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PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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This invention relates to photography, and more particularly to photographic silver halide emulsions containing a non-optical sensitizing agent having at least one polyoxyalkylene group containing at least two oxyalkylene radicals. Still more particularly, it relates to such emulsions containing a hydrocarbon-substituted mononuclear monohydric phenol of at least ten carbon atoms wherein the hydrocarbon substituent is in one of the positions ortho or meta to the hydroxyl groups and the other positions are unsubstituted. 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.

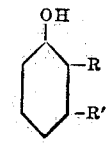
As is well known, the sensitivity of photographic emulsions can be increased in a number of ways. One of these is by adding derivatives of alkylene oxides, such as polyethylene oxide or condensation products of polyethylene oxide with acids, alcohols or amines such as taught, for instance, by Blake et 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 emulsions 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 antifoggants 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 relatively small amounts of at least one hydrocarbon-substituted mononuclear monohydric phenol of at least nine carbon atoms wherein said substituent is in the ortho or meta position to the phenolic hydroxyl group, with 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.

The mononuclear monohydric phenols used in accordance with the invention can be represented by the general formula:



wherein one of the radicals R and R' is hydrogen and the other is a hydrocarbon radical of at least 3 carbon atoms. The hydrocarbon radicals may be alkyl, cycloalkyl, aryl and aralkyl. The alkyl radicals may contain 3 to 12 or more carbon atoms and suitable alkyl radicals are t-butyl, sec-amyl, t-amyl and t-octyl, n-nonyl and n-dodecyl. Suitable cycloalkyl radicals are cyclopentyl and cyclohexyl. Useful aryl radicals include phenyl, naphthyl and biphenyl. Suitable aralkyl radicals include benzyl, α-cumyl and naphthylmethyl.

In an important specific embodiment of the invention the hydrocarbon-substituted mononuclear monohydric phenols have a hydrocarbon substituent attached to the nuclear carbon atom through a saturated hydrocarbon radical which is attached to at least two additional hydrocarbon radicals. Suitable such substituents are isoalkyl, t-alkyl and cycloalkyl.

It has been discovered that when 5 to 50 millimoles of at least one hydrocarbon substituted mononuclear monohydric phenol of the type described above is used per mole of silver halide in the sensitized emulsions 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 said 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 hydrocarbon-substituted mononuclear monohydric phenols are preferably 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 gelatino silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with .53 g. of a polyethylene oxide having an average molecular weight of 6000–7500 (I) ("Carbowax 6000" manufactured by the Carbide and Carbon Chemical Company), per mole of silver halide. To a second portion was added .53 g. of the polyethylene oxide per mole of silver halide together with 20 millimoles of o-benzylphenol (II).

The coatings were tested fresh, after one month of room aging, and after one week at 120° F. and 65% R.H. (relative humidity). The exposed photographic films were then processed (*a*) by being developed for 5 minutes in a developer of the following composition:

	Grams
N-methyl-p-aminophenol hydrosulfate	3
Anhydrous sodium sulfite	50
Hydroquinone	9
Anhydrous potassium carbonate	50
Potassium bromide	4.5
Water to make 1000 ml.	

and (*b*) by being fixed for 5 minutes in a fixing solution of the following composition:

Sodium thiosulfate, anhydrous	grams	153
Sodium sulfite, anhydrous	do	15
Borax	do	18
Glacial acetic acid	ml	12
Potassium alum ($12H_2O$)	grams	20
Water to make 1 liter.		

Results of tests for speed, gamma and fog, before and after storage treatment 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	680	2.41	320	2.15	.29
Polyethylene oxide I.	.53 g.					.56
I plus II	53 g. 20 millimoles.	630	2.36	320	2.92	.31

[One month room aging]

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control	640	2.38	350	2.27	.38
I					.88
I plus II	685	2.36	340	1.83	.35

[One week at 120° F. and 65% R.H. (Relative humidity)]

	Fog
Control	.24
I	1.84
I plus II	.28

Example 2

A gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with .53 g. of (I) the polyethylene oxide described in Example 1 per mole of silver halide. To a second portion was added .53 g. of the polyethylene oxide together with 20 millimoles of (II) o-phenylphenol per mole of silver halide. Coating, exposure, processing and aging 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	3.06	420	2.53	.29
Polyethylene oxide I.	.53 g.					
I plus II	.53 g. 20 millimoles.	820	2.54	450	2.17	.36

[One 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	800	2.46	440	2.35	.32

[One week at 120° F. and 65% R.H.]

	Fog
Control	.30
I	2.16
I plus II	.54

Example 3

A gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 1.1 g. of the condensation products of polyethylene oxide with oleyl alcohol (I) having a molecular weight of approximately 900 ("Emulphor" ON–870 manufactured by the Antara Chemicals Division, General Aniline and Film Corp.), per mole of silver halide. To a second portion was added 1.1 g. of the above condensation product together with 20 millimoles of o-phenylphenol (II) per mole of silver halide.

Coating, exposure, processing and aging 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	690	2.54	480	2.19	.37
Polyoxyethylated oleyl alcohol I.	1.1 g.					.48
I plus II	1.1 g. 20 millimoles.	890	2.65	550	2.28	.36

[One month room aging]

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control	670	2.25	400	1.93	.28
I	850	2.58	400	2.05	.36
I plus II	880	2.43	500	1.83	.20

[One week at 120° F. and 65% R.H.]

	Fog
Control	.57
I	.90
I plus II	.42

Example 4

A gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of the polyoxyethylated oleyl alcohol condensation product (I) of Example 2 per mole of silver halide. To a second portion was added 0.5 g. of the above condensation product per mole of silver halide together with 20 millimoles of o-cyclohexylphenol (II).

Coating, exposure, processing and aging 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	690	2.54	480	2.19	.37
I polyoxyethylated oleyl alcohol.	0.5 g.					.48
I plus II	0.5 g. 20 millimoles.	910	2.45	490	2.35	.27

[One month room aging]

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control	670	2.25	400	1.93	.28
I	850	2.58	400	2.05	.36
I plus II	880	2.17	440	1.94	.16

[One week at 120° F. and 65% R.H.]

	Fog
Control	.57
I	.90
I plus II	.42

Example 5

A gelatino-silver iodobromide emulsion, digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of the condensation product of Example 3 per mole of silver halide. To a second portion there was added 0.5 g. of the above condensation product per mole of silver halide together with 10 millimoles of m-cyclohexylphenol.

Coating, exposure, processing and aging 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	2.40	420	2.40	.25
I polyoxyethylated oleyl alcohol.	0.5 g.					.50
I plus II	0.5 g. millimoles.	910	2.49	360	2.49	.21

[One month room aging]

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control	690	2.18	350	1.83	.20
I					.44
I plus II	840	2.41	390	2.04	.18

[One week at 120° F. and 65% R.H.]

	Fog
Control	.34
I	.96
I plus II	.38

Example 6

A gelatino-silver iodobromide emulsion digested with sulfur and gold compounds, was divided into three portions. One portion was treated with 0.5 g. of the polyethylene oxide of Example 1 (I) per mole of silver halide. To a second portion was added 0.5 g. of the polyethylene oxide per mole of silver halide together with 20 millimoles of m-phenylphenol (II). Neither of these additions was made to a third portion. Coating, exposure, processing, and aging 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	860	2.70	380	2.34	.15
I	0.5 g.	1,010	2.35	490	1.91	.36
I plus II	0.5 g. 20 millimoles.	720	2.76	420	2.54	.15

[One month room aging]

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control	700	2.19	320	2.11	.13
I					.70
I plus II	700	2.31	330	1.99	.10

[One week at 120° F. and 65% R.H.]

	Fog
Control	.22
I	1.98
I plus II	.32

Example 7

A gelatino-silver iodobromide emulsion, digested with sulfur and gold sensitizing compounds, was divided into three portions. One portion was treated with 0.5 g. of the polyethylene oxide compound (I) of Example 1 per mole of silver halide. A second portion was treated with (I) and 20 millimoles of m-tertiary butyl phenol (II). Neither of these additions was made to a third portion of the emulsion.

Coating, exposure, processing and aging were carried out as in Example 1 except that the aging was for 2 months.

[Fresh results]

Compound	Amount per mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control	none					.45
I	0.5 g					.58
I plus II	0.5 g. 20 millimoles.	830	3.39	400	2.68	.28

[Two months' aging]

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control					.46
I	740	2.87	330	2.49	.38
I plus II	880	3.23	400	2.49	.30

Example 8

A gelatino-silver iodobromide emulsion, digested with sulfur and gold sensitizing compounds was divided into three portions. One portion was treated with 0.5 g. per mole of silver halide of the polyethylene oxide compound (I) of Example 3. To a second portion there was added 0.5 g. of (I) and 20 millimoles of o-isopropylphenol (II) per mole of silver halide. Neither of these additions was made to the third portion. Coating, exposure, processing and aging were carried out as in Example 7.

[Fresh results]

Compound	Amount per mole	No. 2 Exposure		No. 1 Exposure		Fog
		Speed	Gamma	Speed	Gamma	
Control	none					.45
I	0.5 g					.58
I plus II	0.5 g. 20 millimoles.	830	3.31	400	2.75	.40

[Two months' aging]

Compound	No. 2 Exposure		No. 1 Exposure		Fog
	Speed	Gamma	Speed	Gamma	
Control					.46
I	740	3.29	330	2.49	.38
I plus II	760	3.83	420	2.82	.36

In place of the specific hydrocarbon-substituted mononuclear monohydric phenols used in the foregoing examples there may be substituted one or more other such compounds falling within the generic characterization given above. Suitable additional compounds include ortho-n-butylphenol, ortho-t-butylphenol, and o-sec-amylphenol. These compounds are generally added after digestion and after addition of the polyoxyalkylene sensitizing compound. At the same time other compounds having antifogging properties can be added to the emulsions. 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 aforedescribed silver halide emulsions to light of various intensities is not affected to the same degree as known non-phenolic antifogging agents. A related advantage is that while the hydrocarbon-substituted mononuclear monohydric phenols have an antifogging action in photographic silver halide emulsions sensitized with amphiphilic compounds, they do not have a significant affect on other photographic properties, e.g., contrast, graininess, resolution, optical sensitization and latent image stability.

This application is a continuation-in-part of my copending application Ser. No. 656,181, filed May 1, 1957.

What is claimed is:

1. A water-permeable colloid silver halide emulsion containing per mole of silver halide (1) from 0.1 to 2.0 grams 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 to 50 millimoles of a hydrocarbon-substituted mononuclear monohydric phenol of at least 9 carbon atoms wherein the hydrocarbon substituent contains 3 to 12 carbon atoms and is in one of the positions ortho- and meta- to the hydroxyl group and the other positions of the benzene ring are unsubstituted.

2. An emulsion as set forth in claim 1 wherein said hydrocarbon substituent is an alkyl radical of 4 to 12 carbon atoms.

3. An emulsion as set forth in claim 1 wherein said hydrocarbon substituent is a cyclohexyl substituent.

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

5. An emulsion as set forth in claim 1 wherein said sensitizing agent is a polyethylene oxide having an average molecular weight of at least 1500.

6. An emulsion as set forth in claim 1 wherein said agent is a condensation product of ethylene oxide with oleyl alcohol.

7. An emulsion as set forth in claim 1 wherein said phenol is o-benzylphenol.

8. An emulsion as set forth in claim 1 wherein said phenol is o-phenylphenol.

9. An emulsion as set forth in claim 1 wherein said phenol is m-tertiary butylphenol.

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

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

12. An element as set forth in claim 11 wherein said support is a hydrophobic film base.

13. An element as set forth in claim 11 wherein said support embodies a polyethylene terephthalate film base.

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