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2,955,038

SENSITIZED SILVER HALIDE EMULSIONS

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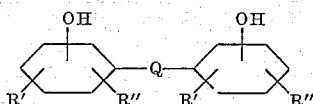
This invention relates to photographic silver halide emulsions and more particularly to such emulsions containing a non-optical sensitizing agent having at least one polyoxyalkylene group containing at least two oxyalkylene radicals and a small amount of a bisphenol. The invention also relates to photographic elements, e.g., films and papers bearing at least one layer of such an emulsion.

It is known that photographic silver halide emulsions which have been sensitized to very high levels tend to produce fog on development. This photographic fog is due to the existence in the emulsion of silver halide grains which are developable without exposure to light. In addition, fog may be produced in photographic emulsions during storage, particularly under adverse conditions of temperature and humidity.

As is well known, the sensitivity of photographic emulsions can be increased in a number of ways. One of these is by adding derivatives of alkylene oxides, such as polyoxide with acids, alcohols, or amines such as taught, for instance, by Blake et al. U.S. 2,400,532; Blake U.S. 2,423,549, Blake U.S. 2,441,389 and Carroll et al. 2,716,062. However, these compounds tend to cause fog when photographic materials, the emulsion of which contain them, are stored for any length of time. Attempts to reduce this fog have involved the use of antifogging agents which are frequently detrimental to certain photographic properties. In particular, such antifogging agents tend to reduce the photographic speed of film exposed to relatively low intensity illumination.

It is therefore an object of this invention to provide means for reducing fog in photographic emulsions. Another object is to reduce fog produced on storage of emulsions, particularly in tropical climates or under other adverse conditions of temperature and humidity. A further object of this invention is to provide silver halide emulsions sensitized with alkylene oxide polymers of improved stability and less tendency to form an objectionable amount of fog on normal storage of photographic elements embodying such emulsions. Still other objects are to achieve the above results without reducing speed or contrast and, in particular, without reducing the speed of the emulsion to low intensity illumination.

The above objects are attained and photographic emulsions and emulsion layers of good stability, speed and contrast which exhibit low fog values upon aging at normal temperatures for extended periods are provided, in accordance with the invention, by admixing (a) fog-inhibiting amounts of a bisphenol of the general formula



wherein Q is a direct carbon-to-carbon linkage —S—, —O—, (—CH₂—)_n where n is 1 to 10, or



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where each of R and R₁ is an alkyl radical of 1 to 18 carbon atoms, R' and R'' are the same or different and are hydrogen, alkyl of 1 to 18 carbon atoms, cycloalkyl, or aryl, and the hydroxyl groups preferably are in the o- or p-position to the radical —Q— with (b) a photographic silver halide emulsion containing sensitizing amounts of a non-optical or chemical emulsion sensitizing agent having a molecular weight of at least 282 and containing at least two, and preferably at least six, oxyalkylene units of two to four carbon atoms.

In the above formula suitable alkyl radicals include methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, pentyl, n-hexyl, n-octyl and t-octyl. Useful aryl radicals include phenyl and naphthyl, and suitable cycloalkyl radicals are cyclopentyl and cyclohexyl.

Many of the bis-type phenols useful in the invention are commercially available and others can be made in like manner by the known prior art procedures including those described in British specification 621,004 and 622,977; U.S. Patent 2,506,486 and those described in J. Am. Chem. Soc. vol. 54, 4325–34 (1932) and vol. 59, 1114 (1937) and Proc. Roy. Soc. vol. 129B, 528–538 (1940).

It has been found that when one or more of the bis-type phenols are added to a sensitized emulsion, as described above, in an amount of 4.7 to 30 millimoles per mole of silver halide, that the speed (i.e., the response of the emulsion to radiation of both high and low intensity), contrast and fog values of the resulting emulsions remain substantially at the initial values of the emulsion prior to the addition of the bis-type phenol, even when the emulsions or emulsion layers, are maintained under adverse storage conditions for a short or extended period of time, e.g., at an elevated temperature and/or under conditions of high humidity.

The invention is not limited to any particular type of light-sensitive silver halide as it is useful with silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver iodide, etc., emulsions and mixed emulsions of these types. It is particularly efficacious in silver iodobromide emulsions containing about 2 mole percent iodide and the rest bromide. These emulsions may be sensitized by means of chemical sensitizing agents other than the polyoxyalkylene polymers mentioned above. Thus, noble metal sensitizers, e.g., gold salts, e.g., chlorauric acid and auric trichloride, may be present in association with sulfur sensitizers, e.g., sodium sulfite, thiosinamine, allylthiourea, sodium thiosulfate, allyl thiocarbamate, alkali metal thiocyanates and sodium sulfide, these sensitizers to be used in amounts up to 0.005% based on the weight of the silver halide. Moreover, the silver halide emulsions may contain one or more optical sensitizing agents, e.g., cyanine, carbocyanine, merocyanine, pseudocyanine, cyazine etc., dyes.

With regard to the non-optical sensitizers which contain at least one polyoxyalkylene group, there are a relatively large number of such compounds known to the art, suitable compounds being described in the above patents. These compounds include not only the polyalkylene oxides or glycols wherein the oxyalkylene groups contain 2 to 4 carbon atoms but also the condensation products of alkylene oxides of 2 to 4 carbon atoms with glycols, fatty acids, saturated aliphatic amines, and hexitol ring dehydration products, said compounds having a molecular weight of at least 282, suitable specific compounds of which are disclosed in the aforesaid patents. In general, these sensitizing compounds are present in amounts from 0.1 to 2.0 g. per mole of silver halide.

While gelatin is the preferred binding agent for the silver halide grains, other water-permeable amphoteric protein protective colloids, e.g., albumin and casein, can be used. Also, agar-agar, alginic acid and the alginates, polyglycuronic acid, polyvinyl alcohol, polyvinyl acetals

including those containing color-forming nuclei, and other natural or synthetic water-permeable colloids useful in making photographic emulsions can be used as the original colloid during the precipitation, or in the final emulsion as bulking agents.

The bis-type phenols preferably are added to the silver halide emulsion after it has been brought to its maximum sensitivity and the conventional adjuvants are added just prior to coating onto a suitable support to form a photographic element. They can, of course, be added at an earlier stage, that is, at the time of second digestion.

The invention will now be further illustrated by but is not intended to be limited to the following examples, wherein the silver halide weight ratio, unless otherwise indicated, is 1.6 mole percent iodide and the remainder bromide. In these examples the emulsions were prepared and coated in the essential absence of actinic radiation, as is customary in the photographic art.

Example 1

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of a condensation product of polyethylene oxide with oleyl alcohol (I) having an average molecular weight of approximately 900 ("Emulphor" ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.5 g. of the condensation product (I) per mole of silver halide together with 5.5 millimoles of 2,2'-methylenebis(4-methyl-6-t-butyl-phenol) (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control. The emulsions were coated on cellulose acetate film base and were exposed to X-rays in the presence of an intensifying screen at two different intensity levels. The exposure of greater intensity has been designated as No. 2 and that of lower intensity and longer time as No. 1.

The coatings were developed for 5 minutes in a developer of the following composition:

	Grams
Metol	3
Anhydrous sodium sulfite	50
Hydroquinone	9
Anhydrous potassium carbonate	50
Potassium bromide	4.5
Water to make 1000 ml.	

The coatings were tested fresh, after two months of room aging, and after one week at 120° F. and 65% R.H. (relative humidity). The aged materials were exposed and developed as described above. Results of tests for speed, gamma and fog, before and after the storage treatment of each of the samples, are given below. Speed is given in terms of a reciprocal of exposure at a density of 0.7. If fog is greater than 0.40 the speed and gamma numbers are of no significance and are therefore not included in such cases.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	820	2.38	420	2.36	.12
I.....	0.5 g.....	940	3.07	400	2.70	.40
I plus II.....	0.5 g.+5.5 millimoles.	940	2.60	420	2.46	.18

1 MONTH ROOM AGING

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	720	2.28	370	1.97	.15
I.....	0.5 g.....	810	2.96	390	2.54	.38
I plus II.....	0.5 g.+5.5 millimoles.	890	2.54	400	2.08	.17

ONE WEEK AT 120° F. AND 65% R.H.

						Fog
Control.....						.14
I.....						1.04
I plus II.....						.24

Example 2

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of polyethylene oxide (I) having an average molecular weight of from 6000-7500 ("Carbowax 6000") per mole of silver halide. To a second portion were added 0.5 g. of the polyethylene oxide per mole of silver halide together with 30 millimoles of 4,4'-methylenebis(2-t-butyl-6-methylphenol) (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	740	2.29	370	2.11	.26
I.....	0.5 g.....					.60
I plus II.....	0.5 g.+30 millimoles.	830	2.70	400	2.33	.23

ONE MONTH ROOM AGING

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control.....	640	2.10	340	1.87	.24
I.....					.71
I plus II.....	650	2.43	360	2.05	.24

ONE WEEK AT 120° F. AND 65% R.H.

						Fog
Control.....						.46
I.....						2.30
I plus II.....						.48

Example 3

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of polyethylene oxide (I) having an average molecular weight of from 6000-7500 ("Carbowax 6000") per mole of silver halide. To a second portion were added 0.5 g. of the polyethylene oxide per mole of silver halide together with 30 millimoles of 2,2'-methylenebis(4-t-butyl-6-methylphenol) (M.P. 137°-139° C.) (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	720	2.37	390	2.09	.26
I.....	0.5 g.....					.58
I plus II.....	0.5 g.+ 30 millimoles.	860	2.79	450	2.69	.22

1 MONTH ROOM AGING

Compound		No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....		750	2.29	410	2.12	.25
I.....						1.02
I plus II.....		880	2.78	430	2.44	.24

ONE WEEK AT 120° F. AND 65% R.H.

						Fog
Control.....						.24
I.....						2.18
I plus II.....						.24

Example 4

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.67 g. of Emulphor ON (I) having an average molecular weight of approximately 900 (Emulphor ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.67 g. of the Emulphor ON per mole of silver halide together with 20.8 millimoles of 2,2'-methylenebis(4-ethyl-6-t-butylphenol) (II) (Manufactured by the American Cyanamid Company) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	880	2.53	410	2.20	.15
I.....	0.67 g.....	1,044	2.91	440	2.37	.26
I plus II.....	0.67 g.+20.4 millimoles.	960	2.50	415	2.11	.17

1 MONTH ROOM AGING

Compound		No. 2 Exposure		Fog
		Speed	Gamma	
Control.....		920	2.45	.16
I.....		1,108	2.88	.26
I plus II.....		920	2.52	.17

ONE WEEK AT 120° F. AND 65% R.H.

						Fog
Control.....						.15
I.....						.74
I plus II.....						.14

Example 5

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.67 g. of Emulphor ON (I) having an average molecular weight of approximately 900 (Emulphor ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.67 g. of the Emulphor ON per mole of silver halide together with 10.4 millimoles of 2,2'-methylenebis(3,4-dimethyl-6-n-octylphenol) (II) (amorphous solid melting at room temperature) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	732	2.46	404	2.09	.26
I.....	0.67 g.....					.56
I plus II.....	0.67 g.+10.4 millimoles.	1,010	2.70	456	2.19	.28

1 MONTH ROOM AGING

Compound		No. 2 Exposure		Fog
		Speed	Gamma	
Control.....		818	2.29	.26
I.....				.52
I plus II.....		1,036	2.68	.30

ONE WEEK AT 120° F. AND 65% R.H.

						Fog
Control.....						.30
I.....						.94
I plus II.....						.60

Example 6

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of polyethylene oxide (I) having an average molecular weight of from 6000-7500 ("Carbowax 6000") per mole of silver halide. To a second portion were added 0.5 g. of the polyethylene oxide per mole of silver halide together with 7.5 millimoles of 2,2'-n-butylidenebis(4,6-di-t-butylphenol), M.P. 113°-114° C., (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	790	3.04	430	2.53	.29
I.....	0.5 g.....					.63
I plus II.....	0.5 g.+7.5 millimoles.	860	2.62	450	2.29	.19

1 MONTH ROOM AGING

Compound		No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....		640	2.48	410	2.35	.33
I.....						1.06
I plus II.....		770	2.30	390	2.19	.16

ONE WEEK AT 120° F. AND 65% R.H.

	Fog
Control.....	.30
I.....	2.16
I plus II.....	.24

Example 7

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of a condensation product of polyethylene oxide with oleyl alcohol (I) having an average molecular weight of approximately 900 ("Emulphor" ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.5 g. of the condensation product (I) per mole of silver halide together with 15 millimoles of 2,2'-ethylidenebis(4-methyl - 6-t - octylphenol) (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

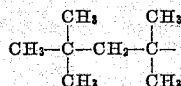
FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	650	2.26	380	2.18	.39
I.....	0.5 g.....					.61
I plus II.....	0.5 g.+ 15 millimoles.	940	2.34	410	2.06	.20

ONE WEEK AT 120° F. AND 65% R.H.

	Fog
Control.....	.60
I.....	1.10
I plus II.....	.74

The t-octyl radical has the formula

**Example 8**

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds was divided into three portions. One portion was treated with 0.5 g. of a condensation product of polyethylene oxide with oleyl alcohol (I) having an average molecular weight of approximately 900 ("Emulphor" ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.5 g. of the condensation product (I) per mole of silver halide together with 15 millimoles of 4,4'-isopropylidenebisphenol manufactured by the Dow Chemical Company (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	650	2.26	380	2.18	.39
I.....	0.5 g.....					.61
I plus II.....	0.5 g.+15 millimoles.	760	2.22	410	2.33	.18

5 MONTHS ROOM AGING

Compound	No. 2 Exposure		Fog
	Speed	Gamma	
Control.....	570	2.11	.36
I.....			.44
I plus II.....	650	2.29	.18

ONE WEEK AT 120° F. AND 65% R.H.

	Fog
Control.....	.60
I.....	1.10
I plus II.....	.60

Example 9

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds was divided into three portions. One portion was treated with 0.67 g. of Emulphor ON (I) having an average molecular weight of approximately 900 (Emulphor ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.67 g. of the Emulphor ON per mole of silver halide together with 4.7 millimoles of 2,2'-n-butylidenebis(6-cyclohexyl-4-ethyl phenol) (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	910	2.19	430	2.23	.32
I.....	0.67 g.....					.64
I plus II.....	0.67 g.+4.7 millimoles.	1,028	2.59	470	2.20	.34

1 MONTH ROOM AGING

Compound	No. 2 Exposure		Fog
	Speed	Gamma	
Control.....	878	2.39	.36
I.....			.65
I plus II.....	1,000	2.50	.34

ONE WEEK AT 120° F. AND 65% R.H.

	Fog
Control.....	.34
I.....	1.25
I plus II.....	.74

Example 10

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds was divided into three portions. One portion was treated with 0.67 g. of Emulphor ON (I) having an average molecular weight of approximately 900 (Emulphor ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.67 g. of the Emulphor ON per mole of silver halide together with 5.2 millimoles of 2,2'-n-butylidenebis(4-isopropylphenol) (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	910	2.19	430	2.23	.32
I.....	0.67 g.....					.64
I plus II.....	0.67 g. + 5.2 millimoles.	1,000	2.41	458	2.59	.28

1 MONTH ROOM AGING

Compound	No. 2 Exposure		Fog
	Speed	Gamma	
Control.....	878	2.39	.36
I.....			.68
I plus II.....	996	2.62	.28

ONE WEEK AT 120° F. and 65% R.H.

Compound	No. 2 Exposure		Fog
	Speed	Gamma	
Control.....			.34
I.....			1.25
I plus II.....			.28

Example 11

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds was divided into three portions. One portion was treated with 0.67 g. of Emulphor ON (I) having an average molecular weight of approximately 900 (Emulphor ON-870—General Aniline & Film Corp.) per mole of silver halide. To a second portion were added 0.67 g. of the Emulphor ON per mole of silver halide together with 10.4 millimoles of 2,2'-n-butyldienebis(4-methylphenol) (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	910	2.19	430	2.23	.32
I.....	0.67 g.....					.64
I plus II.....	0.67 g. + 10.4 millimoles.	1,000	2.91	468	2.64	.32

1 MONTH ROOM AGING

Compound	No. 2 Exposure		Fog
	Speed	Gamma	
Control.....	878	2.39	.36
I.....			.68
I plus II.....	960	3.10	.36

ONE WEEK AT 120° F. AND 65% R.H.

Compound	No. 2 Exposure		Fog
	Speed	Gamma	
Control.....			.34
I.....			.25
I plus II.....			.42

Example 12

A high-speed gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds was divided into three portions. One portion was treated with 0.5 g. of polyethylene oxide (I) having an average molecular weight of from 6000-7500 ("Carbowax" 6000—Carbide

and Carbon Chemicals) per mole of silver halide. To a second portion were added 0.5 g. of the polyethylene oxide per mole of silver halide together with 7.5 millimoles of bis(2-methyl-4-hydroxy-5-t-butylphenyl)sulfide (II) per mole of silver halide. Neither of these additions were made to a third portion, which was used as a control.

Coating, exposure, and development were carried out as in Example 1.

FRESH RESULTS

Compound	Amount per Mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control.....	None.....	720	2.37	390	2.09	.26
I.....	0.5 g.....					.58
I plus II.....	0.5 g. + 7.5 millimoles.	830	2.30	430	2.34	.16

1 MONTH ROOM AGING

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control.....	750	2.29	410	2.12	.25
I.....					1.02
I plus II.....	830	2.13	440	2.12	.14

ONE WEEK AT 120° F. AND 65% R.H.

Compound	No. 2 Exposure		Fog
	Speed	Gamma	
Control.....			.24
I.....			2.18
I plus II.....			.16

In the foregoing examples, the Exposure No. 2 is obtained by using an X-ray tube operated at 71 kvp., 150 milliamps. for $\frac{1}{10}$ second (i.e., 15 milliamp. seconds). A Dupont Par Speed Intensifying Screen is used together with a 1 mm. aluminum filter, and the samples are exposed at a distance of 55 inches from the tube. The Exposure No. 1 is obtained by using an X-ray tube operated at 60 kvp., 7 milliamps. for 9 seconds (i.e., 63 milliamp. seconds). A Dupont Par Speed Intensifying Screen is used. The samples are exposed at a distance of 38 inches from the tube with a $\frac{1}{2}$ mm. aluminum filter in place.

Similar results can be obtained by substituting for the particular bis-type phenols equivalent amounts within the range specified above of p,p'-bisphenol, 4,4'-sec-butylidenebisphenol, 4,4'-n-butyldienebis(2-t-butyl-5-methylphenol), 2,2'-n-butyldienebis(4-ethyl-6-t-butylphenol), 4,4'-n-butyldienebis(2-cyclohexylphenol), 4,4'-n-butyldienebis(2-phenylphenol) or 2,2'-methylenebis(3,4-dimethyl-6-t-butylphenol). Other useful bisphenols include 2,2'- and 4,4'-ethylenebisphenols and higher polymethylenebisphenols which contain 3 to 10 methylene groups between the phenol nuclei wherein the hydroxyl groups are in the ortho- and para-positions. These compounds can be prepared as described in J. Am. Chem. Soc., vol. 62, pp. 413-15 (1940) and J. Chem. Soc. 1942, p. 6849. An important class of compounds is that which contains a chalcogen of atomic number not greater than 16 between two hydroxyphenyl groups which are in the o- or p-position to the ether linkage. While it is preferable to use a single phenolic compound in the emulsions, mixtures of any two or even more of any of the above bis-type phenols can be used in the emulsions.

The bis-type phenols used in accordance with the invention are generally added to the emulsions after digestion and after addition of the polyoxyalkylene sensitizing compound. At the same time other compounds having antifogging properties can be added to the emul-

sions. Suitable antifogging agents which can be used include benzotriazole nitrobenzimidazole, 1-phenyl-5-mercaptotetrazole, and benzothiazole.

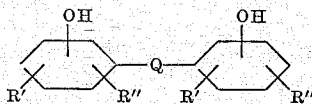
The resulting photographic emulsions can be coated onto any suitable support to make the desired type of photographic element. Suitable supports include cellulose esters, e.g., cellulose acetate, cellulose nitrate, cellulose acetate butyrate, cellulose propionate; super polymers, e. g., nylon, polyethylene terephthalate, polyvinyl chloride, poly(vinyl chloride co vinyl acetate) and vinylidene chloride copolymers with vinyl acetate, acrylonitrile, etc.; metal sheets or foils, e.g., aluminum and zinc; and paper including resin-coated and baryta-coated paper; as well as glass plates, inter alia.

An advantage of this invention is that it provides photographic emulsions and elements with improved stability and aging characteristics. It enables one to obtain the useful sensitizing action of the polyoxyalkylene compounds without an undue degree of fog being formed upon storage of the photographic elements for long periods.

Another advantage is that the improved emulsions and emulsion layers can be made by the addition of readily available chemical compounds. A further advantage is that the improved emulsions do not require the use of expensive chemicals or tedious procedures. A still further advantage is that the speed of the afore-described silver halide emulsions to light of various intensities is not affected to the same degree as known non-phenolic antifogging agents. A closely related advantage is that while the bis-type phenols have an adequate antifogging action in photographic silver halide emulsions sensitized with the polyoxyalkylene compounds referred to above and disclosed in the cited patents, they do not have any significant adverse effect on other photographic properties, e.g., contrast, graininess, resolution, optical sensitization and latent image stability. Hence, once the emulsion is adjusted to have its optimum desired properties, the admixture of the bis-type phenols confers additional stabilizing and antifogging characteristics.

What is claimed is:

1. A water-permeable colloid silver halide emulsion containing per mole of silver halide (1) from 4.7 to 30.0 millimoles of a non-optical sensitizing agent having a molecular weight of at least 282 and containing at least one polyoxyalkylene group having at least two oxyalkylene radicals of 2 to 4 carbon atoms taken from the group consisting of condensation products of alkylene oxides of 2-4 carbon atoms with glycols, fatty acids, saturated aliphatic amines and hexitol ring dehydration products, and (2) from 5-50 millimoles of at least one compound of the general formula



wherein Q is a member taken from the group consist-

ing of a direct carbon-to-carbon linkage, —O—, —S—, —(CH₂)_n— where n is 1 to 4, and



where each of R and R₁ is an alkyl radical of 1 to 18 carbon atoms, and R' and R'' are each a member taken from the class consisting of H, alkyl of 1 to 18 carbon atoms, cycloalkyl and aryl.

2. An emulsion as set forth in claim 1 wherein said sensitizing agent is a polyethylene ether glycol having a molecular weight of at least 1500.

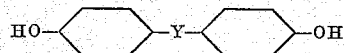
3. An emulsion as set forth in claim 1 wherein said silver halide is silver iodobromide.

4. An emulsion as set forth in claim 1 wherein said colloid is gelatin.

5. A water permeable colloid silver halide emulsion containing per mole of silver halide (1) from 4.7 to 30.0 millimoles of a non-optical sensitizing agent having a molecular weight of at least 282 and containing at least one polyoxyalkylene group having at least two oxyalkylene radicals of 2 to 4 carbon atoms taken from the group consisting of condensation products of alkylene oxides of 2-4 carbon atoms with glycols, fatty acids, saturated aliphatic amines and hexitol ring dehydration products, and (2) from 0.1 to 2.0 grams of an unsubstituted o,o'-alkylidenebisphenol.

6. An emulsion as set forth in claim 5 wherein said colloid is gelatin.

7. A water-permeable colloid silver halide emulsion containing per mole of silver halide (1) from 4.7 to 30.0 millimoles of a non-optical sensitizing agent having a molecular weight of at least 282 and containing at least one polyoxyalkylene group having at least two oxyalkylene radicals of 2 to 4 carbon atoms taken from the group consisting of condensation products of alkylene oxides of 2-4 carbon atoms with glycols, fatty acids, saturated aliphatic amines and hexitol ring dehydration products, and (2) from 0.1 to 2.0 grams of a bisphenol of the formula



where Y is a chalcogen of atomic number not greater than 16.

8. A photographic element comprising a support bearing at least one layer composed of a photographic emulsion as set forth in claim 1.

9. An element as set forth in claim 8 wherein said support is a hydrophobic film base.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,955,038

October 4, 1960

Thomas David Smith

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 11, lines 45 and 46, for "4.7 to 30.0 millimols" read -- 0.1 to 2.0 grams --; line 53, for "5-50" read -- 4.7 to 30.0 --; column 12, lines 19 and 20, for "4.7 to 30.0 millimoles" read -- 0.1 to 2.0 grams --; line 27, for "0.1 to 2.0 grams" read -- 4.7 to 30.0 millimoles --; lines 32 and 33, for "4.7 to 30.0 millimoles" read -- 0.1 to 2.0 grams --; line 40, for "0.1 to 2.0 grams" read -- 4.7 to 30.0 millimoles --.

Signed and sealed this 14th day of November 1961.

(SEAL)

Attest:

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