art. The color developing solution has usually a pH of at least 7, most commonly in the range of from about 10 to 13. The temperature for color development is usually 15°C or more, commonly in the range of 20 - 50°C. For high-speed development, the temperature is preferably at least 30°C. The conventional processing lasts for 3 - 4 min but to achieve rapid access, which is the primary objective of the present invention, color development is preferably performed for a time period of 10 - 60 sec, more preferably in the range of 20 - 50 sec.

The silver halide photographic material of the present invention can be developed rapidly without a drop in maximum density on the characteristic curve even if the color developing solution contains less than 2 ml per liter of benzyl alcohol which is commonly used in rapid development.

After color development, the photographic material is subjected to bleaching and fixing steps. Bleaching may be performed simultaneously with fixing. After fixing, the photographic material is usually washed with water. In place of washing with water, stabilization may be performed. If desired, both washing with water and stabilization may be performed.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1

A support was prepared by laminating one side of a paper base with polyethylene and the other side with TiO_2 containing polyethylene. Layers having the compositions shown in Table 1 below were coated on the side of the support where the TiO_2 containing polyethylene layer was provided, thereby preparing sample No. 101 of multi-layered silver halide color photographic material. Coating solutions for the respective layers were prepared by the following methods.

Coating solution for the first layer:

Ethyl acetate (60 ml) was added to a mixture of yellow coupler (EY-1, 26.7 g), a dye image stabilizer (ST-1, 10.0 g), a dye image stabilizer (ST-2, 6.67 g), an anti-stain agent (HQ-1, 0.67 g) and a high-boiling point organic solvent (DNP, 6.67 g). The resulting solution was dispersed wigh an ultrasonic homogenizer into a 10% aqueous gelatin solution (220 ml) containing 20% surfactant (SU-2, 7 ml), thereby preparing a dispersion of yellow coupler.

The dispersion was mixed with a blue-sensitive silver halide emulsion (see below; containing 8.67 g Ag) and, thereafter, an anti-irradiation dye (AIY-1) was added to prepare a coating solution for the first layer.

The same procedure was repeated to prepare coating solutions for the second to seventh layers. A hardener (HH-1) was added to the second and fourth layers and a hardener (HH-2) was added to the seventh layer. Surfactants (SU-1) and (SU-3) were added as coating aids for surface tension adjustment.

Table 1

Layer	Composition	Amount added (g/m^2)
7th layer (protective layer)	gelatin	1.00
6th layer (uv absorbing layer)	gelatin	0.40
	uv absorber (UV-1)	0.10
	uv absorber (UV-2)	0.04

Table 1 (continued)

Layer	Composition	Amount added (g/m^2)
6th layer (uv absorbing layer)	uv absorber (UV-3)	0.16
	anti-stain agent (HQ-1)	0.01
	DNP	0.20
	PVP	0.03
	anti-irradiation dye (AIC-1)	0.02
5th layer (red-sensitive layer)	gelatin	1.30
	red-sensitive AgClBr emulsion (Em-R)	0.21
	cyan coupler (EC-1)	0.24
	cyan coupler (EC-2)	0.08
	dye image stabilizer (ST-1)	0.20
	anti-stain agent (HQ-1)	0.01
	HBS-1	0.20
	DOP	0.20
4th layer (uv absorbing layer)	gelatin	0.94
	uv absorber (UV-1)	0.28
	uv absorber (UV-2)	0.09
	uv absorber (UV-3)	0.38
	anti-stain agent (HQ-1)	0.03
	DNP	0.40

Table 1 (continued)

Layer	Composition	Amount added (g/m^2)
3rd layer (green-sensitive layer)	gelatin	1.40
	green-sensitive AgClBr emulsion (Em-G)	0.17
	magenta coupler (EM-1)	0.75*
	DNP	0.20
	dye image stabilizer (II-5)	0.75*
	anti-irradiation dye (AIM-1)	0.01
2nd layer (intermediate layer)	gelatin	1.20
	anti-stain agent (HQ-2)	0.03
	anti-stain agent (HQ-3)	0.03
	anti-stain agent (HQ-4)	0.05
	anti-stain agent (HQ-5)	0.23
	DIDP	0.06
	mold inhibitor (F-1)	0.002
1st layer (blue-sensitive layer)	gelatin	1.20
	blue-sensitive AgClBr emulsion (Em-B)	0.26
	yellow coupler (EY-1)	0.80
	dye image stabilizer (ST-1)	0.30
	dye image stabilizer (ST-2)	0.20
	anti-stain agent (HQ-1)	0.02
	anti-irradiation dye(AIY-1)	0.01
	DNP	0.20

Table 1 (continued)

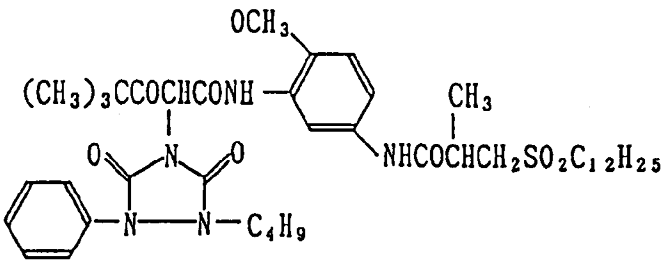
Layer	Composition	Amount added (g/m^2)
support	polyethylene laminated paper	

*mmol/m^2

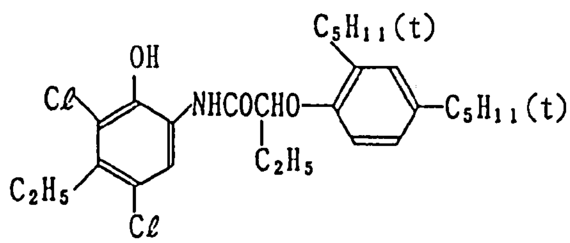
The amount of addition of each silver halide emulsion is shown in terms of silver.

Shown below are the structural formulas of the compounds used in the respective layers of sample No. 101.

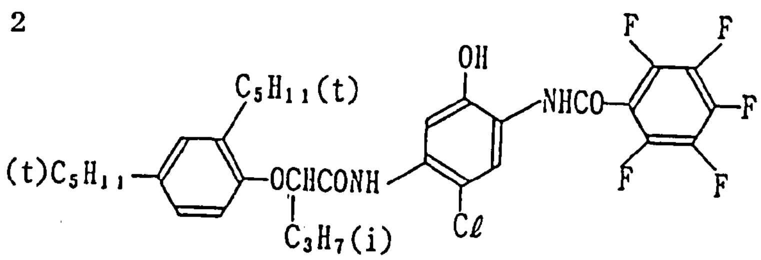
EY - 1



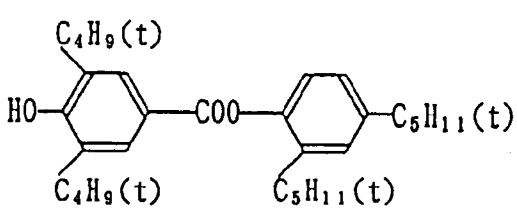
EC - 1



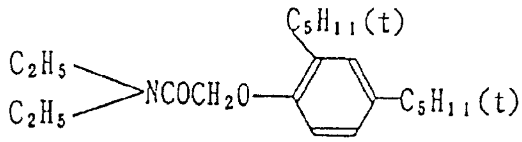
EC - 2



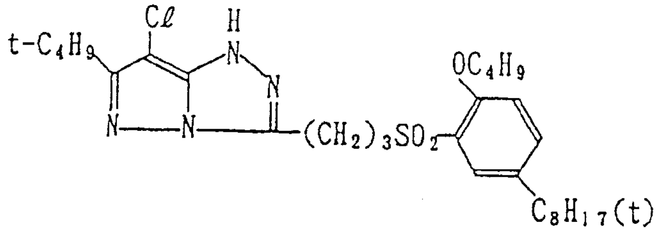
ST - 1



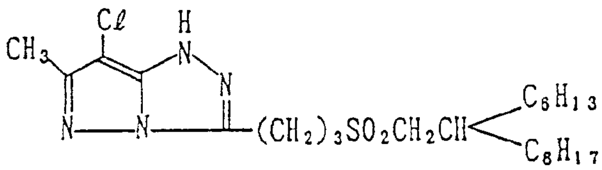
ST - 2



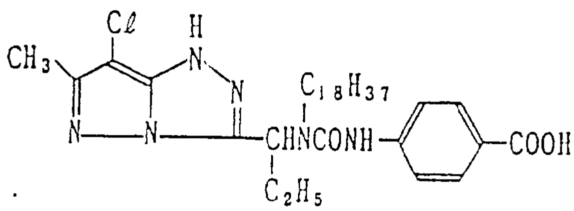
EM - 1



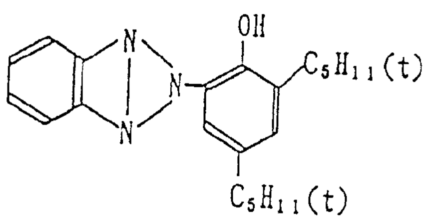
EM - 2



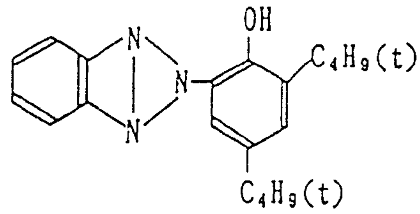
EM - 3



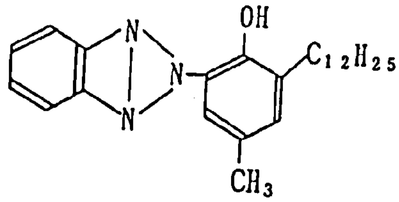
UV - 1



UV - 2

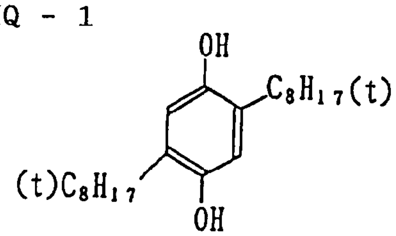


UV - 3

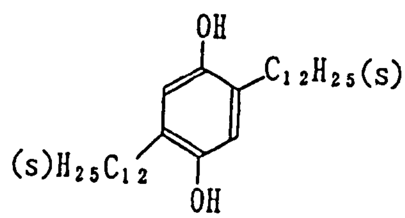


DOP dioctyl phthalate
DNP dinonyl phthalate
DIDP diisodecyl phthalate
PVP polyvinyl pyrrolidone

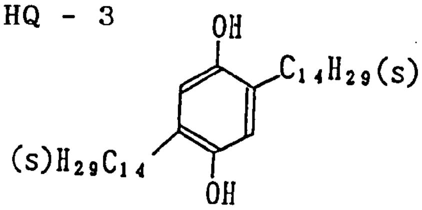
HQ - 1



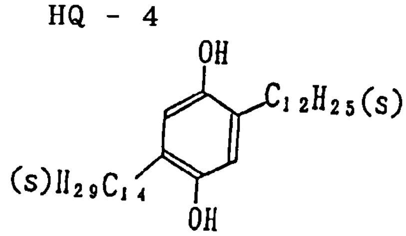
HQ - 2



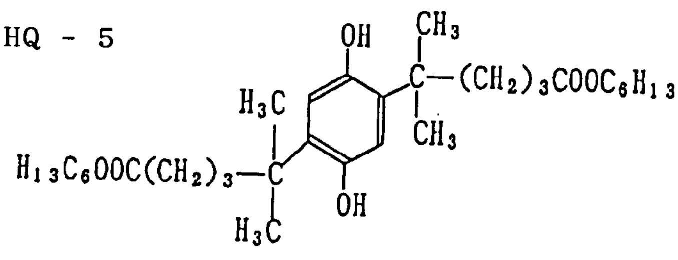
HQ - 3



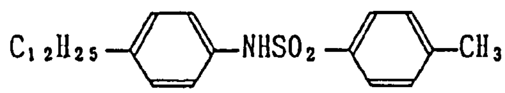
HQ - 4



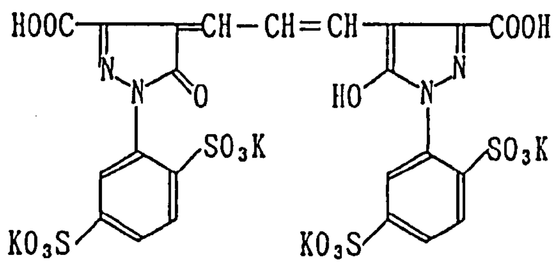
HQ - 5



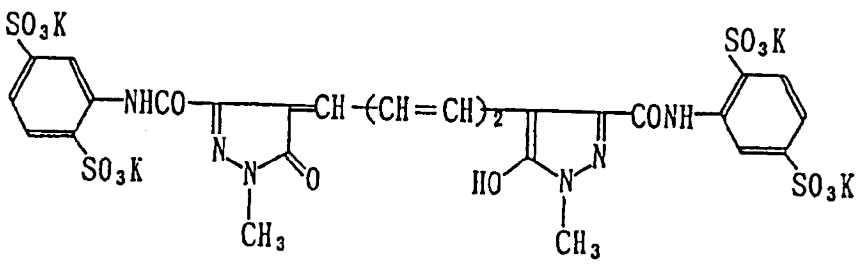
HBS-1



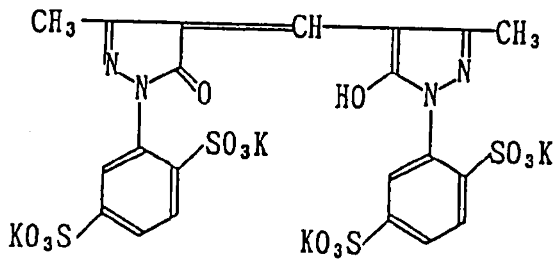
AIM-1



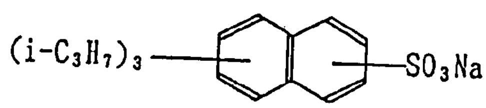
AIC-1



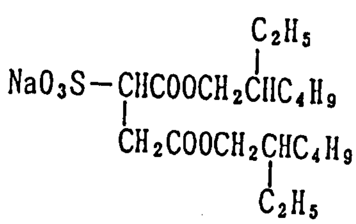
AIY-1



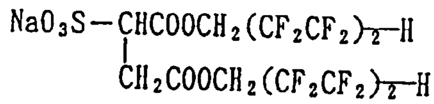
SU-1



SU-2



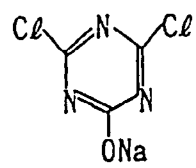
SU-3



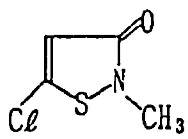
HH-1

$C(CH_2SO_2CH=CH_2)_4$

HH-2



F-1



Blue-sensitive silver halide emulsion (Em-B):

Monodispersed cubic emulsion having an average grain size of 0.85 μm, C.V. of 0.07 and containing 99.5 mol% AgCl

Sodium thiosulfate	0.8 mg/mol AgX
Chloroauric acid	0.5 mg/mol AgX
Restrainer (STAB-1)	6×10^{-4} mol/mol AgX
Sensitizer (BS-1)	4×10^{-4} mol/mol AgX
Sensitizer (BS-2)	1×10^{-4} mol/mol AgX

Green-sensitive silver halide emulsion (Em-G):

Monodispersed cubic emulsion having an average grain size of 0.43 μm, C.V. of 0.08 and containing 99.5 mol% AgCl

Sodium thiosulfate	1.5 mg/mol AgX
Chloroauric acid	1.0 mg/mol AgX
Restrainer (STAB-1)	6×10^{-4} mol/mol AgX
Sensitizer (GS-1)	4×10^{-4} mol/mol AgX

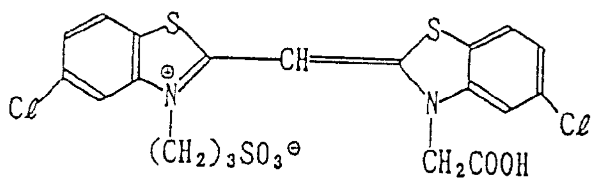
Red-sensitive silver halide emulsion (Em-R):

Monodispersed cubic emulsion having an average grain size of 0.50 μm, C.V. of 0.08 and containing 99.5 mol% AgCl

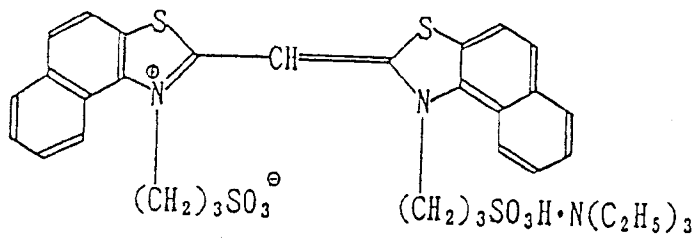
Sodium thiosulfate	1.8 mg/mol AgX
Chloroauric acid	2.0 mg/mol AgX
Restrainer (STAB-1)	6×10^{-4} mol/mol AgX
Sensitizer (RS-1)	1×10^{-4} mol/mol AgX

Shown below are the structural formulas of the compounds used in the respective monodispersed cubic emulsions.

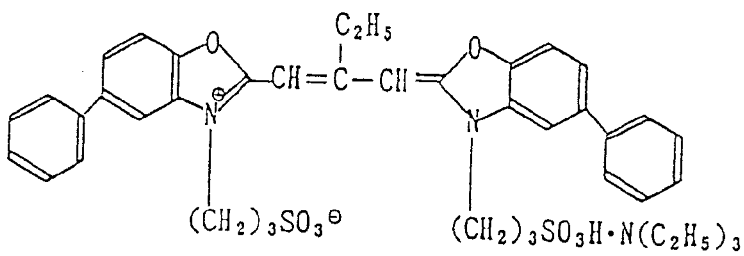
BS-1



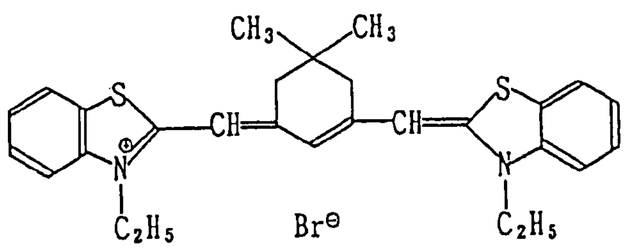
BS-2



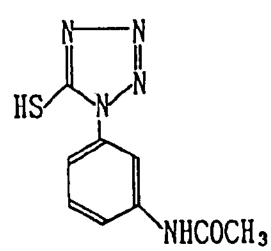
GS-1



RS-1



STAB-1



Sample Nos. 1 - 45 were prepared by repeating the procedure of preparing sample No. 101 except that the restrainer in Em-B and the sensitizer in Em-R were replaced by equal moles of the compounds of the present invention shown in Tables 3 and 4.

The samples thus prepared were exposed to red light through an optical wedge in the usual manner and subsequently processed by the following procedure.

Steps	Temperature (°C)	Time (sec)
Color development	35.0±0.3	45
Bleach-fixing	35.0±0.5	45
Stabilization	30~34	90
Drying	60~80	60

Shown below are the formulations of the processing solutions used. Each of the processing solutions was replenished in an amount of 80 ml per square meter of the silver halide photographic material.

Color developing solution	Tank solution	Replenisher
Pure water	800ml	800ml
Triethanolamine	10g	18g
N,N-Diethylhydroxylamine	5g	9g
Potassium chloride	2.4g	
1-Hydroxyethylidene-1, 1-diphosphonic acid	1.0g	1.8g
N-Ethyl-N-β-methane-sulfonamidoethyl-3-methyl-4-aminoaniline sulfate	5.4g	8.2g
Optical brightening agent (4,4'-amino-stilbene-sulfonic acid derivative)	1.0g	1.8g
Potassium carbonate	27g	27g
Water		to make 1,000ml
pH	10.10	10.60

Bleach-fixing solution (tank solution was of the same composition as replenisher)

Ethylenediaminetetraacetic acid	60g
iron (III) ammonium dihydrate	3g
Ethylenediaminetetraacetic acid	100ml
Ammonium thiosulfate (70% aq. sol.)	27.5ml
Ammonium sulfite (40% aq. sol.)	
Water	to make 1,000ml

pH adjusted with potassium carbonate or glacial acetic acid to 5.7

Stabilizing solution (tank solution was of the same composition as replenisher)	
5-Chloro-2-methyl-4-isothiazolin-3-one	1.0g
Ethylene glycol	1.0g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0g
Ethylenediaminetetraacetic acid	1.0g
Ammonium hydroxide (20% aq. sol.)	3.0g
Optical brightening agent (4,4'-diamino-stilbenesulfonic acid derivative)	1.5g
Water	to make 1,000ml

pH adjusted with sulfuric acid or potassium hydrodide to 7.0

The processed samples were evaluated for the following parameters.

(1) Fog

Unexposed sample was processed in accordance with the scheme described above. After the end of processing, the density of the sample was measured with a Model PDA-65 densitomer (Konica Corp.), with the fog density being expressed in relative values with the absorption by raw paper being set at zero.

(2) Relative sensitivity

Each sample was exposed to red light through a three-color separating filter on a Model KS-7 sensitometer (Konica Corp.) and subsequently processed in accordance with the scheme shown above. After the end of processing, the samples were subjected to sensitometry with a Model PDA-65 densitometer (Konica Corp.).

The results are expressed in terms of relative values, with the sensitivity of sample No. 1 being taken as 100. The reference point for the optical density at which sensitivity was determined was (fog + 0.20).

The results of the two evaluations are shown collectively in Table 2 below.

Table 2

Sample No.	Restrainer	Sensitizer	Fog	Sensitivity	Remarks
1	STAB-1	RS-1	0.05	100	Comparison
2	STAB-1	2-4	0.05	98	do.
3	1-1	RS-1	0.05	100	do.
4	1-1	2-4	0.01	115	Invention
5	1-4	2-4	0.01	110	do.
6	1-6	2-4	0.02	115	do.
7	1-10	2-4	0.02	110	do.
8	1-11	2-4	0.02	110	do.
9	1-12	2-4	0.01	113	do.

Table 2 (continued)

Sample No.	Restrainer	Sensitizer	Fog	Sensitivity	Remarks
10	1-13	2-4	0.01	130	do.
11	1-16	2-4	0.02	120	do.
12	1-20	2-4	0.02	125	do.
13	1-22	2-4	0.02	116	do.
14	1-24	2-4	0.02	118	do.
15	1-25	2-4	0.01	116	do.
16	1-26	2-4	0.03	104	do.
17	1-28	2-4	0.01	109	do.
18	1-33	2-4	0.01	108	do.
19	1-36	2-4	0.01	117	do.
20	1-40	2-4	0.00	130	do.
21	1-44	2-4	0.01	121	do.
22	1-45	2-4	0.02	125	do.
23	1-47	2-4	0.03	105	do.
24	1-1	2-7	0.01	114	do.
25	1-3	2-7	0.01	108	do.
26	1-6	2-7	0.02	113	do.
27	1-13	2-7	0.01	125	do.
28	1-14	2-7	0.01	122	do.
29	1-16	2-7	0.02	120	do.
30	1-20	2-7	0.02	123	do.
31	1-24	2-7	0.02	117	do.

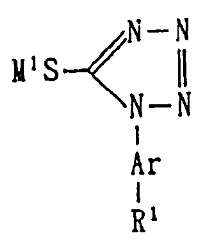
Table 2 (continued)

Sample No.	Restrainer	Sensitizer	Fog	Sensitivity	Remarks
32	1-25	2-7	0.01	118	do.
33	1-26	2-7	0.03	103	do.
34	1-27	2-7	0.01	110	do.
35	1-32	2-7	0.01	113	do.
36	1-36	2-7	0.01	115	do.
37	1-40	2-7	0.01	133	do.
38	1-42	2-7	0.01	126	do.
39	1-44	2-7	0.01	120	do.
40	1-47	2-7	0.03	106	do.
41	1-40	2-8	0.01	120	do.
42	1-40	2-9	0.01	124	do.
43	1-40	2-10	0.01	119	do.
44	1-40	2-11	0.01	120	do.
45	1-40	2-14	0.01	105	do.

The data in Table 2 shows that by using the restrainer of the present invention in combination with the sensitizing dye of the present invention, there is offered a silver halide photographic material that has high sensitivity and which experiences less fog.

Claims

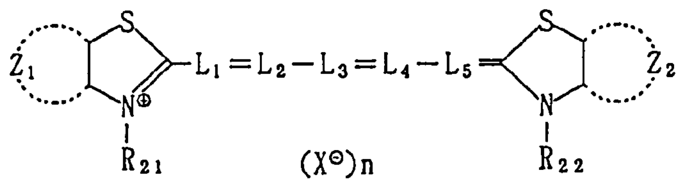
1. A silver halide photographic material containing a compound represented by the following general formula [I] and a compound represented by the following general formula [II]:



[I]

where Ar is an aromatic group; M^1 is a hydrogen atom, an alkali metal atom, an alkaline earth metal atom or an ammonium group; and R^1 is OR^2, $NR^3SO_2R^4$ or $COOM^2$ (where R^2 is a hydrocarbon group having

2 or more carbon atoms; R^3 is a hydrogen atom or a hydrocarbon group; R^4 is a hydrocarbon group; and M^2 is the same as M^1);



[II]

where Z_1 and Z_2 each represent the atomic group necessary to form an aromatic ring; R_{21} and R_{22} are each an alkyl group or an aryl group; L_1, L_2, L_3, L_4 and L_5 are each a methine group; $X^{\ominus}$ is an anion; n represents the integer necessary for neutralization of the charges in the molecule, provided that the total number of carbons in R_{21} and R_{22} and in the substituents on Z_1 and Z_2 is at least 6.

2. A silver halide photographic material according to claim 1 wherein Ar in said general formula [I] is a phenyl group.

3. A silver halide photographic material according to claim 1 wherein R^1 in said general formula [I] is OR^2 or $NR^3SO_2R^4$.

4. A silver halide photographic material according to claim 1 wherein R^2 in said general formula [I] is an alkyl group.

5. A silver halide photographic material according to claim 1 wherein R^3 is said general formula [I] is a hydrogen atom.

6. A silver halide photographic material according to claim 1 wherein R^4 in said general formula [I] is an alkyl group.

7. A silver halide photographic material according to claim 1 wherein Z_1 in said general formula [II] represents the atomic group necessary to form a benzene ring.

8. A silver halide photographic material according to claim 1 wherein Z_2 in said general formula [II] represents the atomic group necessary to form a benzene ring.

9. A silver halide photographic material according to claim 1 wherein R_{21} in said general formula [II] is an alkyl group or an alkoxyalkyl group.

10. A silver halide photographic material according to claim 1 wherein R_{22} in said general formula [II] is an alkyl group or an alkoxyalkyl group.

11. A silver halide photographic material according to claim 1 wherein at least one of L_1, L_3 and L_5 in said general formula [II] is an unsubstituted methine group.

12. A silver halide photographic material according to claim 1 wherein L_2, L_3 and L_4 in said general formula [II] form a dimethylcyclohexene ring.

13. A silver halide photographic material according to claim 1 which contains a silver halide emulsion composed of silver halide grains at least 90 mol% of which is silver chloride.

14. A silver halide photographic material according to claim 13 wherein said silver halide grains are silver chlorobromide grains having a silver bromide content of 0.1 - 2 mol%.

15. A silver halide photographic material according to claim 1 which is a color paper.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 2566

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X Y	EP-A-0 421 464 (FUJI PHOTO FILM CO., LTD.) * page 25, formula V-42 * * page 26, formulas V-43 - V-45 * * page 58, line 16 - line 18 * * page 64, line 15 - line 28; claim 11 * * page 67, formulas X-7, X-8 *	1-3,7-13 4-6	G03C1/20 G03C1/34
X Y	EP-A-0 421 452 (FUJI PHOTO FILM CO., LTD.) * page 20, line 1 - line 12; claims 1-4 * * page 18, formula IV-36 *	1,2,7-14 4-6	
X Y	EP-A-0 402 087 (KONICA CORPORATION) * page 13, formula I-19 * * page 33, formula VI-32 * * page 33, line 50 - line 53; claim 1 *	1,2, 7-11,15 4-6	
Y	EP-A-0 462 579 (KONICA CORPORATION) * page 5, formula S-4 * * page 6, formula S-9 * * example 2 *	4-6	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 MAY 1993	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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