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PHOSPHATE ANTIFOGGANTS FOR PHOTOGRAPHIC EMULSIONS

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ABSTRACT OF THE DISCLOSURE

A photographic silver halide emulsion or photographic element containing as an antifoggant an aryl, alkyl or mixed alkyl-aryl phosphate.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to new and improved antifoggants for photographic elements and to photographic silver halide emulsions containing said antifoggants therein.

Description of the prior art

During development of a silver halide emulsion, small amounts of unexposed silver halide are reduced to metallic silver. This reduction of unexposed silver halide produces an objectionable background fog.

It is often desirable to use developers of high activity to develop photographic films. In addition, certain films such as aerographic and color negative films are often developed for long times even in developers of high activity in order to obtain more information or speed. Kodak D-19 Developer—a high sulfite, high-bromide, Elon-hydroquinone developer—is typical of such developers used with black-and-white emulsions whereas paraphenylene diamine-type developers are used with color films. In the past, such developers have often given rise to excessive fog at long development times with certain spectrally sensitized emulsions.

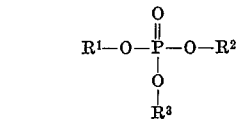
Development fog has been reduced by prior art methods of processing exposed silver halide material in the presence of compounds which restrict development of unexposed silver halide. Such compounds can be incorporated in the silver halide emulsion or in the processing solutions for developing such silver halide emulsions. Although a large number of emulsion antifoggants have been used in the prior art, many of these compounds cause undesirable losses in emulsion speed and contrast while others lack adequate compatibility with the emulsion gelatin.

SUMMARY OF THE INVENTION

According to this invention, there is incorporated into the silver halide emulsion of a photographic element or in a layer contiguous to the silver halide emulsion, from about 0.1 to about 5.0 grams, preferably from about 0.5 to about 1.0 gram, per mole of silver in the emulsion of an aryl phosphate, an alkyl phosphate, a mixed aryl-alkyl phosphate or mixtures thereof. The phosphate may be added to the emulsion or coated onto the element either as an alcoholic solution or in the form of a fine dispersion in gelatin. Use of the phosphate compound results in control of excessive fog formed on forced development of the silver halide emulsion.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred fog stabilizing compounds of this invention have the formula



wherein R^1, R^2 and R^3 may each be the same or different radicals and are alkyl radicals having up to 10 carbon atoms or mononuclear aryl radicals, either or both of which may or may not be substituted. Examples of such radicals include phenyl, cresyl, ethyl, butyl, 2-ethylhexyl, etc. Examples of phosphates falling within the formula include trinonyl phosphate, trioctyl phosphate, chlorophenyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, tributyl phosphate, tri(2-ethylhexyl) phosphate, dicresylmethyl phosphate, diphenylbutyl phosphate, etc.

The silver halide emulsion of a photographic element containing the antifoggants of this invention can contain conventional addenda such as gelatin plasticizers, coating aids, anti-foggants such as the azaindines and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis(sodium bisulfate), maleic dialdehyde, aziridines, dioxane derivatives and oxypolysaccharides. Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Pats. 2,526,632 of Brooker and White issued Oct. 24, 1950, and 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, and hemicyanines. Developing agents can also be incorporated into the silver halide emulsion if desired or can be contained in a separate underlayer. Various silver salts can be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide.

The silver halide emulsion layer of a photographic element containing the antifoggants of the invention can contain any of the hydrophilic, water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumin, polyvinyl compounds, cellulose derivatives, acrylamide polymers, etc. Mixtures of these binding agents can also be used. The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Pats. 3,142,568 of Nottorf issued July 28, 1964; 3,193,386 of White issued July 6, 1965; 3,062,674 of Houck, Smith and Yudelson issued Nov. 6, 1962; and 3,220,844 of Houck, Smith and Yudelson issued Nov. 30, 1965; and include the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The silver halide emulsion of a photographic element containing the antifoggants of the invention can be coated on a wide variety of supports. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthalate) film and related films or resinous materials as well as glass, paper, metal and the like. Supports such as paper which are coated with α-olefin polymers, particularly polymers of α-olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylenebutene copolymers and the like can also be employed.

The speed of photographic emulsions containing the antifoggants of the invention can be further increased

by including in the emulsions a variety of hydrophilic colloids such as carboxymethyl protein of the type described in U.S. Pat. 3,011,890 of Gates, Jr., Miller and Koller issued Dec. 5, 1961, and polysaccharides of the type described in Canadian Pat. 635,206 of Koller and Russell issued Jan. 23, 1962.

Photographic emulsions containing the antifoggants of the instant invention can also contain speed-increasing compounds such as quaternary ammonium compounds, polyethylene glycols or thioethers. Frequently, useful effects can be obtained by adding the aforementioned speed-increasing compounds to the photographic developer solutions instead of, or in addition to, the photographic emulsions.

Photographic elements containing the antifoggants of the invention can be used in various kinds of photographic systems. In addition to being useful in X-ray and other nonoptically sensitized systems they can also be used in orthochromatic, panchromatic and infrared sensitive systems. The sensitizing addenda can be added to photographic systems before or after any sensitizing dyes which are used.

Silver halide emulsions containing the antifoggants of the invention can be used in color photography for example emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type such as described in U.S. Pat. 2,698,794 of Godowsky issued Jan. 4, 1955; in silver dye-bleach systems; and emulsions of the mixed-grain type such as described in U.S. Pat. 2,592,243 of Carroll and Hanson issued Apr. 8, 1952.

Silver halide emulsions containing the antifoggants of the invention can be sensitized using any of the well-known techniques in emulsion making, for example, by digesting with naturally active gelatin or various sulfur, selenium, tellurium compounds and/or gold compounds. The emulsions can also be sensitized with salts of noble metals of Group VIII of the Periodic Table which have an atomic weight greater than 100.

Silver halide emulsions containing the antifoggants of the invention can be used in diffusion transfer processes which utilize the undeveloped silver halide in non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a silver layer in close proximity to the original silver halide emulsion layer. Such processes are described in U.S. Pats. 2,352,014 of Rott issued June 20, 1944; 2,543,181 of Land issued Feb. 27, 1951; and 3,020,155 of Yackel, Yutzy, Foster and Rasch issued Feb. 6, 1962. The emulsions can also be used in diffusion transfer color processes which utilize a diffusion transfer of an imagewise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another.

While it is preferred to utilize the antifoggants of the invention by incorporating them directly into a photographic element, the antifoggants could also be utilized by incorporating them into a photographic developer, since image formation would still take place in the presence of the antifoggants and they would still perform their antifoggant function.

The invention can be further illustrated by the following examples or preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention.

EXAMPLE 1

Triphenyl phosphate is added as a one percent alcoholic solution in an amount of 0.5 gram per silver mole to a panchromatically sensitized, medium-speed silver bromoiodide (3.1 mole percent iodide) emulsion. This emulsion and a control are coated on a polyethylene terephthalate support at a silver coverage of 474 milligrams per square foot, exposed on an intensity scale sensitometer and developed in Kodak D–19 developer with the following results:

	Fog, time in developer—		Relative speed, time in developer—	
	8 min.	20 min.	8 min.	20 min.
Control	0.05	0.56	100	195
Control plus triphenyl phosphate	0.03	0.25	83	148

Kodak D–19 developer employed in this example has the following composition:

	Grams
N-methyl-p-aminophenol sulfate	2.0
Hydroquinone	8.0
Sodium sulfite, desiccated	90.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0

Water to make 1 liter.

EXAMPLE 2

Coatings similar to those in Example 1 are made on a cellulose triacetate support. They are similarly evaluated with the following results:

	Fog, time in developer—		Relative speed, time in developer—	
	8 min.	20 min.	8 min.	20 min.
Control	0.02	0.26	100	200
Control plus triphenyl phosphate	0.03	0.17	91	191

EXAMPLE 3

Triphenyl and tricresyl phosphates are added to emulsions, coated and tested as described in Example 1 with the following results:

	Phosphate, g./silver mole	Fog, time in developer—			Relative speed, time in Developer—		
		8 min.	20 min.	36 min.	8 min.	20 min.	36 min.
Control		0.13	0.67	1.46	100	174	174
Control plus							
Triphenyl phosphate	0.5	0.08	0.42	0.97	82	155	166
Do	1.0	0.07	0.35	0.83	78	148	166
Tricresyl phosphate	0.5	0.08	0.45	1.09	91	166	166
Do	1.0	0.06	0.39	0.93	87	155	166

EXAMPLE 4

Triphenyl phosphate at 0.5 gram per silver mole is added to a high speed silver bromoiodide (4.1 mole percent iodide) panchromatically sensitized emulsion. This emulsion and a control are coated on a polyethylene terephthalate support at a coverage of 667 milligrams

silver per square foot. They are developed in Kodak DK–50 developer with the following results:

	Fog, time in developer—			
	5 min.	12 min.	24 min.	36 min.
Control	0.03	0.22	0.38	0.65
Control plus triphenyl phosphate	0.03	0.04	0.16	0.30

The Kodak DK–50 developer used in this example has the following composition:

	Grams
N-methyl-p-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite, desiccated	30.0
Sodium metaborate	10.0
Potassium bromide	0.5

Water to make 1 liter.

Samples of the films of this example are also developed in Kodak D–19 developer with the following results:

	Fog, time in developer—			
	5 min.	12 min.	24 min.	36 min.
Control	0.06	0.11	0.55	0.94
Control plus triphenyl phosphate	0.06	0.07	0.20	0.36

EXAMPLE 5

Triphenyl phosphate at 0.5 gram per mole of silver is added to a high speed panchromatically sensitized, silver bromoiodide (6.5 mole percent iodide) emulsion. This emulsion and a control are coated on a polyethylene terephthalate support at a coverage of 515 milligrams silver per square foot. They are developed in Kodak D–19 developer with the following results:

	Fog, time in developer—			
	5 min.	12 min.	24 min.	36 min.
Control	0.01	0.07	0.21	0.42
Control plus triphenyl phosphate	0.03	0.08	0.15	0.23

EXAMPLE 6

The process of Example 5 is repeated substituting cellulose acetate for the polyethylene terephthalate support and using the phosphates indicated below with the following results:

	Phosphate, g. per silver mole	Time in developer					
		8 min.		24 min.		36 min.	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
Control		100	0.03	155	0.09	170	0.23
Control plus triphenyl phosphate	1.0	94	0.03	148	0.08	170	0.18
Control plus tributyl phosphate	1.0	97	0.03	155	0.08	174	0.19
Control plus tri(2-ethylhexyl) phosphate	1.0	105	0.02	159	0.09	182	0.21

EXAMPLE 7

The process of Example 5 is repeated using the phosphates indicated below with the following results:

	Phosphate, g. per silver mole	Time in developer					
		8 min.		24 min.		36 min.	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
Control		100	0.04	151	0.14	166	0.33
Control plus tributyl phosphate	1.0	91	0.02	155	0.10	162	0.24
Control plus tri(2-ethylhexyl) phosphate	1.0	95	0.03	148	0.12	162	0.29

Examples 8 and 9 illustrate that optimum results are obtained at concentrations of about 5 grams or below of phosphate in the photographic emulsion. While higher amounts of phosphate may be utilized to control fog, they have a tendency to decrease the speed obtained.

EXAMPLE 8

The process of Example 5 is repeated substituting cellulose acetate for the polyethylene terephthalate support and using the amounts of triphenyl phosphate indicated below with the following results:

	Phosphate, g. per silver mole	Time in developer			
		8 min.		36 min.	
		Relative speed	Fog	Relative speed	Fog
Control		100	0.28	115	0.50
Control plus triphenyl phosphate	0.5	100	0.22	126	0.40
Do	1.0	95	0.20	115	0.34
Do	2.0	87	0.18	100	0.28
Do	4.0	83	0.16	91	0.24
Do	8.0	83	0.12	87	0.18
Do	16.0	80	0.12	87	0.16

EXAMPLE 9

The process of Example 8 is repeated substituting polyethylene terephthalate for the cellulose acetate support with the following results:

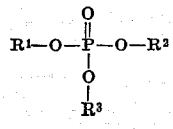
	Phosphate, g. per silver mole	Time in developer			
		8 min.		36 min.	
		Relative speed	Fog	Relative speed	Fog
Control		100	0.40	129	0.82
Control plus triphenyl phosphate	0.5	105	0.29	115	0.54
Do	1.0	95	0.23	110	0.40
Do	2.0	83	0.18	91	0.32
Do	4.0	76	0.15	80	0.22
Do	8.0	73	0.12	80	0.16
Do	16.0	69	0.12	76	0.16

Although the invention has been described in considerable detail with reference to certain embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A photographic silver halide emulsion containing from about 0.1 to about 5.0 grams per mole of silver in said silver halide emulsion of an aryl phosphate, an alkyl phosphate, a mixed aryl-alkyl phosphate or mixtures thereof.

2. The emulsion of claim 1 wherein said phosphate has the formula



wherein R^1, R^2 and R^3 may each be an alkyl radical having up to 10 carbon atoms or a mononuclear aryl radical.

3. The emulsion of claim 1 wherein said phosphate is present in an amount of from about 0.5 gram to about 1.0 gram per mole of silver in said silver halide emulsion.

4. The emulsion of claim 1 wherein said phosphate is triphenyl phosphate.

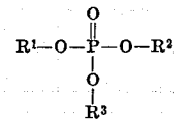
5. The emulsion of claim 1 wherein said phosphate is tricresyl phosphate.

6. The emulsion of claim 1 wherein said phosphate is tributyl phosphate.

7. The emulsion of claim 1 wherein said phosphate is tri(2-ethylhexyl) phosphate.

8. A photographic element comprising a support coated with a silver halide emulsion, said element containing from about 0.1 to about 5.0 grams per mole of silver in said silver halide emulsion of an aryl phosphate, an alkyl phosphate, a mixed aryl-alkyl phosphate or mixtures thereof.

9. The photographic element of claim 8 wherein said phosphate has the formula



wherein R^1, R^2 and R^3 may each be an alkyl radical having up to 10 carbon atoms or a mononuclear aryl radical.

10. The photographic element of claim 8 wherein said phosphate is present in a layer contiguous to said silver halide emulsion.

11. The photographic element of claim 8 wherein said phosphate is present in said silver halide emulsion.

12. The photographic element of claim 8 wherein said phosphate is present in an amount of from about 0.5 to about 1.0 gram per mole of silver in said silver halide emulsion.

13. The photographic element of claim 8 wherein said phosphate is triphenyl phosphate.

14. The photographic element of claim 8 wherein said phosphate is tricresyl phosphate.

15. The photographic element of claim 8 wherein said phosphate is tributyl phosphate.

16. The photographic element of claim 8 wherein said phosphate is tri(2-ethylhexyl) phosphate.

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