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A photographic material.

A photographic material is described which comprises a support and:

- (a) a light-sensitive silver halide,
- (b) a substantially light-insensitive metallic salt whose solubility is greater than that of the light-sensitive silver halide and whose surface has been made relatively insoluble to said substance by a dissolution retarder, and
- (c) a physical development nucleus, present in one or more constituent layers thereon characterised in that a constituent layer contains a compound having the formula:



wherein M is an alkali metal, an alkaline earth metal or an ammonium group; X is a halogen; and n is 1 or 2.

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A PHOTOGRAPHIC MATERIALDETAILED DESCRIPTION OF THE INVENTION

The invention relates to a negative type silver halide photographic light-sensitive material and, more particularly, to a negative type silver halide photographic light-sensitive material the preservability 5 of which before it is exposed to light is improved while having excellent photographic characteristics.

Metallic silver is a natural product which is an essential raw material for a silver halide photographic light-sensitive material; its supply is on 10 the decrease year by year, while the industrial world has increasing demands for it. Accordingly, attempts at the present time to reduce the amount of silver used, i.e. the so-called "silver-saving" attempts, have become very important in production technologies for 15 silver halide photographic light-sensitive materials. From the abovementioned view point, we have previously disclosed, in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 48544/1979, a light- 20 sensitive material containing a small amount of silver, high sensitivity, and high maximum density.

In the preparation of this material, a light-sensitive material containing light-sensitive silver halide grains, substantially non-light-sensitive 25 metallic salt particles which have been made scarcely soluble with a dissolution retarder and physical development nuclei, are processed by a developer containing materials capable of dissolving the abovementioned metallic salt particles. Light-sensitive 30 materials such as those mentioned above deteriorate in their photographic characteristics on storage before

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they are exposed to light and subsequently possess lower light-sensitivity and gamma etc., as well as an increased tendency to fog. In particular, fog is considerably increased under high temperature and low humidity conditions. When preserving such light-sensitive materials in a high temperature and high humidity condition, fog is also apt to occur even with the use of a safe-light; such fog is the so-called "safe-light-fog".

10 We have further proposed, in Japanese Patent O.P.I. Publication Nos. 166642/1980 and 66846/1981, a light-sensitive material containing a dissolution retarder as a precursor in the aforementioned processing method and a light-sensitive material
15 containing a dissolution retarder as a non-diffusion type compound. Improvements in sensitivity on storage can be made by selecting the dissolution retarder, but it has, however, been found that any increase in fogging cannot be prevented when the light-sensitive materials
20 are kept unexposed to light under high temperature and low humidity conditions as mentioned above.

Following the abovementioned publication, we have also proposed, in Japanese Patent Application No. 15078/1982, that 1-phenyl-5-mercaptotetrazole
25 derivatives can be used as the aforementioned dissolution retarder, and in Japanese Patent Application No. 16764/1982 that a 1,3-dihydroxybenzene derivative or a 1,3-dihydroxynaphthalene derivative is used in combination with a heterocyclic mercapto compound. It
30 has become clear that the abovementioned methods are capable of inhibiting fog increase when storing the light-sensitive materials unexposed under high temperature and low humidity conditions, but that, on the contrary, the improved methods are not effective
35 to prevent a safety-light-fog when the light-sensitive

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materials are prestored unexposed to light in a high temperature and high humidity condition.

Accordingly, it is an object of the invention to provide a negative type light-sensitive material, such as mentioned above, containing light-sensitive silver halide grains, substantially non-light-sensitive metallic salt particles which have been made hardly soluble with a dissolution retarder and physical development nuclei, and wherein, in particular, the photographic characteristics thereof are prevented or hindered from deteriorating on storage while remaining unexposed to light in a high temperature and low humidity condition and fog is prevented from occurring.

We have found, after considerable research, that the abovementioned objects can be achieved by a photographic material having a support and a constituent layer containing a component selected from the group consisting of (a) a light-sensitive silver halide, (b) a substantially light-insensitive metallic salt whose solubility is larger than that of the light-sensitive silver halide and whose surface is made insoluble with a dissolution retarder, and (c) a physical development nucleus, the improvement comprising that the constituent layers contain a compound having the formula below:

Formula $M(X)_n$

wherein M is selected from the group consisting of an alkali metal, an alkaline earth metal or an ammonium group; X is a halogen; and n is 1 or 2.

According to the invention, it has been discovered that, when a compound of the specified formula is contained in a negative type light-sensitive material having constituent layers containing the component (a), (b) and (c), in any one of the constituent layers coated on the support, the preservability of the resulting light-sensitive material as it remains

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unexposed to light is significantly improved both in a high temperature and low humidity condition and in a high temperature and high humidity condition.

It is already known to those skilled in the art that the compounds having the specified formula will decrease fog when present in a light-sensitive material in a high temperature and a low humidity condition, and will cause serious fog when present in a high temperature and high humidity condition. In the meantime, as is apparent from the invention, when the compounds having the abovementioned formula are applied to a negative type light-sensitive material having the abovementioned composition, fog is effectively inhibited from occurring not only when the material is preserved in a high temperature and low humidity, but also when preserved in a high temperature and high humidity condition and using a safe-light. These facts have never been disclosed before.

In the invention, the compounds having the abovementioned formula are used effectively in the negative type silver halide photographic light-sensitive materials of the invention (hereinafter referred to as the negative type light-sensitive materials of the invention). In the formula, examples of alkali metals represented by M include Li, Na, K and Cs; alkaline earth metals include Ca, Sr, Ba, Be and Mg, as well as Zn included therein. Halogen atoms represented by X may be exemplified by chlorine and bromine. Accordingly, the specified compounds are inorganic compounds providing, generally, chlorine ions or bromine ions in water. Typical examples of the compounds having the aforementioned formula are given below.

- | | | |
|----------------------------|---------------------|---------------------|
| (1) LiCl | (2) NaCl | (3) KCl |
| (4) NH_4Cl | (5) MgCl_2 | (6) CaCl_2 |
| 35 (7) ZnCl_2 | (8) BaCl_2 | (9) LiBr |

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- | | | |
|--|--|-----------------------------|
| (10) NaBr | (11) KBr | (12) NH_4Br |
| (13) $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ | (14) $\text{CaBr}_2 \cdot 2\text{H}_2\text{O}$ | (15) ZnBr_2 |
| (16) $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ | | |

The compounds used in this invention are usually incorporated into the constituent layers of the negative type light-sensitive layers of the invention, such as a constituent layer containing light-sensitive silver halide grains, metallic salt particles and physical development nuclei, and preferably into a layer containing light-sensitive silver halide grains. Water or a hydrophilic organic solvent such as methanol, ethanol, acetone, dimethyl formamide or tetrahydrofuran is generally used as solvent for incorporating the compounds in a constituent layer of the abovementioned light-sensitive material. The desired amount of the specified compounds is suitably 1×10^{-3} mol to 5×10^{-1} mol per mol of silver halide when the compound is a chloride and 1×10^{-5} mol - 1×10^{-2} mol when it is a bromide. The compounds may be added at any time in the process for preparing the light-sensitive silver halide emulsions; preferably they are added after completing chemical ripening and before coating the emulsions.

Under the conditions mentioned above, the grains of a light-sensitive silver halide which is an essential component in the negative type light-sensitive materials of the invention, include those of silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide, silver chloriodobromide, or mixtures thereof; inter alia a highly sensitive silver iodobromide is preferably used; silver iodobromide containing no more than 50 mol% of silver iodide is particularly suitable for the invention.

The light-sensitive silver halide grains such as mentioned above can be applied in the form of a silver halide emulsion. Such emulsions can be prepared in a

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variety of processes including common and customary processes such as that described in Japanese Patent Publication No. 7772/1971, or the so-called conversion emulsion processes described in U. S. Patent No.

5 2,592,250, such as a single jet emulsion process or a double jet emulsion process.

The light-sensitive silver halide grains to be used in the invention may have various crystal habits such as a cubic system, an octahedron system or a
10 spherulite system. These crystal structure may be uniform from the interior to the exterior or may be layered crystals.

The required sizes of these grains depend on the application or use of the photographic element,
15 but suitable sizes are generally from 0.1μ to 3.0μ ; the grain sizes may be distributed either widely or narrowly.

These light-sensitive silver halide emulsions can be chemically sensitized by the use of a variety of
20 chemical sensitizers. Such chemical sensitizers include not only well-known ones such as an active gelatin, a sulphur sensitizer, a selenium sensitizer, a noble metal sensitizer or a polyamine but also a reduction sensitizer, such as stannous chloride or a polyalkylene oxide
25 sensitizer which are being used independently or in combination.

The light-sensitive materials may also be spectrally sensitized by the single or combination use of various kinds of sensitizing dyes, for example a
30 cyanine dye or a merocyanine dye, and they may further be stabilized by the use of, for example, a nitrogen-containing heterocyclic compound such as an imidazole, a triazole, a tetrazaindene or a tetrazole, for example, to serve as a photographic additive. Besides the above,
35 a hardener, a gradient adjuster and a coating assistant,

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for example, may be used.

The metallic salt particles which are to be used in the invention comprise metallic salts having substantially no light-sensitivity, and when the surfaces thereof are not covered with a dissolution retarder, the dissolution rate of the particles to the substance capable of dissolving the metallic salt particles is higher than that of the abovementioned light-sensitive silver halide grains. To be more precise, when the respective dissolution rates (the mass dissolved for a unit period of time) of metallic salt particles (A) and of light-sensitive silver halide grains (B) are measured in the presence of at least one metallic salt dissolving agent mentioned below, on condition that the total masses of the corresponding particles (A) and grains (B) are equal to each other, it is necessary that the dissolution rate of the particles (A) is faster than that of the grains (B).

The following method is suitable for practically verifying whether or not this requirement is satisfied.

First, two emulsions are prepared so that the hydrophilic colloids thereof may contain light-sensitive silver halide particles and metallic salt particles, respectively. Then, two samples are prepared by coating the respective emulsions and drying. In the preparation of these two samples, the amounts of the light-sensitive silver halide, metallic salts and hydrophilic colloids to be coated per unit area are made equal to each other between the two samples.

For the measurements, sodium thiosulfate is used as the control metallic salt dissolving agent and the samples prepared are dipped in a 5% (by weight) aqueous solution of sodium thiosulfate at 20°C without agitation. The dipping periods are severally set, for

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example, at 2 seconds, 5 seconds and 8 seconds. Next, the samples are transferred into a water tank to be washed and are then dried. With the samples processed as mentioned above, analytical measurements on the residual amounts of the light-sensitive silver halide and the metallic salts are made in known manner and the respective percentages of the residues are obtained. A graph is drawn to indicate the relation between the residual percentages and the dipping periods of time to obtain a dipping period t_1 for the light-sensitive silver halide sample and a dipping period t_2 for the metallic salt sample, which periods correspond to a 50% residue, from which the value of t_2/t_1 is determined.

The value of t_1/t_2 obtained should not be larger than 1 and preferably not be larger than 0.7.

The metallic salt particles are relatively easily soluble, but on the other hand they are not substantially light-sensitive.

The expression "substantially not light-sensitive or light-insensitive" as used herein means that they are "not light-sensitive" in relation to the abovementioned light-sensitive silver halide; more specifically, when the light energy sufficient to make the light-sensitive silver halide light-sensitive is applied to a light-sensitive material of the invention, then the metallic salt particles are "not substantially made light-sensitive".

The metallic salt particles used in the invention are preferably very fine ones having a light sensitivity of at most only about one tenth of that of the abovementioned light-sensitive silver halide.

In one preferred embodiment of the invention, the metallic salt particles are silver halide grains substantially light-sensitive and are capable of being dissolved in a substance dissolving silver halide at a

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faster rate than that of the aforementioned light-sensitive silver halide.

More specifically, it is desirable that the metallic salt particles used in the invention are pure
5 silver bromide, pure silver chloride or a mixture thereof, which are not chemically sensitized, and their crystals are finer than those of the abovementioned light-sensitive silver halide.

The metallic salt particles are suitably used
10 in the invention in an amount of 0.1 mol to 100 mol per mol of a light-sensitive silver halide.

A metal ion or metal complex ion resulting from the dissolution of such metallic salt particles as mentioned above in the presence of the metallic salt
15 dissolving agent, is reduced to a metal on a physical development nucleus as described below, in the presence of a reducing agent.

The surface of each metallic salt particle to be used in the invention is covered with a dissolution
20 retarder. The dissolution retarder is a compound which slows down the dissolution rate of the particle in the presence of the abovementioned metallic salt dissolving agent by adsorbing to the surface of the metallic salt particle or by adsorbing to a part of the surface of the
25 particle that becomes the active site of a dissolution reaction; dissolution retarders also include compounds adsorbing to the surface of an easily soluble metallic salt particle to precipitate a rarely soluble salt or a complex salt with the metal ions of the metallic salt.

30 According to one of the preferred embodiments of the invention, the dissolution retarder is a compound capable of adsorbing to non-light-sensitive silver halide grains, which are easily soluble metallic salt particles, thereby lowering the solubility thereof.

35 A mercapto compound is one of the preferred

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examples of these compounds. Typical examples include cysteine, 1-phenyl-5-mercaptopotetrazole, mercaptobenzthiazole, mercaptobenzselenazole, mercaptobenzoxazole, mercaptobenzimidazole, benzylmercaptan, 4-ethyl-2-thio-
5 oxazoline, 2-mercapto-6-azauracil, 4-hydroxy-2-mercapto-6-methyl-pyrimidine or 3-mercapto-4-phenyl-5-methyl-1,2,4-triazole. A thiourea, an indazole, a triazole or an imidazole are also preferred, specifically a mercaptopotetrazole compound.

10 Along with the above, noble metals such as gold, silver, and platinum, and more preferably, colloids thereof, a metal sulfide such as silver sulfide, palladium sulfide or zinc sulfide, or a metal selenide may be used as physical development nuclei.

15 A metallic silver particle obtained by reducing a silver compound such as silver nitrate or a silver halide; a noble metal colloid; palladium sulfide; or silver sulfide are particularly preferred.

 These physical development nuclei need not
20 necessarily have a particulate form but may be substances which act by catalytically accelerating the process in which a metallic ion or metallic complex ion produced by dissolving the aforementioned metallic salt is reduced to a metal reducing agent, or they may be substances
25 containing a chemically active site for this purpose.

 The amount of the physical development nuclei used in the light-sensitive material depends on the nature of the nuclei. In using silver sulfide, for example, a suitable content is 0.001 g to 1.0 g per sq.
30 meter in the form of a metallic silver, and in using a metallic silver which is prepared by reducing fine particles of silver chloride, a suitable content is 0.01 g to 3.0 g per sq. meter.

 The constitution of the light-sensitive materials
35 of the invention can be varied in accordance with the intended use.

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The light-sensitive material of the invention has, on a support, a layer containing (a) light-sensitive silver halide grains, (b) metallic salt particles which are more easily soluble than the abovementioned silver halide and are substantially non-light-sensitive and also are covered by a dissolution retarder, and (c) physical development nuclei. The abovementioned materials (a) through (c) may be contained in different layers, or any two or more materials (a) through (c) may be contained in one and the same layer.

For example, it is possible to provide not only an arrangement in which the following constituent layers are laminated on a support, in order from the support; a layer containing physical development nuclei, a layer containing metallic salt particles and, if necessary, a layer containing a silver halide developer as described below, but also an arrangement in which the order of the layer lamination is reversed, as well as a double-layer arrangement in which a layer containing physical development nuclei and, if necessary, a silver halide developer is coated on a support and thereon another layer containing a mixture of light-sensitive silver halide grains and metallic salt particles is laminated, or still further, a single-layer arrangement in which one layer containing the mixture of light-sensitive silver halide grains, metallic salt particles and physical development nuclei is coated on a support.

Besides the above, constituent layers may be coated on both sides of a support; two supports can be provided and the respective constituent layers formed on each of the supports; or three supports can be provided and one constituent layer is coated on every three pieces of the supports.

The preferred arrangement of the light-sensitive materials of the invention is one in which a single layer

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containing the mixture of light-sensitive silver halide grains, metallic salt particles and physical development nuclei is coated on a support, or a layer containing the mixture of metallic salt particles and physical

5 development nuclei is coated on a support and thereon another layer containing light-sensitive silver halide grains only is coated to provide a double-layer constitution.

In the invention, it is preferred that the
10 compounds having the specified formula are added to a layer containing light-sensitive silver halide grains, as abovedescribed.

The layer constitution of the light-sensitive materials of the invention may be as described above.

15 However, the light-sensitive materials of the invention may be provided, if necessary, with such auxiliary layers as a protective layer, an interlayer, or an anti-halation layer at a suitable position, and these layers may also contain other photographic additives.

20 In the invention, light-sensitive silver halide grains, metallic salt particles and physical development nuclei may be dispersed independently or in the form of the mixture of two or more thereof in a suitable binder so that they may be incorporated in a specific
25 constituent layer.

A variety of hydrophilic colloids such as a gelatin derivative or polyvinyl alcohol including gelatin itself may be used as the abovementioned binders; gelatin is typically and preferably used. It is also desirable
30 to use a variety of physical property layer improving agents such as hardeners, if necessary, with the purpose of improving the physical properties of a coated layer in which the abovementioned hydrophilic colloid serves as the binder of the layer.

35 There may be incorporated in the composition of

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a coated layer in which a hydrophilic colloid serves as a binder thereof photographic additives other than the abovementioned hardener, such as a gelatin plasticiser, a surfactant, an ultra-violet-ray absorbing agent, an anti-staining agent, a pH adjuster, an antioxidant, an antistatic agent, a thickener, a graininess improver, a dye, a mordant, a whitener, a developing speed adjuster, a matting agent or a silver halide developer as described below, on condition that the effects of the invention are not adversely affected.

Supports to be used for the light-sensitive materials of the invention typically include baryta paper, polyethylene coated paper, synthetic polypropylene paper, glass plate, cellulose acetate film, cellulose nitrate film, polyester film such as polyethylene terephthalate film, polyamide film, polypropylene film, polycarbonate film or polystyrene film. These supports are suitably selected in accordance with the intended use of the light-sensitive material.

The light-sensitive materials of the invention are suitably processed with a developer containing both a reducing agent and a substance capable of dissolving metallic salt particles.

Developing agents are advantageously used as the abovementioned reducing agent to be contained in the developers. Suitable developing agents include the following compounds which are well-known in the art; a polyhydroxy benzene such as hydroquinone, toluyhydroquinone and 2,5-dimethyl hydroquinone; a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone or 1-phenyl-4-methyl-3-pyrazolidone; an aminophenol such as o-aminophenol or p-aminophenol; a 1-aryl-3-aminopyrazoline such as 1-(p-hydroxy phenyl)-3-aminopyrazolidone or 1-(p-methylaminophenyl)-3-pyrazoline; ascorbic acid; as well as the compounds described as developing agents in C.E. K. Mees

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& T. H. James, "The Theory of the Photographic Process", 3rd edition, 1966, Published by Macmillan Co., N.Y., Chapter 13 and L. P. A. Mason, "Photographic Processing Chemistry", 1966, pp. 13 - 30, Published by The Focal
5 Press, London. These compounds can be used singly or in combination.

The substance capable of dissolving the metallic salt particles, i.e. the metallic salt dissolving agent, which is to be used in the developer is one capable of producing metal ions or soluble metal complex ions
10 through the action of the substance on the metallic salt particles. The substance may be a solvent of the developer itself such as water.

It is preferred that these metallic salt dissolving agents are substances not substantially
15 dissolving light-sensitive silver halide, or those dissolving metallic salt particles such as fine grains of silver halide whose solubility is different from that of the light-sensitive silver halide as far as the amount of the metallic salt dissolving agent added by
20 which light-sensitive halide is not substantially dissolved.

Typical examples of the metallic salt dissolving agents mentioned above include a sulfite such as sodium sulfite; a thiosulfate such as sodium thiosulfate,
25 potassium thiosulfate, and ammonium thiosulfate; a cyanate such as potassium cyanate, and sodium cyanate; a thiocyanate such as sodium thiocyanate and potassium thiocyanate; an amino acid compound such as cystine and cysteine; a thiourea compound such as thiourea, and
30 phenyl thiourea or a thioether compound such as 3,6-di-thio-1,8-octadiol.

These metallic salt dissolving agents are usually contained in developers; however, they may be contained in light sensitive materials according to
35 circumstance, as described above.

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Among these metallic salt dissolving agents, sodium sulfite in particular is commonly used as a preservative for developers. The amount used, per litre of developer, is preferably 0.1 g to 100 g 5 and more preferably 1 g to 70 g.

The pH value of developers of this kind is usually not lower than and, most suitably, is from 5.5 to 13.2.

If necessary, such developers may contain a 10 variety of additives, for example, an alkaline agent, a pH buffer, a development accelerator or an antifoggant. A suitable processing temperature for the abovementioned developer is from 20°C to 50°C.

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The following Examples further illustrate the present invention.

Example 1

[Preparation of a light-sensitive silver halide emulsion]

5 The emulsion of light-sensitive silver halide grains was prepared in an ordinary process that 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene of 1.5 g per mol of a silver halide, and which serves as a stabilizer, were added to a highly light-sensitive silver iodobromide emulsion containing 4.0 mol
10 of silver iodide and which were ripen up to the maximum light-sensitivity thereof by gold sensitization and sulfur sensitization processes. The average grain size of the silver halide grains obtained was about 1.3 μ .

[Preparation of metallic salt particles which are silver halide
15 grains substantially light-insensitive]

The pure silver chloride emulsion was prepared from silver nitrate and sodium chloride in a neutralizing process. The average grain diameter of the silver chloride particles obtained was about 0.1 μ and the grains were easily soluble.

20 [Preparation of physical development nuclei]

Physical development nuclei of gold colloid were prepared in the process that 50 ml of 0.2% of chloroauric acid were

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added to 10 ml of 1% aqueous solution of polyvinyl alcohol of which the polymer saponification degree was at 99% and the polymerization degree was 1000 and the mixture thereof was stirred at room temperature and then 10 ml of 1% solution of 5 sodium borohydride were added thereto.

Then, the silver chloride emulsion substantially light-insensitive was thereto added 1-phenyl-5-mercaptotetrazole of 1.2 g per mol of silver halide, to serve as a dissolution retarder. Succeedingly, the aforementioned physical development 10 nuclei were added so that chloroauric acid as the nuclei may amount to 120 mg, and then a suitable amount of saponin was further added to prepare a coating liquid.

In the coating process, the coating liquid was uniformly coated on the both surfaces of a polyethylene terephthalate 15 film support having been sublayered.

Succeedingly, the light-sensitive silver halide emulsion thus prepared was taken to divide into equal parts and thereto the compounds relating to the invention having the aforementioned formula were added respectively as shown in the 20 following Table 1 and at the same time the control samples to which the compounds relating to the invention were not added were also respectively prepared. Next, suitable amounts of saponin were added thereto to serve as a coating agent and the mixture thus prepared were coated uniformly onto the both 25 surfaces of the aforementioned silver chloride emulsion layer.

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Further, a variety of negative type silver halide photographic light-sensitive materials were prepared in the process that a 2.5% aqueous gelatin solution containing suitable amounts of a hardener, i.e., formalin, and a coating agent, 5 i.e., sodium-2-ethyl hexyl succinate monosulfonate, the gelatin solution was overlaid as a protect layer on the abovementioned layer.

Concerning the amount coated on the both surfaces of the each samples prepared, the amount of silver contained in the 10 silver chloride layer to serve as the non-light-sensitive silver halide emulsion layer was 1.0 g/m^2 , the amount of gold contained in the physical development nuclei was 0.5 g/m^2 , and the amount of silver contained in the silver iodobromide layer to serve as the light-sensitive silver halide emulsion layer 15 was 3.0 g/m^2 .

With respect to each of the samples prepared in the above-mentioned process, preservation tests of the unexposed samples were respectively tried under the conditions exhibited in the Table 1 below and the respective film pieces of the above- 20 mentioned samples were exposed to light of 3.2 CMS through a wedge, and then development was made by the developer of the undermentioned composition at 35°C for 30 seconds and further the fixation, washing and drying were made in succession, and thus the sensitometry was tried.

25[Composition of Developer]

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	Hydroquinone	12.0 g
	Sodium sulfite, anhydrous	65.0 g
	Phenidone	1.0 g
	Sodium hydroxide	15.0 g
5	5-methylbenzotriazole	0.5 g
	Potassium bromide	2.0 g
	Add water to make	1 ltr.

The results obtained are shown in Table 1 below, wherein the sensitivity values are expressed as the percentages to the 10value of Sample No. 1.

Table 1

Sample No.	Compound added	Amt. added Mol/l Mol of Light-sensitive Emulsion	Allowed to stand for 3 days			60°C RH20% for 3 days			50°C RH80% for 3 days		
			Relative sensitivity	Gamma	Fog	Relative sensitivity	Gamma	Fog	Relative sensitivity	Gamma	Fog
1	Null	0	100	3.0	0.21	95	2.9	0.30	99	2.8	0.25
2	Exemplified Compound (1)	0.025	100	3.0	0.21	99	3.0	0.21	100	3.1	0.20
3	"	0.05	99	3.1	0.20	101	3.0	0.19	100	3.0	0.20
4	"	0.10	98	3.0	0.19	100	3.1	0.18	98	3.0	0.19
5	" (2)	0.025	100	3.1	0.21	100	3.1	0.21	100	3.0	0.21
6	"	0.05	100	3.2	0.20	102	3.1	0.20	99	3.1	0.20
7	"	0.10	98	3.1	0.20	99	3.0	0.19	98	3.0	0.20
8	" (4)	0.025	100	3.1	0.20	101	3.1	0.21	100	3.0	0.20
9	"	0.05	100	3.0	0.19	100	3.1	0.19	99	3.0	0.19
10	"	0.10	97	3.0	0.19	98	3.0	0.19	96	3.0	0.19
11	" (11)	0.001	99	3.0	0.20	99	3.0	0.22	100	3.0	0.21
12	"	0.002	98	2.9	0.19	98	2.8	0.20	98	2.9	0.20
13	" (14)	0.0005	100	3.1	0.20	101	3.2	0.21	100	3.1	0.20
14	"	0.001	99	3.0	0.20	100	3.0	0.20	98	3.0	0.19

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As is obvious from the Table above, it was found that every sample containing the compounds of the invention has the effect that the occurrence of fog can be reduced during the preservation thereof under the conditions of a high temperature and a low humidity or a high temperature and a high humidity.

Example 2

Some of the samples prepared in Example 1 were provided, and at the same time there were prepared the control samples for this example 2, one group of the control sample was uniformly coated on the both surfaces of a polyethylene terephthalate support with only the light-sensitive emulsion which had been prepared in the case of Example 1 and another group of the control samples was uniformly coated on the both surfaces of a polyethylene terephthalate base with the abovementioned light-sensitive emulsion but to which such a compound as shown in Table 2 below was added.

Onto the respective light-sensitive emulsion layers coated thereon with the abovementioned control coating materials, protective layers were coated further on, to provide the control samples. The aggregate amounts of the emulsion coated on the both surfaces were 3.0 g of silver per sq. meter.

The conditions for the preservation tests of unexposed samples were applied to each of the samples obtained and the

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exposures and the development processes were applied thereto in the same manner as taken in Example 1. The results obtained are shown in Table 2 below. Wherein, the sensitivity values are expressed as the percentages to the value of Sample No. 15.

Table 2

Sample No.	Compound added	Amt. added Mol/l mol of Light- sensitive Emulsion	Allowed to stand for 3 days			50°C 80%RH for 3 days		
			Relative sensi- tivity	Gamma	Fog	Relative sensi- tivity	Gamma	Fog
15	Null	0	100	3.0	0.21	98	2.8	0.25
16	Exemplified Compound (1)	0.05	99	3.1	0.20	100	3.0	0.20
17	" (2)	0.05	100	3.2	0.20	99	3.1	0.20
18	" (4)	0.05	100	3.0	0.19	99	3.0	0.19
19	" (11)	0.001	99	3.0	0.20	100	3.0	0.21
Control 1	Null	0	80	1.2	0.22	79	1.1	0.22
" 2	Exemplified Compound (1)	0.05	79	1.1	0.21	80	1.2	0.28
" 3	" (2)	0.05	79	1.2	0.21	79	1.1	0.27
" 4	" (4)	0.05	78	1.1	0.21	79	1.1	0.29
" 5	" (11)	0.001	78	1.0	0.21	79	1.0	0.27

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As is understandable from the results shown in the above table, it is apparent that the samples of the invention (No. 16 through 19) are effective to inhibit the increase of fog without lowering the sensitivity particularly during the period of preserving light-sensitive materials under the conditions of a high temperature and a high humidity. Also, as is observed in the conventional and publicly known technologies, it has been proved that, even if the compounds of the invention are added to a silver halide light-sensitive emulsion, there causes but the increase of fog during the period of the preservation of light-sensitive materials under the conditions of a high temperature and a high humidity.

Example 3

Samples each prepared in the same manner as in Example 1 were preserved for three days under the conditions of high temperature of 50°C and high humidity of 80%RH, and were then allowed to stand for 20 minutes under a safe-light, i.e., Sakura-Highlight, a 20 watt tungsten lamp, from 1.0 meter. After developing the samples in the same manner as in Example 201, the fog density of each sample was measured. The measurement results obtained are shown in Table 3 below.

In the table, the values of the fog are expressed as the difference between the values of fog caused when the samples were exposed to light and the values of fog caused when the

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samples remain unexposed.

Table 3

5	Sample No.	Compound added	Amt. added Mol/1 Mol of light-sensitive Emulsion	Safe-light Fog	
				Allowed to stand for 3 days	50°C 80%RH for 3 days
	20	Null	0	0.04	0.34
10	21	Exemplified Compound (1)	0.05	0.03	0.04
	22	" (2)	0.05	0.02	0.04
	23	" (3)	0.05	0.02	0.03
	24	" (4)	0.05	0.03	0.04

As is obvious from the above table, the every sample (No. 15 21 through 24) which was added with the compounds of the invention is capable of effectively reducing fog that is apt to cause when being exposed to a safe-light in the course of preservation under the conditions of a high temperature and a high humidity, in particular.

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CLAIMS

1. A photographic material having a support
and:

- (a) a light-sensitive silver halide,
- (b) a substantially light-insensitive metallic salt whose
5 solubility is greater than that of the light-sensitive
silver halide and whose surface has been made
relatively insoluble to said substance by a
dissolution retarder, and
- (c) a physical development nucleus, present in one or
10 more constituent layers thereon characterised in that
a constituent layer contains a compound having the
formula: $M(X)_n$
wherein M is an alkali metal, an alkaline earth metal,
including beryllium, magnesium and zinc,
15 or an ammonium group; X is a halogen; and n is 1 or 2.

2. A photographic material according to claim
1 wherein the halogen is chlorine or bromine.

3. A photographic material according to claim
1 or 2 wherein the said compound is present in the
20 constituent layer containing the light-sensitive silver
halide.

4. A photographic material according to claim
2 or 3 wherein the said compound is present in the
material in the amount from 1×10^{-3} to 5×10^{-1} mol per mol
25 of the silver halide when the compound is a chloride, and
from 1×10^{-5} to 1×10^{-2} mol per mol of the silver halide
when it is a bromide.

5. A photographic material according to any
one of claims 1 to 4 wherein the light-sensitive silver
30 halide is a silver iodobromide.

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6. A photographic material according to claim 5 wherein the silver iodobromide contains no more than 50 mol% of silver iodide.

7. A photographic material according to claim 5 7 wherein the said compound is incorporated in the constituent layer in an emulsion of the light-sensitive silver halide after chemical ripening thereof and before coating.

8. A photographic material according to any 10 one of the preceding claims, wherein the metallic salt is pure silver bromide or pure silver chloride, the crystal size of which is smaller than that of the light-sensitive silver halide.

9. A photographic material according to any one of the preceding claims, wherein the metallic salt is 15 present in an amount from 0.1 mol to 100 mol per mol of the light-sensitive silver halide.

10. A photographic material according to any one of the preceding claims, wherein the dissolution retarder is a mercapto compound, a thiourea, an indazole, 20 a triazole or an imidazole.

11. A photographic material according to claim 16 wherein the dissolution retarder is a mercaptotetrazole compound.

12. A photographic material according to any one 25 of the preceding claims wherein the physical development nuclei are of a noble metal colloid, palladium sulfide or silver sulfide.

13. A photographic material according to any one of the preceding claims wherein the light-sensitive silver halide, the metallic salt and the physical development 30 nuclei are present in one and the same constituent layer.

14. A photographic material according to any one of claims 1 to 12 wherein one constituent layer contains

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a mixture of the metallic salt and the physical development nuclei coated on the support, another constituent layer containing the light-sensitive silver halide only being coated thereover.

- 5 15. A photographic material according to any one of the preceding claims wherein the components are dispersed in a gelatin binder.