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SENSITIZED PHOTOGRAPHIC CELLULOSE
ESTER SILVER HALIDE EMULSION

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This invention relates to photographic emulsions and more particularly to photographic cellulose ester silver halide emulsions. This application is substantially identical with and replaces our application Serial No. 426,486, filed January 12, 1942, now abandoned.

Photographic silver halide emulsions prepared in solutions of far hydrolyzed cellulose esters are known (see, for example, United States Patent 2,110,491, dated March 8, 1938.) However, such emulsions have hitherto been found to be only of moderate sensitivity unless heat treatment to induce silver halide grain growth is used in their preparation, or unless nitrogen-containing peptizers (which permit the use of sulfur sensitizers) are used in the preparation of the emulsions. Polyvinyl acetals in which a portion of the acetal groups are p-dimethylamino-benzaldehyde acetal groups are suitable nitrogen-containing peptizers. See United States Patent No. 2,276,322 dated March 17, 1942. However, the above methods of obtaining higher sensitivity have disadvantages, in that ordinary heat treatment or the use of nitrogen-containing peptizers produces emulsions of low contrast which are unsuitable for certain photographic work where high contrast is necessary, as in the case of the preparation of film for cine positive, microfilm and other copying work. Thus, while gammas of 4 or 5 can be obtained readily on slow unripened emulsions, these same emulsions if ripened to higher speeds or if prepared with nitrogen-containing peptizers may increase their speed as much as fifty times or more, but show gammas of less than one.

We have now found that the speed of cellulose-ester-silver halide emulsions can be increased many fold while maintaining high contrast. It is, accordingly, an object of our invention to provide new and improved photographic cellulose-ester-silver-halide emulsions. A further object is to provide a process for preparing such emulsions. Other objects will become apparent hereinafter.

In accordance with our invention, we prepare cellulose-ester-silver-halide emulsions in the presence of ethylene diamine. The speed of the emulsions is greatly increased owing to the ethylene diamine while the contrast of the emulsion remains high. Hydrazine and hydroxylamine have some slight action of this kind, but are markedly inferior to ethylene diamine. Ammonia is, of course, a ripening agent with cellulose-ester-emulsions as it is with gelatino-emulsions, but it lacks the ability to keep the contrast of the cellulose-ester-emulsions up to the desired figure.

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We have found that the presence of ethylene diamine makes possible the use of sulfur sensitizers in cellulose-ester emulsions, i. e., in the presence of ethylene diamine, sulfur sensitizers, such as thiourea, thiocarbonyl, and especially alkali metal thiocyanates and ammonium thiocyanates, act to increase the speed of cellulose-ester-silver-halide emulsions even above the speed increases that can be obtained with ethylene diamine alone.

The following examples will serve to illustrate our invention.

Example 1

Far hydrolyzed cellulose acetate propionate of high viscosity, containing 19% to 33% by weight of acyl groups, was dissolved in a 1:1 (volumes) acetone-water mixture to make an 8½% solution by weight. 20 g. of this solution was diluted with 40 cc. of water and 100 cc. of ethanol. The resulting mixture was warmed to 80° C. The following two solutions, A and B, both at 80° C., were then allowed to run simultaneously into the aforesaid mixture over a period of three minutes while stirring rapidly:

(A) 20 cc. of a 50% (by weight) aqueous solution of silver nitrate.

(B) 20 cc. of a 40% (by weight) aqueous solution of potassium bromide and 1 cc. of a 25% (by weight) aqueous solution of potassium iodide.

180 g. of the aforesaid 8½% solution of cellulose acetate propionate was then added to the resulting emulsion and thoroughly stirred into the emulsion. The emulsion was then precipitated by pouring into water, and the shreds thus formed were freed of organic solvents and of excess salts by washing with several changes of water. The emulsion was then pressed to a weight of 135 g. and dissolved by stirring into the following solvent mixture:

	Cc.
Water	110
Acetone	90
Monoethyl ether of ethylene glycol	50
Monoacetin	6

The emulsion was then spectrally sensitized with 4 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbo-cyanine iodide. The sensitized emulsion was then coated onto film. The emulsion showed the following properties:

H and D speed	0.14
Gamma	3.8

developed for four minutes with Eastman Kodak Company "D-16" developer.

Example 2

The emulsion of Example 1 was modified by the addition of 30 cc. of a 10% (by weight) aqueous solution of ethylene diamine after the addition of solutions A and B. The resulting mixture was allowed to stand at 80° F. for five minutes before the final 180 g. of cellulose acetate propionate solution were added. After spectrally sensitizing and coating as in Example 1, this emulsion showed the following properties:

H and D speed----- 1.0
Gamma----- 2.3

developed for four minutes with Eastman Kodak Company "D-16" developer.

Example 3

An emulsion like that of Example 2 was prepared, but with 2 cc. of a 10% (by weight) aqueous solution of potassium thiocyanate added along with the ethylene diamine. After spectrally sensitizing and coating, the emulsion had the following properties:

Hand D speed----- 3.9
Gamma----- 1.9

developed for four minutes with Eastman Kodak Company "D-16" developer.

Our invention is directed especially to the far hydrolyzed cellulose-ester-silver-halide emulsions containing from 19% to 33% by weight of acyl groups. Far hydrolyzed cellulose esters containing from 20% to 26% by weight of acyl groups are most advantageously employed. Cellulose acetate and acetate-propionates are especially useful. Emulsions made from such cellulose esters are described in United States Patent 2,110,491, dated March 8, 1938. Cellulose esters hydrolyzed to an acyl group content of below 30% are described in United States Patents 1,896,145, dated February 7, 1933; and 1,954,336, dated April 10, 1934. Cellulose esters hydrolyzed to an acyl group content of below 30% are described in United States Patent 2,129,052, dated September 6, 1938.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 19% to 33% by weight of acyl groups, said emulsion containing ethylene diamine.

2. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 20% to 26% by weight of acyl groups, said emulsion containing ethylene diamine.

3. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 19% to 33% by weight of acyl groups, said emulsion containing ethylene diamine and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates.

4. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 20% to 26% by weight of acyl groups, said emulsion containing ethylene diamine and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates.

5. A process for increasing the speed of a pho-

tographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 19% to 33% by weight of acyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine.

6. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 20% to 26% by weight of acyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine.

7. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 19% to 33% by weight of acyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates.

8. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose carboxylic ester containing from 20% to 26% by weight of acyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates.

9. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate containing from 19% to 33% by weight of acetyl groups, said emulsion containing ethylene diamine.

10. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate containing from 20% to 26% by weight of acetyl groups, said emulsion containing ethylene diamine.

11. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate propionate containing from 19% to 33% by weight of acyl groups, said emulsion containing ethylene diamine.

12. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate propionate containing from 20% to 26% by weight of acyl groups, said emulsion containing ethylene diamine.

13. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate propionate containing from 19% to 33% by weight of acyl groups, said emulsion containing ethylene diamine and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates.

14. A photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate propionate containing from 20% to 26% by weight of acyl groups, said emulsion containing ethylene diamine and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates.

15. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate containing from 19% to 33% by weight of acetyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine.

16. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate containing from 20% to 26% by weight of

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acetyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine.

17. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate propionate containing from 19 to 33% by weight of acetyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine.

18. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate propionate containing from 20 to 26% by weight of acyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine.

19. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in cellulose acetate propionate containing from 19 to 33% by weight of acyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine and a thiocyanate selected from the group con-

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sisting of alkali metal and ammonium thiocyanates.

20. A process for increasing the speed of a photographic silver halide emulsion in which the silver halide is dispersed in a hydrolyzed cellulose acetate propionate containing from 20 to 26% by weight of acyl groups, said process comprising digesting the emulsion in the presence of ethylene diamine and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates.

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REFERENCES CITED

The following references are of record in the file of this patent:

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20 Number	Name	Date
2,184,023	Sheppard et al.	Dec. 19, 1939