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PHOTOGRAPHIC ELEMENTS AND EMULSIONS STABILIZED AGAINST THERMAL FOG

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ABSTRACT OF THE DISCLOSURE

A photographic silver halide emulsion or photographic element containing as stabilizers against thermal fog, cadmium chloride and either citric acid or tartaric acid.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photographic materials, their preparation and use. One aspect of the invention relates to new and improved stabilizers against thermal fog for photographic elements. Another aspect of the invention relates to photographic silver halide emulsions containing the stabilizers therein.

Description of the prior art

During development of a silver halide emulsion, small amounts of silver halide are reduced to metallic silver regardless of whether or not they have been exposed. This reduction of silver ion produces a background fog which is more specifically referred to as chemical fog. This fog is particularly noticeable when the film is given more development than intended either because of longer processing time or higher processing temperature or a combination of both. Fog produced by a photographic emulsion which has been subjected to high temperatures is also a chemical fog and is commonly referred to as "thermal fog." When ordinary photographic elements are heated to high temperatures, e.g., 100° C., considerable thermal fog is produced after processing. Moreover, if the element has been exposed before heating, this thermal fog can completely obscure the latent image.

U.S. Pat. 2,839,405 of Jones issued June 7, 1958, discloses various emulsion stabilizers such as the water-soluble inorganic acid salts of cadmium, cobalt, manganese and zinc. While these fog inhibitors are effective at temperatures which are ordinarily encountered, these and other prior art emulsion stabilizers will not stabilize an emulsion for very long when the emulsion is heated to 100° C. It would be desirable to have an emulsion stabilizer which would protect a photographic emulsion exposed to temperatures over 100° C. A photographic element with great heat resistance could be commercially used in airplanes to record all the characteristics of the flight and could be kept intact even though the airplane has crashed and the photographic element has been heated for a long time.

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, a fog-stabilizing amount of cadmium chloride and an acid selected from the group consisting of citric acid, tartaric acid or mixtures thereof. This particular emulsion-stabilizer combination is a synergistic stabilizer combination as will be shown by the examples hereinafter.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The emulsion stabilizers of this invention may be incorporated into the silver halide emulsion of a photographic element or in a layer contiguous to the silver halide emulsion, in any amount which will stabilize the silver halide emulsion against thermal fog. In general, a concentration of the cadmium chloride in an amount of from about 10 to about 150 grams per mole of silver in the silver halide emulsion and a concentration of the acid in an amount of from about 5 to about 55 grams per mole of silver in the silver halide emulsion can be used with good results. Particularly good results are obtained when the cadmium chloride is employed in a concentration of from about 12 to about 60 grams per mole of silver in the silver halide emulsion and the acid is employed in a concentration of from about 7 to about 20 grams per mole of silver in the silver halide emulsion.

The preparation of photographic silver halide emulsions such as are suitably stabilized with the emulsion stabilizers of this invention typically involves three separate operations:

(1) Emulsification and digestion of the silver halide,

(2) The freeing of the emulsion of excess water-soluble salts, suitably by washing with water, and

(3) The second digestion or "after ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.)

The emulsion stabilizers of the invention can be added to the emulsion before this final digestion or "after ripening" or it can be added immediately prior to the coating step.

The silver halide emulsion of a photographic element containing the stabilizers of this invention can contain conventional addenda such as gelatin plasticizers, coating aids, and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis-(sodium bisulfite), maleic dialdehyde, aziridines, dioxane, derivatives and oxypolysaccharides. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, and hemicyanines. Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Pat. 2,526,632 of Brooker and White issued Oct. 24, 1950, and 2,503,776 of Sprague issued Apr. 11, 1950. Developing agents can also be incorporated into the silver halide emulsion if desired or can be contained in a contiguous layer. 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 halides used can be those which form latent images predominantly on the surface of the silver halide grains or those which form latent images inside the silver halide crystals such as described in U.S. Pat. 2,592,250 of Davey and Knott issued Apr. 8, 1952.

The silver halide emulsion layer of a photographic element containing the stabilizers 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 stabilizers of the invention can be used on a wide variety of supports. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthaate) 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, ethylene-butene copolymers and the like can also be employed.

The speed of the photographic emulsions containing the stabilizers of the invention can be further enhanced 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 stabilizers of the 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 stabilizers of the instant invention can be used in various kinds of photographic systems. In addition to being useful in X-ray and other non-optically 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 stabilizers 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 stabilizers 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 stabilizers 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. Silver halide emulsions containing the stabilizers of the invention can be processed in stabilization processes such as the ones described in U.S. Pat. 2,614,927 of Broughton and Woodward issued Oct. 21, 1952, and as described in the article "Stabilization Processing of Films and Papers" by H. D. Russell, E. C. Yackel and J. S. Bruce in PSA Journal, Photographic Science and Technique, volume 16B, October 1950.

The stabilizers of this invention can be incorporated to advantage during manufacture in silver halide emulsions representing the variations described above. Moreover, fog control in binderless silver halide films prepared by vapor deposition of silver halide on a suitable support can be achieved by coating the stabilizing agents of the invention over the vapor deposited layer of silver halide.

Combinations of all the above-mentioned addenda can be used if desired.

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 illustratiton and are not intended to limit the scope of the invention.

Example 1.—A coarse-grain, ammonical, gelatino-silver bromoiodide emulsion is prepared containing about 99 mole percent bromide and 1 mole percent iodide. The emulsion is sensitized with conventional sulfur and gold compounds and then a portion of it coated on a baryta paper support (250 grams baryta per square decimeter) at a silver coverage of about 40 milligrams per square decimeter and a gelatin coverage of about 80 milligrams per square decimeter. Similar portions of the emulsion are coated in the same manner containing the stabilizers listed in the following table. The coated elements are then exposed on an intensity scale sensitometer and enclosed in an impervious package of a composite aluminum-polyethylene sheet. The coated elements are then heated to 100° C. After the various heating periods listed in the following table, samples are removed, developed in Kodak D–19b Developer for 4 minutes at 20° C., fixed, washed and dried. Fog and Relative Speed values are then determined and compared with an unheated control sample with the following results:

Thermal fog stabilizers (grams per silver mole)	Fresh		Fog after heating at 100° C. for						
	Rel. speed	Fog	1 hr.	4 hrs.	6 hrs.	9 hrs.	15 hrs.	20 hrs.	25 hrs.
None	100	0.07	0.59	[1] 1.15					
$CdCl_2$ (58)	126	0.03	0.04	0.24	0.49	[1] 1.15			
Citric acid (17.5)		0.03	0.04	0.05	0.06	0.80	[1] 1.15		
$CdCl_2$ (58) plus citric acid (17.5)	126	0.02	0.02	0.02	0.06	0.08	0.10	[2] 0.18	0.55

[1] Fogged to D_{max}.
[2] Relative speed of this sample was 126.

The above results show that the synergistic stabilizer combination of the invention provides antifoggant protection which is greater than the sum of the protection provided by the individual components taken separately. In addition, the synergistic stabilizer combination of the invention does not affect sensitometric properties.

The formula for Kodak D–19b Developer used in the above example is as follows:

Water at 125° F.—500 cc.
N-methyl-p-aminophenol sulfate—2 grams
Sodium sulfite (desiccated)—72 grams
Hydroquinone—8 grams
Sodium carbonate (monohydrated)—56 grams
Potassium bromide—4 grams
Water to make 1 liter.

Example 2.—Example 1 is repeated but with the impervious package containing 0.3 gram of water per liter of air, which corresponds to saturation at that temperature. Results similar to those of Example 1 are obtained.

Example 3.—Coated elements similar to those of Example 1 are prepared but are not exposed before enclosing in the impervious package. Instead the coated elements are heated for various times and then exposed on an intensity scale sensitometer, developed, washed and fixed as in Example 1 with the following results:

Thermal fog stabilizers (grams per silver mole)	Fresh		Heating at 100° C.		
	Rel. speed	Fog	Hours	Rel. speed	Fog
None	100	0.07	1	126	0.21
$CdCl_2$ (58)	126	0.03	4	63	0.46
Citric acid (17.5)	100	0.03	7	63	0.20
CdC'_2 (58) plus Citric acid (17.5)	126	0.02	20	100	0.20

The above results given the duration of resistance to drying with heat of the various tested samples, before the appearance of serious fogging. It is seen that the stabilizer combination of the invention is a synergistic combination in providing protection for the longest period of time.

Example 4.—Although a cellulose triacetate film support undergoes deformation at 100° C., it is still possible to study changes of characteristics of an emulsion coated on such a support. To illustrate, an emulsion similar to that of Example 1 is prepared and the various stabilizers listed in the following table are added. The various samples are then coated on a cellulose triacetate support, 0.2 millimeter thick, at the same coverage as in Example 1 and then processed in the same manner as in Example 1 with the following results:

Thermal fog stabilizers (grams per silver mole)	Fog after heating at 100° C. for—					
	0 hrs.	1 hr.	2 hrs.	4 hrs.	5 hrs.	6 hrs.
None	0.18	0.38	0.41	2.52		
$CdCl_2$ (14)	0.16	0.56	0.60	1.40		
Citric acid (8.8)	0.18	0.17	0.17	0.23	1.20	2.50
$CdCl_2$ (14) plus Citric acid (8.8)	0.16	0.17	0.17	0.20	0.24	1.00
$CdCl_2$ (14) plus 2N Sulfuric acid (26 ml.)	0.16	0.27	0.29	1.26		
Citric acid (8.8) plus KCl (5.6)	0.17	0.18	0.19	2.58		
Citric acid (8.8) plus Cd $(NO_3)_2.5H_2O$ (22)	0.16	0.16	0.16	2.64		
$CdCl_2$ (14) plus Tar taric acid (8.8)	0.16		0.17		0.30	

The above results again illustrate that the stabilizer combination of the invention is a synergistic combination and also point out the unobviousness of the invention in that acids other than citric and tartaric acid are not effective, chlorides other than cadmium chloride are not effective and cadmium salts other than cadmium chloride are not effective.

Example 5.—Coated elements similar to those of Example 4 are prepared but are not exposed before enclosing in the impervious package. Instead, the coated elements are heated for various times and then exposed on an intensity scale sensitometer, developed, washed and fixed as in Example 4 with the following results:

Thermal fog stabilizers (grams per silver mole)	Fresh		Heating at 100° C.		
	Rel. speed	Fog	Hours	Rel. speed	Fog
None	100	0.18	1	100	0.20
$CdCl_2$ (14)	126	0.16	1	145	0.24
Citric acid (8.8)	50	0.18	4	100	0.36
$CdCl_2$ (14) plus citric acid (8.8)	71	0.16	4	100	0.20
$CdCl_2$ (14) plus 2N Sulfuric acid (26 ml.)	112	0.16	2	159	0.30
Citric acid (8.8) plus KCl (5.6)	40	0.17	2	63	0.18
Citric acid (8.8) plus $Cd(NO_3)_2$-$5H_2O$	57	0.16	2	63	0.18

$CdCl^2$ (14) plus 2N Sulfuric acid

The above results indicate that samples stabilized according to the invention can be heated for 4 hours before any significant fogging occurs while samples stabilized with other similar materials can tolerate only 2 hours.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and as defined in the appended claims.

I claim:

1. A composition comprising a photographic silver halide emulsion containing a fog-stabilizing amount of cadmium chloride and an acid selected from the group consisting of citric acid, tartaric acid or mixtures thereof.

2. The composition of claim **1** wherein said cadmium chloride is present in a concentration of from about 10 to about 150 grams per mole of silver in said silver halide emulsion and said acid is present in a concentration of from about 5 to about 55 grams per mole of silver in said silver halide emulsion.

3. The composition of claim **2** wherein said acid is citric acid.

4. The composition of claim **2** wherein said acid is tartaric acid.

5. A photographic element comprising a support coated with a silver halide layer, said element containing a fog-stabilizing amount of cadmium chloride and an acid selected from the group consisting of citric acid, tartaric acid or mixtures thereof.

6. The photographic element of claim **5** wherein said layer is a silver halide emulsion.

7. The photographic element of claim **6** wherein said cadmium chloride is present in a concentration of from about 10 to about 150 grams per mole of silver in said silver halide emulsion and said acid is present in a concentration of from about 5 to about 55 grams per mole of silver in said silver halide emulsion.

8. The photographic element of claim **7** wherein said cadmium chloride and said acid are present in said silver halide emulsion.

9. The photographic element of claim **8** wherein said acid is citric acid.

10. The photographic element of claim **8** wherein said acid is tartaric acid.

11. The photographic element of claim **6** wherein said cadmium chloride and said acid are present in a layer contiguous to said silver halide emulsion.

12. The photographic element of claim **5** in which said silver halide layer comprises coarse grain silver bromoiodide, sensitized with sulfur or gold.

References Cited

UNITED STATES PATENTS

2,384,663	9/1945	Weissberger et al.	96—109 X
2,839,405	6/1958	Jones	96—110

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,539,350 Dated November 10, 1970

Inventor(s) Maurice E. Pfaff

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 2, line 39 (page 3, line 14 of application), after "dioxane", delete ",".

In Column 3, line 7 (page 4, line 18 of application), "terephthaate" should read ---terephthalate---

In Column 4, line 27 (page 6, line 29 of application), "illustratiton" should read ---illustration---

In Column 5, line 19 (page 10, line 1 of application), "given" should read ---give---.

In Column 5, lines 70-71 (page 11, line 23 of application), "$Cd(NO_3)_2$-$5H_2O$" should read ---$Cd(NO_3)_2 \cdot 5H_2O$---

In Column 5, line 72 (page 11 of application), aft the table, "$CdCl^2$(14) plus 2N Sulfuric acid" should be delet

Signed and sealed this 8th day of June 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents