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FOG REDUCTION IN PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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ABSTRACT OF THE DISCLOSURE

Photographic elements having thereon a silver halide emulsion layer, and containing in said layer or an adjacent layer, a 2,2'-(p,p-biphenylene)-3,3',5,5'-tetra-substituted bistetrazolium salt as a fog reducing agent.

This invention relates to photographic silver halide emulsions, and in particular, to reduction therein of fog—especially while applying methods thereto to increase the speed and improve covering power.

More particularly, it relates to photographic elements having thereon a light-sensitive silver halide emulsion layer, and having incorporated in said layer or in an adjacent layer, a non-diffusion bis-tetrazolium salt as hereinafter defined.

It is well known that silver halide emulsions may be sensitized with chemical sensitizers or with optical sensitizers. In the case of optical sensitization, the optical range of sensitivity is increased; that is, the sensitivity to light of longer wavelengths. Chemical sensitization is either the result of the formation of small amounts of silver sulfide or silver on the surface of the silver halide crystal. Examples of this class of chemical sensitizers are $Na_2S_2O_3$ and Na_2SO_3.

For the purpose of increasing the sensitivity of photographic silver halide emulsions, many other compounds have been proposed; e.g., polyoxyalkylene ethers and numerous derivatives thereof, quaternary ammonium, phosphonium, ternary sulfonium salts, also combinations or mixtures of alkylene oxide polymers and quaternary ammonium compounds, also condensation products of alkylene oxide with organic compounds containing an active hydrogen atom.

Certain compounds have been added to or brought in contact with photographic silver halide emulsions for the purpose of increasing the practical speed, improving the contrast and the covering power of the developed silver. One determines covering power by dividing the optical density at maximum density by the grams of silver per square decimeter in the developed image layer.

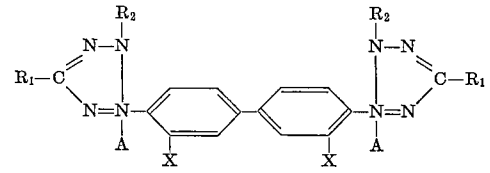
Compounds which have been proposed for this purpose are, e.g., poly-N-vinyl lactams, the water-soluble polyglucose dextran, water-soluble β-hydroxyalkyl ether of a polyvinyl alcohol, water-soluble hydrolyzed glucogen, water-soluble mannan polysaccharide, the water-soluble polyglucose laminarin, hydroxy-ethyl cellulose, and carboxymethylated proteins.

While these compounds serve their purpose well, they nevertheless, have also shortcomings. Some of these compounds cause higher fog and inferior storage stability.

It is an object of this invention to provide improved photographic silver halide emulsions having a reduced tendency to fog and possessing good storage stability—also when they contain compounds as discussed above which increase sensitivity, speed, contrast and/or covering power.

We have discovered that silver halide emulsions having reduced tendency to fog can be obtained by inluding

therein a bis-tetrazolium salt having the following general formula:



wherein R_1 and R_2 are aryl radicals such as phenyl or substituted phenyl radicals wherein the substituents can be, for example, methyl, methoxy, hydroxy, chloro or nitro groups, or heterocyclic radicals such as furyl, thienyl, pyridyl, quinolyl, napthothienyl, or benzothiazolyl; X represents hydrogen or a substituent such as methyl, methoxy or chloro; and A represents the anion of a salt-forming acid such as hydrochloric or acetic acid.

The preparation of compounds of the foregoing class is described in Ann., vol. 58 (1953) pages 16–23 and 29–44.

The compounds which we have described may be used in various types of photographic emulsions, e.g., non-sensitized emulsions, orthochromatic, panchromatic and X-ray emulsions. If used with sensitizing dyes, they may be added to the emulsion before or after the dyes are added. Various silver salts may be used as a sensitive element, such as silver bromide, silver iodide, silver chloride or mixed silver halides. Our compounds are especially suitable because of their non-diffusing properties in multi-layer emulsions such as those intended for color photography, e.g., emulsions containing color-forming components. The dispersing agent in the photographic emulsion may be gelatin, or other colloids, such as collodion, albumen, cellulose derivatives, polyvinyl alcohol, polyvinylpyrrolidone, caseine. The emulsions to which we add our compounds may or may not contain chemical sensitizers, such as gold sensitizers or other noble metal sensitizers, sulfur sensitizers, reduction sensitizers, or accelerators, such as polyoxyalkylenes or their derivatives.

The quantity of the foregoing bis-tetrazolium compounds incorporated in the silver halide emulsions is preferably from 0.05 to 0.5 mg. per mol of silver halide.

The aforesaid compounds may be added directly to the emulsion prior to coating or they may be added to an adjacent—such as an undercoat, a middle coat, an overcoat or a surface coating, which is adjacent to a silver halide emulsion layer of the light-sensitive element.

The following examples illustrate photographic emulsions and light-sensitive materials in accordance with the invention, but are not to be regarded as limiting the scope thereof.

EXAMPLE 1

A silver halide emulsion in gelatin containing 4% silver iodide and 96% silver bromide was prepared in a conventional manner and brought up to its maximum light-sensitivity. It was then readied for coating on film base; that is, melted at 40° C., necessary coating finals were added such as sensitizing dyes, stabilizers and hardeners. A 0.001% solution of 2,2'-(m,m'-dimethoxy-p,p'-biphenylene)- bis-(3,5-diphenyl-tetrazolium chloride) in methanol was prepared and a portion of this solution added to a sample of the above-described emulsion containing about 0.6 mol of silver halide. A sample of the same emulsion, but not containing the compound of our invention, served as a control. The so-prepared emulsion samples were coated on a suitable cellulose ester base or polyester base and dried. Samples of these film coatings were then exposed in a Type I–B sensitometer

and developed in a developer of the following composition:

Water: 500 cc.
Metol: 2.2 g.
Sodium sulfite, anhydrous: 72.0 g.
Hydroquinone: 8.8 g.
Sodium carbonate, monohydrated: 56.0 g.
Potassium bromide: 4.0 g.
Water to make 1.0 liter.

The resulting speed, maximum density and fog after 6 minutes' development were as follows:

Quantity of bis-tetrazolium compound used per 0.6 mol of silver halide, mg.	Relative speed	$D_{max.}$	Fog 6' dev.
0	100	3.42	.23
0.05	108	3.32	.18

EXAMPLE 2

To a silver halide emulsion sample similar to that used in Example 1 and containing 0.6 mol of silver halide, there was added, 1 gram of polyoxyethylene lauryl ether and 5 ml. of an 0.001% solution in methanol of the bis-tetrazolium salt of Example 1. After coating on a film base as described in Example 1, an aqueous gelatin solution containing 20 g. of gelatin per liter was overcoated to provide an antiabrasion layer. As a control, light-sensitive material was similarly prepared, omitting, however, the bis-tetrazolium compound. Samples of the resulting film were exposed and developed in the same manner as in Example 1, yielding the following results in terms of relative speed, maximum density and fog after 12 minutes' development:

Material	Relative speed	D_{max}	Fog 12' development
Control	150	3.04	.34
Material containing bis-tetrazolium salt	150	3.04	.23

EXAMPLE 3

A silver halide emulsion in gelatin containing 2% silver iodide and 98% silver bromide was prepared in a conventional manner and brought up to its maximum light sensitivity. It was then readied for coating as described in Example 1. Also samples were prepared as in Example 1. Test and control were then developed in a commercial rapid processing system (Eastman Kodak M–4 X-Omat system). The results were as follows:

Quantity of bis-tetrazolium compound used, mg.	Relative speed	Fog	D_{max}
0	100	.20	4.00
0.05	108	.15	4.00

EXAMPLE 4

A silver halide emulsion containing 2% silver iodide and 98% silver bromide was prepared. Samples containing about 0.4 mol of silver halide were taken and experiments conducted as follows:

(a) Coated as control and provided with a 4μ surface coating prepared from 20 grams gelatin in 1 liter water.

(b) As (a) but to the 1 liter of surface solution was added 15 grams of propylene oxide treated gelatin (see U.S.P. 3,312,553).

(c) Like (b) but to the emulsion sample were added 0.05 mg. 2,2'-(m,m'-dimethoxy-p,p'-biphenylene)-bis-(3,5-diphenyl-tetrazolium chloride).

The testing material (a), (b) and (c) was sensitometrically exposed and developed in the M–4 X-Omat system, with the following results:

Experiment	Speed	Fog	$D_{max.}$	Ag, g./dm.
(a)	100	.20	3.50	13.1
(b)	140	.22	4.00	13.0
(c)	140	.15	4.00	12.9

Instead of the anti-foggant bis-tetrazolium salt illustrated in the examples, there can be used with similar effectiveness, the following tetrazolium salts corresponding to the above general formula, wherein the radicals represented by letters are the following:

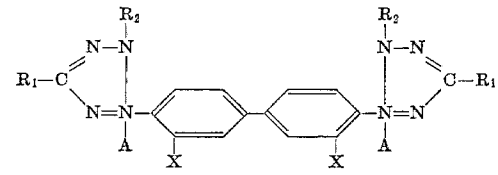
R_1	R_2	X	A
Anisyl	Phenyl	Methoxy	Acetate.
o-Hydroxyphenyl	do	do	Chloride.
3,4-dimethoxyphenyl	do	do	Acetate.
Furyl (2)	do	do	Do.
Thienyl (2)	do	do	Do.
Pyridyl (2)	do	do	Do.
Thionaphthenyl (2)	do	do	Do.
Dibenzothiazolyl (2)	do	do	Chloride.
Phenyl	Pyridyl (2)	do	Acetate.
o-Nitrophenyl	do	do	Do.
o-Chlorophenyl	do	do	Do.
Phenyl	Quinolyl (2)	do	Do.
o-Nitrophenyl	do	do	Do.
o-Chlorophenyl	do	do	Do.
Furyl	Pyridyl (2)	do	Chloride.
Pyridyl (2)	do	do	Acetate.
Pyridyl (4)	do	do	Do.
Thionaphthenyl (2)	do	do	Do.
Furyl	Quinolyl (2)	do	Do.
Thienyl	Phenyl	H	Chloride.

The aforesaid salts are similarly effective when incorporated in a layer adjacent to the silver halide emulsion layer in photographic light-sensitive material.

Variations and modifications which will be obvious to those skilled in the art can be made in the foregoing examples without departing from the scope or spirit of the invention.

We claim:

1. A light-sensitive silver halide emulsion containing a fog-reducing amount of an antifoggant comprising a compound of the following general formula:



wherein R_1 and R_2 are independently selected from the group consisting of aryl and heterocyclic radicals, X represents a member selected from the group consisting of hydrogen, chlorine, methyl and methoxy groups, and A represents the anion of a salt-forming acid.

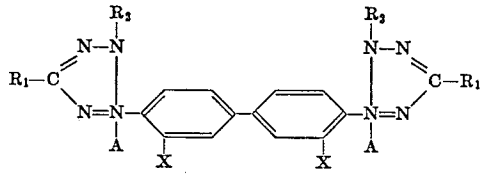
2. A light-sensitive silver halide emulsion as defined in claim **1**, wherein said antifoggant is present in a concentration of 0.05 to 0.5 mg. per mol of silver halide.

3. A light-sensitive silver halide emulsion as defined in claim **1**, wherein said emulsion contains at least one member selected from the group consisting of sensitizers and accelerators.

4. A light-sensitive silver halide emulsion as defined in claim **1**, wherein said antifoggant is 2,2'-(m,m'-dimethoxy-p,p'-biphenylene)-bis-(3,5-diphenyltetrazolium chloride).

5. A light-sensitive photographic material comprising a base and a light-sensitive silver halide emulsion layer thereon, said light-sensitive material containing in a layer selected from the group consisting of said silver halide emulsion layer and a layer contiguous therewith, a fog-

reducing amount of an antifoggant comprising a compound of the following general formula:



wherein R_1 and R_2 are independently selected from the group consisting of aryl and heterocyclic radicals, X represents a member selected from the group consisting of hydrogen, chlorine, methyl and methoxy groups, and A represents the anion of a salt-forming acid.

6. A light-sensitive photographic material as defined in claim 5, wherein said antifoggant is included in said layer contiguous with said silver halide emulsion layer.

7. A light-sensitive photographic material as defined in claim 5, wherein said antifoggant is included in said silver halide emulsion layer.

8. A light-sensitive photographic material as defined in claim 7, wherein said silver halide emulsion layer contains a member selected from the group consisting of sensitizers and accelerators.

9. A light-sensitive photographic material as defined in claim 5, wherein the quantity of said antifoggant is from 0.05 to 0.5 mg. per mol of silver halide.

10. A light-sensitive photographic material as defined in claim 5, wherein said antifoggant is 2,2'-(m,m'-dimethoxy-p,p'-biphenylene) - bis - (3,5 - diphenyltetrazolium chloride).

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