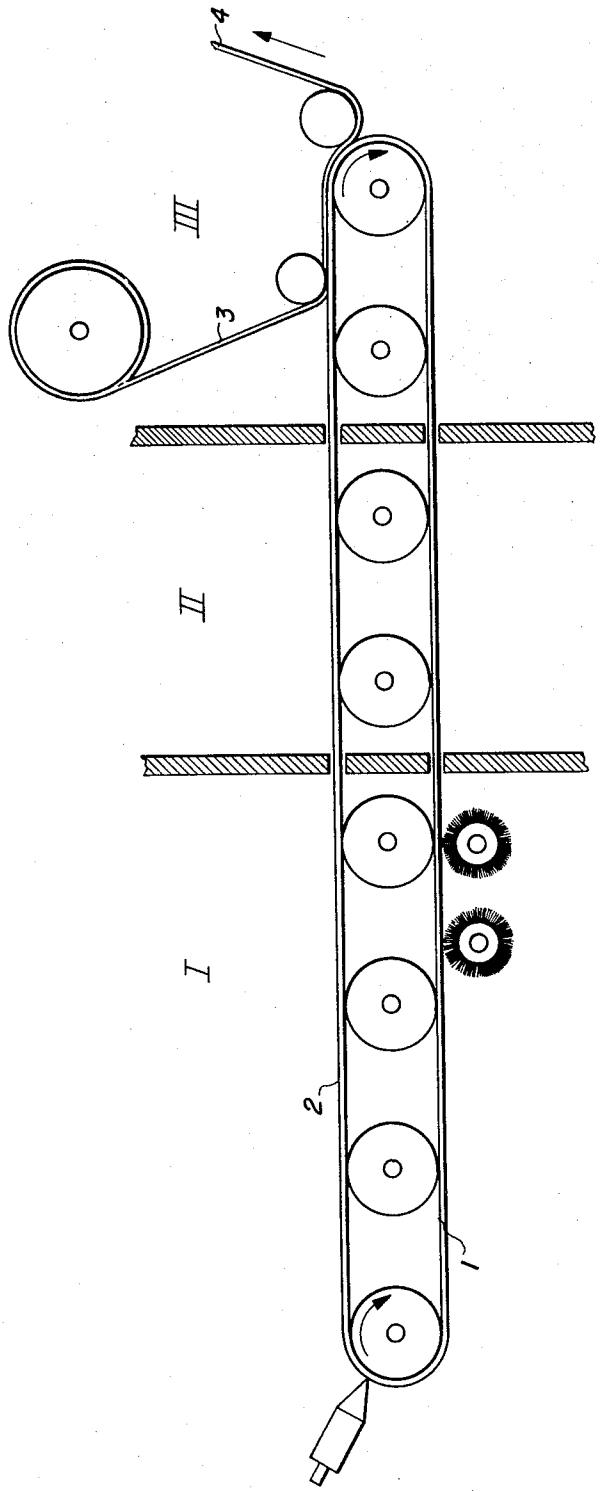
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PHOTOSENSITIVE ELEMENTS HAVING HIGH SURFACE CONCENTRATION OF SILVER HALIDE AND STABILIZED AGAINST CONTAMINATION FOG

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PHOTOSENSITIVE ELEMENTS HAVING HIGH SURFACE CONCENTRATION OF SILVER HALIDE AND STABILIZED AGAINST CONTAMINATION FOG

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ABSTRACT OF THE DISCLOSURE

A photographic element comprising a silver halide emulsion layer in which most of the silver halide has been concentrated at one surface of the emulsion layer wherein the silver halide emulsion contains, after sensitization and before the silver halide grains have been concentrated at one surface, a member selected from the group consisting of glyoxal and mucochloric acid in a concentration to effectively control contamination fog, said concentration being between about 1 to about 20 grams per gram atom of silver with the mean grain size of said silver halide grains being about 0.5μ to about 2.5μ and to provide hardening of the very thin layer of gelatin enveloping the silver halide grains. This fog stabilizing effect appears to be unique to these agents and is not found in other known photographic silver halide emulsion hardeners.

This is a continuation-in-part of application Ser. No. 641,835, filed May 29, 1967, now abandoned.

BACKGROUND OF THE INVENTION

The invention relates to photography and particularly to elements comprising photographic silver halide emulsion layers and to improvements therein. More particularly the invention relates to contamination fog stabilization in certain types of photographic silver halide emulsion layers.

Preparation of photographic recording elements having a high concentration of silver halide at a surface of the emulsion layer may be accomplished by centrifuging a coated silver halide emulsion or, alternatively, may be accomplished by gravity sedimentation of a coated silver halide emulsion. In most embodiments an emulsion is coated on a support and while the emulsion coating is still fluid, the silver halide grains in the emulsion are concentrated at or near the surface of the emulsion layer adjacent to the support, either by centrifugal force or by gravity settling. Usually, but not in every embodiment, the support used will be a stripping support so that the coated emulsion layer, after settling of the silver halide and after the emulsion has at least partially set but not completely dried, can be transferred to a permanent support. The first support is then stripped away leaving the concentrated silver halide in the very outer surface of the emulsion layer on the permanent support. Preparations of silver halide photographic recording elements according to methods just described are described in more detail, for example, in British Pat. 688,980 and in French Pat. 1,112,681.

A problem with emulsion layers of the kind described, i.e., those having most of the silver halide concentrated at the very surface of the emulsion layer has been a serious fogging of the emulsion which appears when the photograph is developed. The kind of fog observed is not the same as the chemical fog observed in ordinary photographic silver halide layers. It is fog of unique nature and we have named this particular type of fog found in sedimented and centrifuged emulsion layers "contamination" fog. Such a contamination fog is very likely the result of high superficial silver halide coverage and of low superficial gelatin coverage coupled wtih the relatively large grain size of the silver halide.

SUMMARY OF THE INVENTION

In accordance with the present invention, in those silver halide emulsion layers in which most of the silver halide has been concentrated at one surface of the emulsion layer, contamination fog is substantially reduced by presence of mucochloric acid or glyoxal in the emulsion layer, added to the emulsion after sensitization and before the silver halide grains have been concentrated at one surface, the antifoggant concentration being in the range of about 1 to about 20 grams per gram atom of silver in the emulsion, with the mean grain size of said silver halide grains being about 0.5μ to about 2.5μ. The mucochloric acid or glyoxal also provides hardening of the very thin layer of gelatin enveloping the silver halide grains. Mucochloric acid and glyoxal are known photographic silver halide emulsion hardeners and in the present use they do function as hardeners to some extent, but their principal value in emulsions of the type considered here and the reason for their use is their utility for reducing contamination fog. The excellent antifogging effect of mucochloric acid and glyoxal is not a general characteristic of most photographic emulsion hardeners. Glyoxal and mucochloric acid have not been found to be generally useful as antifoggants in other types of silver halide emulsions. The concentrations of these agents as they are used for controlling contamination fog are generally much higher than the concentrations ordinarily needed for emulsion hardening. For example, to reduce fog density in a centrifuged or sedimented emulsion of the kind described, to a value of 0.06 or less, we have used to advantage concentrations in the range of from about 1 to about 20 grams mucochloric acid or glyoxal, and preferably from 3 to 10 grams, per gram atom of silver in the emulsion.

According to a preferred mode for carrying out the invention, using the procedure for centrifugation described in French Pat. 1,112,681, there is centrifuged a silver halide dispersion in 5 percent aqueous gelatin solution containing one of the agents of the invention, mucochloric acid or glyoxal, to obtain a centrifuged emulsion in which contamination fog has been considerably reduced. Results are of particular interest for applications involving centrifugation of emulsions of high sensitivity in which grains are generally larger and especially susceptible to contamination. It is particularly useful with silver halide emulsions having a mean grain size of silver halide grains about 0.5μ to about 2.5μ.

According to a second mode for carrying out the invention, a photosensitive layer is prepared by sedimentation in a continuous operation. Referring now to the drawing, the figure represents one scheme for realization of the invention by a continuous process. Onto a continuous polished metal belt **1**, there is deposited, as the belt is transported, a film dispersion **2** of silver halide in a 5 percent gelatin solution containing 0.15 percent by weight of mucochloric acid or glyoxal. The belt **1** bearing the dispersed emulsion **2** passes through Zone I in which humidity conditions are maintained at values sufficient for the emulsion to remain fluid without drying at the temperature necessary for sedimentation (e.g. 40° C. is particularly appropriate). Then the belt passes into the second Zone II maintained at a temperature to effect

setting of the gelatin, e.g., about 5° C. The belt 1 then passes to Zone III where before the sedimented layer has completely dried it is transferred to a gelatin coated film support and drying of the finished film is then completed. In the sedimentation Zone I and the setting Zone II the conditions of operation will determine the time needed for passing through the respective zones. More particularly, the time needed for sedimentation of silver halide grains greater than 0.5 micron and preferably greater than 0.8 micron after application of the emulsion to the temporary support in the customary manner will be relatively short, provided temperature is maintained at about 40° C., in the sedimented Zone I. This period varies, naturally depending on viscosity and nature of the emulsion. Then the sedimentation time will be on the order of one minute.

It is preferable to use for preparation of the emulsion a gelatin of low viscosity and high gel resistance, i.e., high gel strength. Concentration of gelatin is preferably very low, for example, 2–3 percent by weight. The gelatin concentration of the settled silver halide emulsion is of course not uniform throughout the depth of the emulsion layer. At the settled surface, the superficial gelatin coverage is very low, i.e. less than 10^{-6} grams per gram of emulsion. That is, the gelatin concentration at or near the settled surface should be less than 10 grams per gram atom of silver and preferably less than about 5 grams per gram of silver, for at gelatin concentrations higher than about 5 grams per gram atom of silver the ultraviolet light absorption by the gelatin becomes excessive for some intended uses. The whole gelatin content of the silver halide emulsion layer is between about 2 and about 10 percent by weight of the silver halide emulsion. Therefore it is desirable to partially dry the layer in order to obtain a firmer film before transfer to the film support.

After transfer, the exposed surface of the emulsion at which the silver halide has been concentrated is poor in gelatin and so is very fragile and sensitive to mechanical abrasion. For protection of this film before it is turned onto a roll, one may apply a narrow adhesive strip along the borders of the film.

According to one variant, if it is desired to prepare a sedimented emulsion without stripping, the layer may be coated directly on a permanent film support carried on the transport band. Sedimentation and setting are carried out as described, then, upon drying, the gelatin forms a protective coat over the silver halide which is concentrated at the film support interface.

The mechanism by which mucochloric acid and glyoxal inhibit contamination fog is difficult to define precisely. It seems to be especially active when these agents are used in large doses without provoking coagulation of the gelatin in liquid phase. The hardening effect on drying reinforces mechanical resistance of the thin envelope of gelatin formed around the concentrated grains in the surface. Nevertheless, practice of the invention is not limited by lack of a precise theory explaining the action of the contamination inhibitors.

Following are specific examples embodying the invention and illustrating a preferred mode of carrying out the invention.

EXAMPLE I

There is prepared a medical radiographic silver halide emulsion which we call Emulsion A containing 1 gram atom silver and 200 grams gelation per 4 kg. of emulsion. Viscosity of this emulsion at 38° C. is 5 centipoises. Emulsions B and C are prepared like Emulsion A but adding respectively 0.6 gram and 6 grams mucochloric acid per gram atom silver. The coated layers are formed by one of the processes described above, by sedimentation or centrifugation at the coating rate of 25 mg. of Ag per dm.^{2} and transferred to cellulose triacetate film base. A normal coating without concentration of the emulsion is coated on a film base for a control. Each of the finished samples is exposed sensitometrically through a step wedge. Sensitometric curves for determining sensitivity and

chemical fog or contamination fog are obtained for each sample after development for two minutes at 20° C. in Kodak D–19b developer. Results are tabulated in Table 1.

TABLE 1

Example No.		Emulsion	Relative speed	Fog-chemical and/or contamination
1a	Normal layer coated at 25 mg. of Ag per square decimeter	A	100	0.04
1b	Same + 0.6 gram mucochloric acid/mole Ag.	B	89	0.04
1c	Same + 6 grams mucochloric acid/mole Ag.	C	65	0.03
1d	Centrifuged layer coated at 25 mg, Ag per square decimeter.	A	.....	2.55
1e	Same + 0.6 grams mucochloric acid/mole Ag.	B	82	0.61
1f	Same + 6 grams mucochloric acid/mole Ag.	C	71	0.06
1g	Sedimented emulsion layer coated at 25 mg. Ag per square decimeter.	A	.....	1.50
1h	Same + 0.6 grams mucochloric acid/mole Ag.	B	78	0.39
1i	Same + 6 grams mucochloric acid/mole Ag.	C	63	0.03

The values obtained for contamination fog in the sedimented and centrifuged emulsions containing mucochloric acid were acceptably low.

From a consideration of Table 1, in normal nonsettled emulsion layers (Examples 1a, 1b, and 1c), mucochloric acid is effective as a fog inhibitor at concentrations even as low as 0.6 gram of mucochloric acid per mole of silver. However, in the above described centrifuged and sedimented emulsion layers containing 0.6 gram mucochloric acid per mole of silver (Examples 1e and 1h, respectively), the fog jumps to unacceptably high levels of 0.61 and 0.39 respectively.

Comparing Examples 1a, 1b, and 1c in Table 1, the results show what would happen in accordance with the teaching of the prior art when mucochloric acid is used (without centrifuging or sedimenting); the relative speeds are about 11% and 35% lower, respectively, while there is no measurable change in fog. Examples 1d and 1g show what then occurs if Emulsion A (without mucochloric acid) is centrifuged or sedimented: the relative speed could not be measured because of the very high fog levels (2.55 and 1.50 respectively). Examples 1f and 1i illustrate the results of the instant invention: relative speed (while being reduced by only 29% and 37%, respectively) is not reduced to an unmeasurable level, for the fog only slightly increased in Example 1f and slightly decreased in Example 1i.

EXAMPLE II

To compare anticontamination activity of mucochloric acid and glyoxal according to the invention with other conventional emulsion hardening agents, various quantities of chrome alum and formaldehyde were added in Emulsion A. Centrifuged emulsion coatings of the various emulsions were coated at 25 mg. Ag per square dm. on conventional film supports. The films were tested for relative speed and fog as in Example I. Results are tabulated in Table 2.

TABLE 2

Emulsion + hardening agent, grams/gram atom silver	Relative speed	Fog-chemical and/or contamination	Gamma
Emulsion A + mucochloric acid: 6.65 g	100	0.05	2.2
Emulsion A + chrome alum:			
5.4 g	71	0.30	2.2
10.8 g	50	0.10	1.65
16.2 g. (coagulation)			
Emulsion A + formaldehyde at pH 5.5:			
12.5 g	141	0.50	1.3
25 g	141	0.30	1.7
50 g. (coagulation)			
Emulsion A + glyoxal:			
0.10 g	200	0.20	2.2
0.20 g	126	0.15	2.0
1.6 g	79	0.10	2.0
3.2 g	79	0.05	2.0

Mucochloric acid and glyoxal reduced contamination to acceptable values with acceptable changes in sensitivity The other agents did not reduce fog to acceptable levels, even when added in highest practicable concentrations.

EXAMPLE III

Comparison of use of mucochloric acid with use of conventional antifogging agents, methylbenzotriazole and 1-phenyl-5-mercaptotetrazole, shows that contamination fog is a phenomenon distinct from chemical fog. To show this, two like emulsions are prepared and to one is added 25 grams formaldehyde per gram atom silver. To different fractions of the latter emulsion are added different proportions of methylbenzotriazole and 1-phenyl-5-mercaptotetrazole. The emulsions were coated by the centrifugation process at 25 mg. Ag per square dm. of conventional acetate film base, then tested with same as in Example I to measure sensitivity and contamination. Results are tabulated in Table 3.

TABLE 3

Emulsion + adjuvant, grams/gram atom silver	Relative speed	Fog-chemical and/or contamination	Gamma
Emulsion A + mucochloric acid 6.65 g	100	0.05	2.2
Emulsion A + formaldehyde 25 g. + methylbenzotriazole 1 g	85	0.23	1.2
Same, 0.2 g	87	0.12	1.6
Same, 0.1 g	120	0.14	1.7
Emulsion A + formaldehyde 25 g	126	0.15	1.7
Emulsion A + mucochloric acid 6.65 g	100	0.05	2.2
Emulsion A + formaldehyde 25 g. + mercaptotetrazole 1 g	Completely desensitized.		
Same, 0.1 g	42	0.08	1.5
Emulsion A + formaldehyde 25 g	126	0.15	1.7

The classic antifogging agents were tested in presence of formaldehyde without which the antifoggants would have completely desensitized these emulsions. Even then, the agents did not reduce fog to acceptable levels and they caused substantial diminution of sensitivity. The contrast is inferior to that obtained with mucocholoric acid.

The present invention is adaptable to industrial processes, continuous or batch, for making silver halide coatings having silver halide grains concentrated at the surface of the sensitive emulsion layer. The invention practically eliminates risk of contamination fog in such emulsions, making coatings of good sensitivity using high doses of mucochloric acid or glyoxal without coagulation of the emulsion. The sedimentation process is especially advantageous because it is adaptable to a continuous process for making a strip of film with sedimented silver halide layer. Photographic products of the invention are especially adaptable to use in ultraviolet photography. There are other advantages of emulsions having silver halide concentrated at the surface, particularly greater processing speed and generally better definition.

It will be understood that modifications and variations

may be made within the scope of the invention as described above and as defined in the following claims.

We claim:

1. In a photographic recording element having a layer of silver halide emulsion with most of the silver halide grains concentrated at one surface of the emulsion layer, the improvement wherein said silver halide emulsion contains, after sensitization and before the silver halide grains have been concentrated at one surface, a member selected from the group consisting of glyoxal and mucochloric acid in a concentration sufficient to effectively control contamination fog, said concentration being about 1 to about 20 grams per gram atom of silver and the mean grain size of said silver halide grains being about 0.5μ to about 2.5μ.

2. A photographic recording element comprising the improvement defined by claim 1 wherein said selected member is present in a concentration sufficient to reduce fog density in said emulsion to the equivalent of 0.06 or less density after development for two minutes in D–19 developer.

3. A photographic recording element comprising the improvement defined by claim 1 wherein said selected member is present in the emulsion at a concentration in the range from 3 to 10 grams per gram atom silver in the emulsion.

4. A photographic recording element comprising the improvement defined by claim 1 wherein said concentration of silver halide occurs at the outer surface of a silver halide emulsion layer on a support.

5. In a process for concentrating sensitized silver halide grains at a surface of a photographic silver halide emulsion layer by settling such grains at one surface by centrifugal force or gravitational force before setting and drying of the emulsion layer, the improvement which comprises incorporating into said emulsion, after sensitization and before the silver halide grains have been settled at one surface, a member selected from the group consisting of glyoxal and mucochloric acid in a concentration sufficient to effectively inhibit contamination fog in the finished photographic product comprising such emulsion layer, said concentration being between about 1 to about 20 grams per gram atom of silver in the emulsion, and the mean grain size of said silver halide grains being about 0.5μ to about 2.5μ.

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