United States Patent Office 3,671,255 Patented June 20, 1972

3,671,255

SILVER HALIDE EMULSION FOG INHIBITED WITH QUATERNARY AMMONIUM, TRIAZOLE AND TETRAZAINDENE COMPOUNDS

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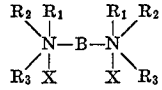
Int. Cl. G03c 1/34
U.S. Cl. 96—109 5 Claims

ABSTRACT OF THE DISCLOSURE

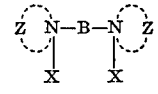
A light-sensitive silver halide photographic material, especially suited for quick development, contains as anti-foggants at least one of the compounds represented by the general Formulas I, II, III and IV

(I)

(II)



(III)

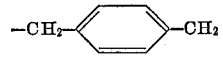


(IV)

wherein R_1 and R_2 are individually an alkyl or hydroxyalkyl group having 1 to 18 carbon atoms; R_3 is an alkyl or hydroxyalkyl group having 1 to 18 carbon atoms, or an aryl or aralkyl group; Z is a non-metallic atomic group necessary for formation of hetero ring by bonding to the nitrogen atom; A is an alkyl, alkenyl, aryl or aralkyl group; B is

$-(CH_2)_n$

$-CH_2O(CH_2)_nOCH_2-$



$-CH_2-O-CH_2-$

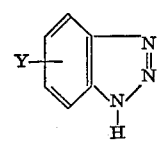
$-CH_2\cdot CH_2-S-CH_2\cdot CH_2-$

$-CH_2\cdot OCH_2-S-CH_2\cdot CH_2\cdot O\cdot CH_2-$

or

$-CH_2\cdot CO\cdot CO\cdot CH_2-$

(where n is a positive integer of 1 to 10); and X is an anion, combined with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene in at least one layer of the photographic material. A compound of the general formula



where Y is a hydrogen atom, a nitro group, a halogen atom or a methyl group, is further incorporated as third component.

The present invention relates to light-sensitive silver halide photographic materials containing as antifoggants compounds represented by the general Formulas I, II, III and IV shown later in combination with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. Further, the present invention involves use of a benzotriazole derivative of the general Formula V as additional ingredient.

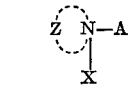
The object of the invention is to provide light-sensitive silver halide photographic materials excellent in anti-fogging property, particularly those which, at the time of quick development, display excellent anti-fogging property and are less in variation of photographic properties as compared with the case of ordinary development.

Recently, the quick treatment of light-sensitive photographic materials has strongly been desired, and the development of photographic materials at an elevated temperature for a short period of time has been effected. When developed at an elevated temperature, however, light-sensitive photographic materials tend to be increased in fog, in general, and are deteriorated in photographic properties.

Heretofore, light-sensitive photographic materials have been sensitized according to various sensitization methods such as sulfur sensitization, reduction sensitization, noble metal sensitization, polyalkylene glycol sensitization, etc. Generally, however, the above-mentioned sensitization methods have a tendency to deteriorate the fog characteristics of the photographic materials, so that anti-foggants have ordinarily been used. As the anti-foggants, there have been known a large number of compounds. Particularly typical among these compounds are 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 1-phenyl-5-mercaptotetrazole. The former compound has an action to inhibit a silver halide emulsion from formation of fog during storage, and is relatively low in anti-fogging effect on an emulsion immediately after preparation. On the other hand, the latter compound has an action to inhibit a silver halide emulsion from formation of fog immediately after preparation. Ordinarily, therefore, the said two compounds are used in combination to accomplish the inhibition of fogging. However, the 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene is injured in anti-fogging effect at the time of high temperature development, while the 1-phenyl-5-mercaptotetrazole is strong in desensitizing action so that a light-sensitive material, which contains said compound in an amount sufficient to inhibit the formation of fog at the time of high temperature development, is greatly desensitized and is not suitable for practical use. Accordingly, conventional light-sensitive photographic materials containing the said anti-foggants are great in variation of photographic properties so that it is difficult to expect sufficient anti-fogging effects.

In view of such actual state as mentioned above, we made various studies on light-sensitive silver halide photographic materials which are suitable not only for quick development but also for ordinary development. As the result, we have found that a light-sensitive silver halide photographic material, which has been incorporated with at least one of the compounds of the general Formulas I, II, III and IV shown below in combination with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and sometimes further with a compound of the general Formula V, is not only markedly less in decrease of speed than the conventional photographic materials but also shows a sufficiently high anti-fogging effect both at the time of high temperature development and at the time of ordinary development.

(I)



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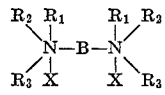

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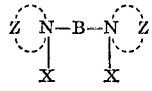


(IV)

wherein

R_1 and R_2 are individually an alkyl or hydroxyalkyl group having 1 to 18 carbon atoms;

R_3 is an alkyl or hydroxyalkyl groups having 1 to 18 carbon atoms, or an aryl or aralkyl group;

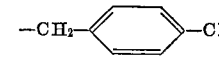
Z is a non-metallic atom grouping capable of forming a hetero ring, together with the adjacent nitrogen atom;

A is an alkyl, alkenyl, aryl or aralkyl group;

B is

$$-(CH_2)_n-$$

$$-CH_2O(CH_2)_nOCH_2-$$



$$-CH_2-O-CH_2-$$

$$-CH_2\cdot CH_2-S-CH_2\cdot CH_2-$$

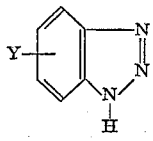
$$-CH_2\cdot O\cdot CH_2\cdot CH_2-$$

$$S-CH_2\cdot CH_2\cdot O\cdot CH_2-$$

or

$$-CH_2\cdot CO\cdot CO\cdot CH_2-$$

(where n is a positive integer of 1 to 10); and X is an anion



(V)

wherein Y is a hydrogen atom, a nitro group, a methyl group or a halogen atom.

Heretofore, the compounds represented by the general Formulas I to IV have been known as sensitizers, as set forth in United States Pat. 2,288,226 and other literature, and scarcely show anti-fogging effects. Further, the compound represented by the general Formula V has been known as an anti-foggant, but is strong in desensitizing action, like in the case of 1-phenyl-5-mercaptotetrazole, and when used in an amount capable of displaying a sufficient anti-fogging effect at the time of high temperature development, it is too strong in desensitizing action to be suitable for practical purpose.

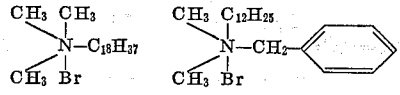
However, when at least one of the compounds represented by the general Formulas I to IV is used in combination with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and further with the compound represented by the general Formula V, there can be attained an excellent anti-fogging effect by effective interaction of the said two or three members, as will be clarified in the examples set forth later.

Processes for synthesizing the compounds represented by the above-mentioned general Formulas I to IV have already been reported in many literatures. For example, processes for synthesizing the compounds from pyridines and alkyl dihalides are disclosed in Journal of the American Chemical Society, 18, 988, and Annalen der Chemie, 121, 254; a process for synthesizing quaternary salts from xylene dihalides is disclosed in Berichte, 34, 2089; processes for synthesizing the compounds from alkylamines or pyridines and alkyl halides are disclosed in Industrial and Engineering Chemistry, 45, 1022, Chemical and Engineering News, 30, 1282, and Journal of the American

Chemical Society, 68, 753 and 63, 147; and processes for synthesizing the compounds from azoles and alkylene dihalides or alkylene halides are disclosed in United States Pats. 2,425,774 and 2,694,716.

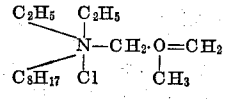
Further, processes for synthesizing the compounds of the aforesaid general Formula V have also been disclosed in, for example, Berichte, 9, 219 and 36, 4028; Annalen der Chemie, 249, 361 and 311, 290; and Journal of the American Chemical Society, 79, 4395 (1957).

Typical examples of the compounds represented by the general Formulas I to IV are as follows:



(1) (2)

(3)



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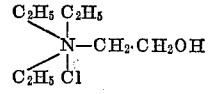

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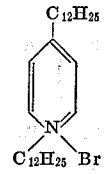

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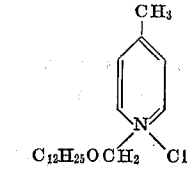

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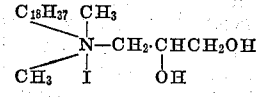

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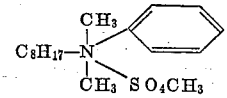

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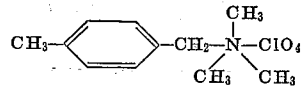

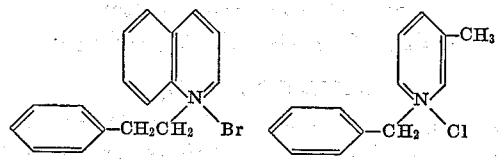

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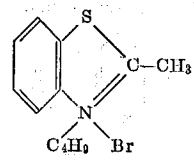

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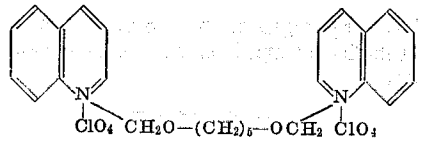

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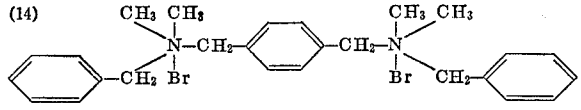

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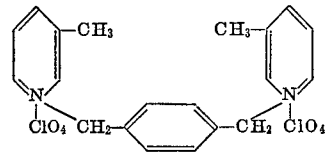

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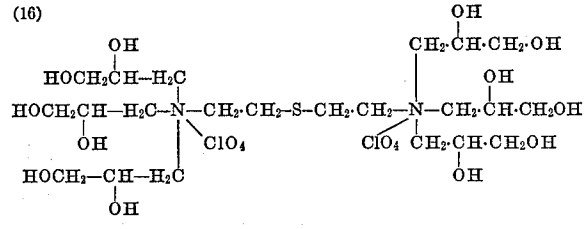

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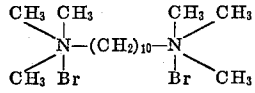

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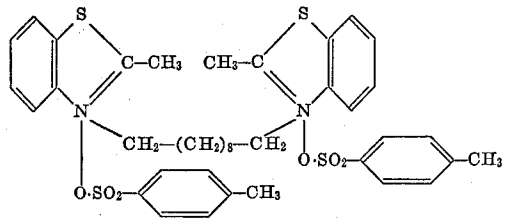

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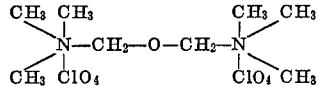

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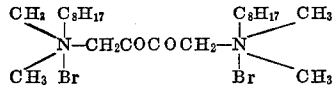

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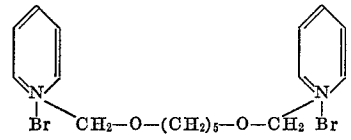

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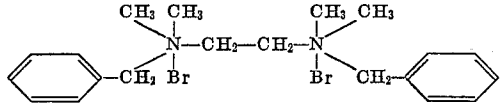

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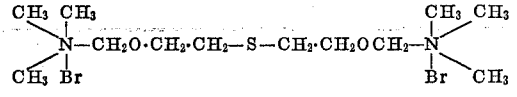
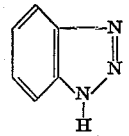


Further, typical examples of the compounds represented by the general Formula V are as follows:



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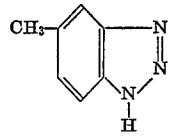

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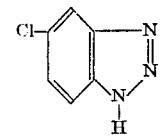

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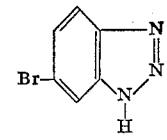

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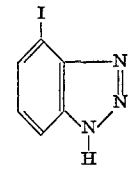

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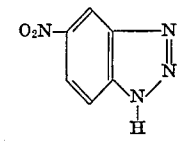


(29)

In adding the above-mentioned compounds to a light-sensitive photographic emulsion in combination with 4 - hydroxy-6-methyl - 1,3,3a,7-tetrazaindene, the compounds are formed, either singly or in admixture, into aqueous solutions, alkali solutions or alcohol solutions, and then added to the emulsion. The amounts of the compounds to be added are preferably such that per 100 g. of silver halide, the amount of the 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene is 0.05 to 6.0 g., the amount of the compound represented by any of the general Formulas I to IV is less than 1 g., and the amount of the compound represented by the general Formula V if used is less than 0.3 g. The compounds may be added to any one of the layers constituting the light-sensitive photographic material such as protective layer, inter layer, filter layer, etc. In this case also, the amounts of the compounds to be added are within the above-mentioned ranges. Further, the compounds may be used in combination with dyes, sensitizers, hardeners and the like known photographic additives.

The present invention is illustrated in further detail below with reference to examples.

EXAMPLE 1

A geltine emulsion of 60 g. of silver iodobromide containing 1.5 mole percent of silver iodide was subjected at the time of second ripening to gold sensitization. After completion of the ripening, the emulsion was equally divided into several portions. One portion was used as a control, and the remaining portions were incorporated with such compounds as shown in Table 1. Subsequently, these emulsions were individually coated on a polyester film base and then dried to prepare samples. The samples were treated according to the sensitometry described in JIS–K–7604, and photographic properties of the treated samples were measured to obtain the results set forth in Table 1. Development was effected under such conditions as shown in Table 1, using developers of the following compositions:

Developer (I):	G.
Sodium sulfite	70
Hydroquinone	10
Boric anhydride	1
Sodium carbonate (monohydrate)	20
1-phenyl-1,3-pyrazolidone	0.35
Sodium hydroxide	5
5-methylbenzotriazole	0.05
Potassium bromide	5
Glutaraldehyde bisulfite	15
Acetic acid	8
Water to make 1 liter.	

Developer (II):	
Metol	3.5
Anhydrous sodium sulfite	60
Hydroquinone	9.0
Sodium carbonate (monohydrate)	53
Potassium bromide	4.0
Water to make 1 liter.	

TABLE 1

	Amount added (mg.)	Developer (I), 40° C., 30 sec. Fog	Developer (I), 40° C., 30 sec. Relative speed	Developer (II), 20° C., 4.5 min. Fog	Developer (II), 20° C., 4.5 min. Relative speed
Control		0.34	100	0.08	85
Compound (A)	750	0.29	96	0.07	82
Compound (A)	750	0.07	48	0.05	45
Compound (B)	30				
Exemplified compound (21)	50	0.22	72	0.08	86
Exemplified compound (26)	30	0.06	55	0.04	50
Exemplified compound (21)	50	0.07	73	0.06	75
Compound (A)	750				
Exemplified compound (21)	50	0.04	70	0.04	71
Exemplified compound (26)	30				
Compound (A)	750				
Exemplified compound (26)	30	0.05	54	0.04	50
Compound (A)	750				

In the table, the Compound A is 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, and the Compound B is 1-phenyl-5-mercaptotetrazole.

As is clear from Table 1, the exemplified Compounds 21 and 26, when used singly, are less in anti-fogging effect or great in desensitizing action, but when the above-mentioned three compounds are used in combination, there can be obtained excellent photographic properties.

EXAMPLE 2

An emulsion prepared in the same manner as in Example 1 was equally divided into several portions. One portion was used as a control, and the remaining portions were incorporated with such compounds as shown in Table 2. Subsequently, these emulsions were individually coated on a cellulose triacetate film base and then dried to prepare samples. The samples were treated in the same manner as in Example 1 to obtain the results set forth in Table 2.

In Table 2, the Developers I and II and the Compounds A and B are the same as in Example 1.

As is clear from Table 2, it is understood that when used in combination with the Compound A, the exemplified Compounds 6 and 27 show market anti-fogging effects and are less in desensitizing action, so that excellent photographic properties can be obtained.

EXAMPLE 3

An emulsion prepared in the same manner as in Example 1 was equally divided into several portions. One portion was used as a control, and the remaining portions were incorporated with such compounds as shown in Table 3. Subsequently, these emulsions were individually coated on a cellulose triacetate film base and then dried to prepare samples. The samples were treated in the same manner as in Example 1 to obtain the results set forth in Table 3.

TABLE 2

	Amount added (mg.)	Developer (I), 40° C., 30 sec. Fog	Developer (I), 40° C., 30 sec. Relative speed	Developer (II), 20° C., 4.5 min. Fog	Developer (II), 20° C., 4.5 min. Relative speed
Control		0.29	100	0.08	82
Compound (A)	750	0.22	91	0.07	80
Compound (A)	750	0.08	49	0.06	47
Compound (B)	20				
Exemplified compound (6)	40	0.18	82	0.08	81
Exemplified compound (27)	20	0.08	53	0.06	50
Exemplified compound (6)	40	0.10	85	0.07	81
Compound (A)	750				
Exemplified compound (6)	40	0.05	71	0.05	75
Exemplified compound (27)	20				
Compound (A)	750				
Exemplified compound (27)	20	0.07	51	0.06	49
Compound (A)	750				

TABLE 3

	Amount added (mg.)	Developer (I), 40° C., 30 sec. Fog	Developer (I), 40° C., 30 sec. Relative speed	Developer (II), 20° C., 4.5 min. Fog	Developer (II), 20° C., 4.5 min. Relative speed
Control		0.30	100	0.08	82
Compound (A)	750	0.26	93	0.06	80
Compound (A)	750	0.06	46	0.05	42
Compound (B)	30				
Exemplified compound (17)	75	0.23	85	0.07	80
Exemplified compound (29)	750	0.07	56	0.06	50
Exemplified compound (17)	75	0.07	81	0.06	79
Compound (A)	15				
Exemplified compound (17)	75	0.03	76	0.03	73
Exemplified compound (29)	15				
Compound (A)	750				
Exemplified compound (29)	15	0.06	52	0.05	48
Compound (A)	750				

In Table 3, the Developers I and II and the Compounds A and B are the same as in Example 1.

From Table 3, it is understood that the exemplified Compounds 17 and 29, which when used singly, are low in anti-fogging effect or great in desensitizing action, become higher in anti-fogging effect when used in combination with the Compound A, but when the exemplified Compound 29 is used in combination with the Compounds 17 and A, not only the anti-fogging effect is further enhanced but also the desensitizing action becomes lower to make it possible to obtain excellent photographic properties.

EXAMPLE 4

A gelatine emulsion of 60 g. of silver iodobromide containing 5.3 mole percent of silver iodide was subjected at the time of second ripening to gold sensitization. After completion of the ripening, the emulsion was equally divided into several portions. One portion was used as a control, and the remaining portions were incorporated with such compounds as shown in Table 4. Subsequently, these emulsions were individually coated on a cellulose triacetate film base and then dried to prepare samples. The samples were treated in the same manner as in Example 1 to obtain the results set forth in Table 4.

TABLE 4

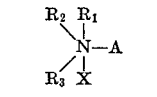
	Amount added (mg.)	Developer (I), 40° C., 30 sec. Fog	Developer (I), 40° C., 30 sec. Relative speed	Developer (II), 20° C., 4.5 min. Fog	Developer (II), 20° C., 4.5 min. Relative speed
Control		0.33	100	0.08	84
Compound (A)	750	0.29	94	0.07	81
Compound (A)	750	0.08	62	0.06	60
Compound (B)	20				
Exemplified compound (1)	35	0.25	90	0 08	83
Exemplified compound (25)	30	0.07	60	0.06	58
Exemplified compound (1)	35	0.09	87	0.07	81
Compound (A)	750				
Exemplified compound (1)	35	0.04	80	0.04	78
Exemplified compound (25)	30				
Compound (A)	750				
Exemplified compound (25)	30	0.06	57	0.06	55
Compound (A)	750				

In the above table, the Developers I and II and the Compounds A and B are the same as in Example 1.

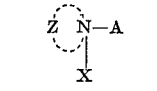
From Table 4, it is understood that when used singly, the exemplified Compounds 1 and 25 and the Compound A are low in anti-fogging effect or great in desensitizing action, but when the three compounds are used in combination, a marked anti-fogging effect is displayed to make it possible to obtain more excellent photographic properties than in the case where any two of the three compounds are used in combination.

What is claimed is:

1. A light-sensitive silver halide photographic material, especially suited for quick development, which contains in at least one layer of the photographic material, as antifoggant: at least one compound represented by the general Formulae I, II, III and IV



(I)



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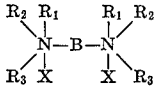
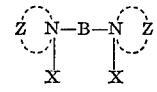


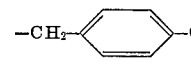
(III)



(IV)

wherein R_1 and R_2 are individually an alkyl or hydroxyalkyl group having 1 to 18 carbon atoms; R_3 is an alkyl or hydroxyalkyl group having 1 to 18 carbon atoms, or an aryl or aralkyl group; Z is a non-metallic atomic group necessary for formation of hetero ring by bonding to the nitrogen atom; A is an alkyl, alkenyl, aryl or aralkyl group; B is

$$-(CH_2)_n-CH_2O(CH_2)_nOCH_2-$$



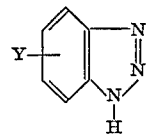
$$-CH_2-O-CH_2-,\ CH_2\cdot CH_2-S-CH_2\cdot CH_2O$$

$$-CH_2OCH_2CH_2-S-CH_2CH_2OCH_2-$$

or

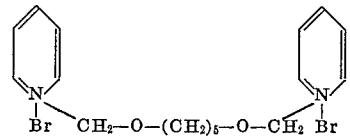
$$-CH_2\cdot CO\cdot CO\cdot CH-$$

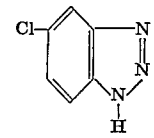
(where n is a positive integer of 1 to 10); and X is an anion, combined with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and a compound of the general formula



where Y is a hydrogen atom, a nitro group, a halogen atom or a methyl group.

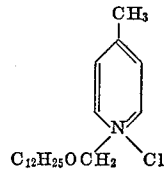
2. A light-sensitive silver halide photographic material as claimed in claim **1**, wherein the antifoggant used is the combination of the following three:

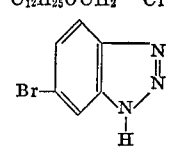




and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

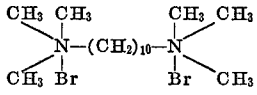
3. A light-sensitive silver halide photographic material as claimed in claim **1**, wherein the antifoggant used is the combination of the following three:

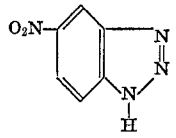




and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

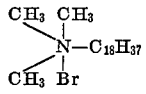
4. A light-sensitive silver halide photographic material as claimed in claim 1, wherein the antifoggant used is the combination of the following three:

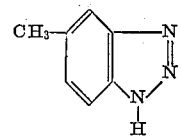




and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

5. A light-sensitive silver halide photographic material as claimed in claim 1, wherein the antifoggant used is the combination of the following three:





and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.

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