Dec. 5, 1961 J. W. GATES, JR., ET AL 3,011,890
PHOTOGRAPHIC EMULSIONS
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Fig. 1

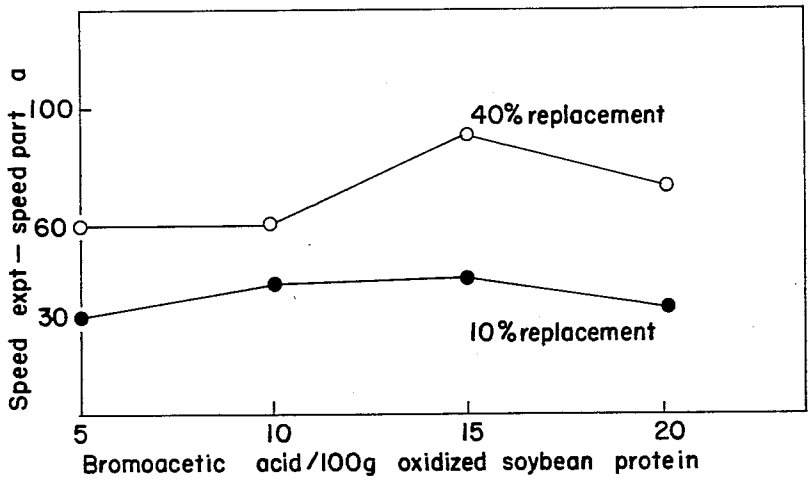
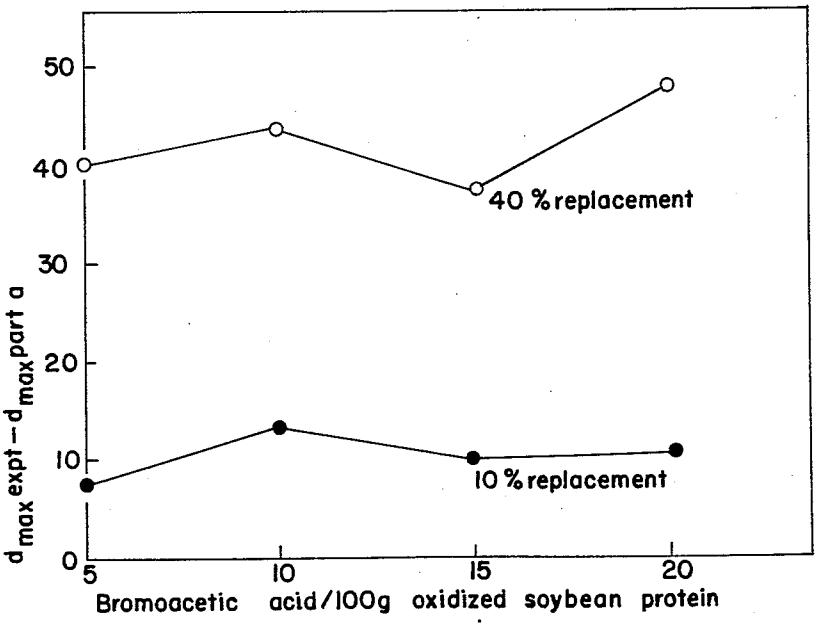


Fig. 2



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PHOTOGRAPHIC EMULSIONS

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This invention relates to photographic emulsions in which certain protein derivatives are employed as a substantial portion of the carrier for the silver halide therein.

Ordinarily, photographic emulsions comprise a dispersion of light-sensitive silver halide grains in a carrier for the silver halide which has usually been gelatin. Additives such as optical sensitizers, sensitizing dyes, hardeners, coating aids, and the like have also been provided to improve the properties of the emulsion in the manner desired.

The maximum optical density of the silver image of a photographic film or paper after exposure, processing, and drying depends on the density which results from the development process and the changes which occur during the processing and drying procedure. The vehicle in which the silver halide grains are suspended exerts an influence on the maximum density during both the processing and the drying of the emulsion layer. For instance, the maximum density of a film may be altered by varying the amount or type of hardening agent added to the photographic emulsion employed.

One object of our invention is to provide photographic emulsions in which certain protein derivatives are employed therein. Another object of our invention is to provide photographic emulsions having greater silver covering power and less density loss upon drying than photographic emulsions in which these certain protein derivatives or their equivalent are absent. A further object of our invention is to increase the speed and contrast of photographic emulsions. Other objects of our invention will appear herein.

We have found that the partial replacement of the gelatin in gelatin-silver halide emulsions with certain modified proteins results in increased covering power, usually in both the wet and dry states, for the silver which may be formed therein by exposure and development. When 10 to 50 percent of the carrier for the silver halide in such emulsions is a derivative of an oxidized protein as will be described herein, the covering power of the developed silver in such emulsions while still in a wet condition after processing is usually greater than that of silver in emulsions containing the full amount of gelatin as a carrier. Furthermore, this difference is even greater after drying because loss of covering power on drying is smaller in emulsions containing these protein derivatives than in full gelatin emulsions. Such an increase of covering power results in increased contrast and maximum density and usually in increased effective speed where the latter is measured at a density significantly above the fog level. In many cases in coarse-grain emulsions, speed gains in the toe regions of the sensitometric curves resulted over and above those which could be attributed to increased covering power. The improvement is noted in use both in coarse-grained and in fine-grained emulsions.

The protein derivatives which have been found to be useful in preparing emulsions in accordance with our invention are carboxymethylated proteins. If the protein is other than gelatin, the sulphur-containing compounds inherent therein are desirably destroyed or removed by oxidation such as by treatment with hydrogen peroxide by the method described in U.S. Patent No. 2,691,582

of Lowe and Gates. Any of the treated proteins described in that patent are useful as material to be carboxymethylated for obtaining protein derivative useful as a supplement to the gelatin in photographic emulsions. The carboxymethyl protein is used in accordance with our invention in an amount 10–50% based on the total protein employed in the emulsion.

The carboxymethylation of the protein is accomplished by reaction upon the protein with an α halo fatty acid such as bromoacetic acid at a pH of 9–12, such as is obtained by the presence of an alkaline buffer material in the reaction mass. The degree of carboxymethylation is usually in the range of 5–25% by weight. Some of the naturally occurring, amino-containing vegetable and animal proteins which may be oxidized and then carboxymethylated and which will be useful in photographic emulsions in accordance with our invention are soybean protein, casein, edestin, glutin, blood albumin, egg albumin, castor bean protein and globulin. Gelatin ordinarily does not need any comparable treatment before forming a useful carboxymethylated product therefrom.

The following examples illustrate methods of preparing carboxymethylated proteins useful in compositions in accordance with our invention.

Example 1

100 parts of casein was thoroughly mixed with 900 parts of distilled water at 45° C. The pH was adjusted to 11.0 by adding 20% sodium hydroxide, whereupon 5 parts of 30% hydrogen peroxide was added and the solution was stirred for 15 minutes. An additional 5 parts of 30% hydrogen peroxide was added and the solution was mixed for 1 hour. Coagulation was caused by adding sulfuric acid to a pH of 3.0. The casein coagulum resulting was separated from the liquid, washed with distilled water, and was redispersed in distilled water at 50° C. at a pH of 9.0 to a volume of 1,000 ml. 10 parts of magnesium oxide and 10 parts of bromoacetic acid were added and the solution was stirred for 3 hours. The solution was then filtered. The casein derivative which formed was obtained by coagulation with sulfuric acid at a pH of 3.0. The carboxymethylated casein thus obtained was separated from the liquid, washed with distilled water, and was redispersed in distilled water at 50° C. and at a pH of 5.5 to a volume of 1 liter.

Example 2

1,000 parts of casein was mixed with 9,000 parts of distilled water at 50° C. 20% sodium hydroxide was added to adjust the pH to 11.0. 50 parts of 30% hydrogen peroxide was added and the solution was stirred for 15 minutes and then an additional 50 parts thereof was added and the solution was stirred for 1 hour. Coagulation was caused by adding sulfuric acid to a pH of 3.0. The casein coagulum which formed was separated, washed with distilled water, and redispersed in water at 50° C. to a volume of 8,500 ml. at a pH of 9. 98.5 parts of bromoacetic acid (dissolved in water) were added and the pH was maintained at 9 for 7 hours with sodium hydroxide. The carboxymethylated casein thus obtained was coagulated by adding sulfuric acid to a pH of 3.0. The coagulum which formed was separated by decanting the liquid, washed with distilled water, and was redispersed in 6,000 parts of 50° C. distilled water to a pH of 5.6. The solution was mixed with 150 parts of carbon for 30 minutes and was then filtered. A clear solution of carboxymethyl casein suitable for use in preparing photographic emulsions was obtained.

Example 3

150 parts of soy protein was stirred into 1,350 parts

of distilled water at 50° C. 20% sodium hydroxide was added to adjust the pH to 11.0. 7.5 parts of 30% hydrogen peroxide was added. The solution was stirred for 15 minutes and then an additional 7.5 parts of 30% hydrgen peroxide was added and the solution was stirred for 1 hour. Half of the solution was stirred for 6 hours with 15 parts of bromoacetic acid dissolved in 50 parts of distilled water, the pH being maintained at 9.5 by the addition of 20% sodium hydroxide. Carboxymethylated protein was coagulated by adding sulfuric acid to a pH of 3.0. The carboxymethylated protein thus obtained was collected, washed with distilled water, and redispersed in 500 parts of 50° C. distilled water at a pH of 6.0. The dispersion was treated with 15 parts of purifying carbon for 30 minutes and was then filtered.

Example 4

300 parts of soy protein was stirred into 2,700 parts of distilled water at 50° C. 20% sodium hydroxide was added to convert the pH to 11.0. There was then added 15 parts of 30% hydrogen peroxide, the solution was stirred for 15 minutes and an additional 15 parts of 30% hydrogen peroxide was added with stirring for 1 hour. 30 parts of bromoacetic acid dissolved in 100 parts of distilled water was added to ½ of the solution, the mass was stirred for 6 hours and the pH was held at 9.5 with sodium hydroxide. Sulfuric acid was then added to impart a pH of 2.5 whereupon the carboxymethylated protein formed coagulated. The coagulum was collected, washed with distilled water, and redispersed in 1,000 parts of 50° C. distilled water at a pH of 6.0. The dispersion was treated with carbon for 30 minutes and was then filtered.

Example 5

450 parts of soy bean protein was stirred into 4050 parts of distilled water at 50° C. 20% sodium hydroxide was added to adjust the pH to 11.0. 22.5 parts of 30% hydrogen peroxide was added, the solution was stirred for 15 minutes, an additional 22.5 parts was added and the solution was stirred for 1 hour. It was then divided into 3 equal parts. One part was stirred for 4 hours with 7.5 parts of bromoacetic acid dissolved in 25 parts of distilled water, the pH being maintained at 9.5 with sodium hydroxide. The carboxymethylated protein thus obtained was coagulated at a pH of 2.5 obtained by adding sulfuric acid. The coagulum was collected, washed with distilled water, redispersed in distilled water which dispersion was mixed with carbon for 20 minutes and was then filtered.

Example 6

There was added to a second part of the soy bean protein solution of the preceding example 15 parts of bromoacetic acid dissolved in water, the procedure otherwise being the same as in Example 5.

Example 7

The third part of the protein dispersion from Example 5 was taken and 22.5 parts of bromoacetic acid was added thereto, the procedure being the same as described in that example.

Example 8

Example 3 was repeated except that blood albumin was employed instead of soy protein.

Example 9

150 parts of soy protein was mixed with 1350 parts of distilled water at 50° C. 20% sodium hydroxide was added to raise the pH to 11. 7.5 parts of 30% hydrogen peroxide was added, the solution was stirred for 15 minutes, an additional 7.5 parts of hydrogen peroxide was added, and the solution was stirred for 1 hour. The pH was maintained at 9.5 for 3 hours after the addition to the solution of 15 parts of bromoacetic acid dissolved in 50 parts of distilled water. The resulting solution was treated with 15 parts of carbon for 20 minutes and was filtered. The protein derivative formed was coagulated by adding sulfuric acid to impart a pH of 2.5. The coagulum was washed and redispersed in distilled water, held at a pH of 5.6 by the occasional addition of sodium hydroxide.

Example 10

100 parts of bone gelatin were plumped and dissolved in 1900 parts of distilled water and the pH of the solution was brought to 9.0 by adding 25 parts of magnesium oxide.

There was then added 20 parts of bromoacetic acid and an additional 25 parts of magnesium oxide was added to keep the pH above 9.0. The mass stood for 18 hours at room temperature, then was warmed to 35° C. and was stirred for 8 hours. The gelatin stood for an additional 18 hours whereupon the temperature was raised to 45° C. The solution was filtered, chilled, sliced, washed and dried in the normal manner to obtain carboxymethylated gelatin, adapted to use in preparing photographic emulsions.

Example 13

400 parts of bone gelatin were plumped in 3600 parts of water. The temperature was raised to 35° C. to melt the gelatin. 50 parts of magnesium oxide and 80 parts of bromoacetic acid were added and the mass was held at 35° C. for 8 hours. An additional 50 parts of magnesium oxide had been added to keep the pH above 9.0. Upon completion of the reaction, the pH was adjusted to 6.0 with sulfuric acid and the product obtained was filtered, chilled, washed and dried in a normal manner.

Example 12

400 parts of bone gelatin ware plumped in 3600 parts of water. The temperature was raised to 35° C., melting the gelatin. 50 parts of magnesium oxide and 40 parts of bromoacetic acid were added and the solution was held at 35° C. for 8 hours. Sulfuric acid was then added to drop the pH to 6.0. The material was removed by filtering and was chilled, washed and dried in the usual manner.

Example 13

200 parts of bone gelatin were plumped in 1800 parts of water. The gelatin was melted at 50° C. and 25 parts of magnesium oxide were added thereto. 10 parts of bromoacetic acid (dissolved in water) was then added and the solution was stirred at 50° C. for 3 hours. The solution was then filtered and sulfuric acid was added to adjust the pH to 6.0. The carboxymethyl gelatin thus obtained was chilled, sliced, washed and dried in the usual manner.

The following examples illustrate the use of carboxymethyl proteins in conjunction with gelatin as a carrier for silver halides in photographic emulsions. Our invention comprises the utilization of carboxymethylated proteins having no photographically active impurities therein or proteins which may be purified by known methods such as oxidation to remove photographically active materials.

Example 14

A coarse-grained gelatin-silver bromoiodide emulsion of a type employed for making a screen X-ray film and containing 36 grams of gelatin per mole of silver halide was prepared for coating by adding a solution of a coating aid and a suitable antifoggant. The emulsion was divided into 2 parts as follows:

(*a*) 1440 ccs. of a 10% solution of gelatin were added per mole of silver halide.

(*b*) 720 ccs. of a 10% solution of gelatin and 950 ccs. of 7.6% solution of carboxymethyl casein, as prepared in Example 1, were added per mole of silver halide.

Suitable hardener was then added to each of these emulsions and they were coated onto a cellulose acetate film support at a coverage of 200 square feet per mole of silver halide. 1 strip of each coating was exposed in an Eastman 1B sensitometer through a continuous "step" wedge, developed 3 minutes in a rapid X-ray developer, fixed and washed. Densities of the steps on each strip were then determined before and after drying. The results obtained were tabulated as follows:

Part	D-max. wet	D-max. dry	Percent D. Loss	Relative Speed	γ
(a)	2.02	1.72	15	100	1.90
(b)	1.98	1.78	10	132	2.08

Example 15

An emulsion similar to that used in Example 14 except that it contained 107 grams of gelatin per mole of silver halide was prepared for coating as in Example 14. The emulsion was divided into 4 parts as follows:

(*a*) 720 ccs. of a 10% solution of gelatin per mole of silver halide was added.
(*b*) 740 ccs. of a 9.8% solution of carboxymethyl casein as prepared in Example 2 was added per mole of silver halide.
(*c*) 900 ccs. of an 8% solution of oxidized soy bean protein prepared as described in the first 6 lines of Example 3 were added per mole of silver halide.
(*d*) 820 ccs. of an 8.8% solution of carboxymethylated oxidized soy bean protein as prepared in Example 3 was added per mole of silver halide.

After addition of hardeners each of these emulsions were coated out onto cellulose acetate film supports and strips thereof were tested as described in Example 14. In addition, unprocessed strips of each coating were analyzed for silver coverage. The results obtained were tabulated as follows:

Part	g. Ag per sq. ft.	D-max. wet	D-max. dry	Percent Loss of D	D dry, g. Ag/ft.²	Relative Speed	γ
(a)	.561	1.99	1.62	19	2.89	100	1.80
(b)	.513	2.00	1.78	11	3.42	142	1.87
(c)	.515	2.36	2.03	14	3.94	118	2.22
(d)	.530	2.43	2.17	11	4.10	166	2.44

Example 16

An emulsion similar to that of Examples 14 and 15 and containing 107 grams of gelatin per mole of silver halide was prepared for coating as in Example 14. The material was divided into 6 parts as follows:

(*a*) 720 ccs. of a 10% solution of gelatin per mole of silver halide was added.
(*b*) 600 ccs. of a 12% solution of carboxymethylated oxidized soybean protein prepared in accordance with Example 9 was added per mole of silver halide. The protein used was known as Drackett 112A.
(*c*) 600 ccs. of a 12% solution of carboxymethylated oxidized soybean protein similar to that prepared in accordance with Example 9 was added per mole of silver halide. The protein used was known as Drackett 112B.
(*d*) 555 ccs. of a 13% solution of carboxymethylated oxidized soybean protein similar to that prepared in accordance with Example 9 was added per mole of silver halide. The protein used was known as Drackett 112C.
(*e*) 570 ccs. of a 12.6% solution of carboxymethylated oxidized soybean protein similar to that prepared in Example 9 was added per mole of silver halide. The protein was known as Drackett 220.
(*f*) 545 ccs. of a 13.2% solution of carboxymethylated oxidized soybean protein similar to that prepared in Example 9 was added per mole of silver halide. The protein used was known as Drackett 410.

These separate emulsions were coated onto cellulose acetate film supports and strips thereof were tested in the manner described in Example 14. The results obtained were tabulated as follows:

Part	D-max. wet	D-max. dry	Percent Loss of D	Relative Speed	γ
(a)	2.15	1.76	18	100	2.00
(b)	2.25	2.01	11	148	2.22
(c)	2.36	2.10	11	152	2.20
(d)	2.23	1.96	12	152	2.02
(e)	2.30	1.95	15	152	1.92
(f)	2.16	1.87	13	142	1.93

Example 17

An emulsion similar to that used in Example 15 was prepared for coating as described in Example 14. The material was divided into 9 parts, to 1 of which was added 720 ccs. of 10% gelatin solution per mole of silver halide (part *a*). To the other parts were added individually:

(*b*) Carboxymethyl oxidized soybean protein prepared with 20 grams of bromoacetic acid per 100 grams of protein in accordance with Example 4.
(*c*) Carboxymethyl oxidized soybean protein prepared with 15 grams of bromoacetic acid per 100 grams of protein in accordance with Example 7.
(*d*) Carboxymethyl oxidized soybean protein prepared with 10 grams of bromoacetic acid per 100 grams of protein in accordance with Example 6.
(*e*) Carboxymethyl oxidized soybean protein prepared with 5 grams of bromoacetic acid per 100 grams of protein as described in Example 5.

in quantities equal in dry weight to that of the gelatin added to part *a* and to the second set of parts (*f*, *g*, *h* and *i*) at ¼ this level but with additional gelatin to keep the total weight of protein in all samples constant. These parts were coated out onto cellulose acetate film supports and strips taken from each were tested as described in Example 14.

The results obtained were plotted on graphs illustrated by FIGS. 1 and 2 of the drawing. In the accompanying drawing FIG. 1 is a graphical representation based on relative speeds and FIG. 2 is a graphical representation based on maximum densities to indicate the improvement upon greater replacement of the gelatin of the photographic emulsion by carboxymethylated soybean protein.

Example 18

A coarse-grained gelatin-silver bromoiodide emulsion suitable for use in the preparaiton of high speed black-and-white negative film was prepared for coating by adding thereto solutions of coating aid and antifoggant. The emulsion was divided into five parts as follows:

(*a*) No further addition.
(*b*) 990 ccs. of a 10% gelatin solution per mole of silver halide was added.
(*c*) 1010 ccs. of a 9.8% solution of carboxymethyl casein prepared as described in Example 2 was added.
(*d*) 1250 ccs. of an 8% solution of oxidized soybean protein prepared as described in the first 6 lines of Example 3 was added.
(*e*) 1130 ccs. of an 8.8% solution of carboxymethyl oxidized soybean protein as prepared in Example 3 was added.

These separate parts were each coated onto cellulose acetate film support and were tested in the manner described in Example 14 except that several strips were exposed and then developed in various developers for

varying periods of time. The results obtained are tabulated below:

Part	Relative Speed			γ		
	4' Kodak D-19 Developer	5' Kodak DK-50 Developer	12' Kodak Rapid X-ray Developer	4' D-19 Developer	5' DK-50 Developer	12' Kodak Rapid X-ray Developer
(a)	110	142	205	0.87	0.69	0.90
(b)	100	159	224	0.77	0.80	1.11
(c)	118	163	191	0.99	1.01	1.37
(d)	126	195	252	0.83	0.88	1.10
(e)	148	205	309	1.00	0.95	1.20

Example 19

A fine-grain gelatin-silver chlorobromide emulsion containing 119 grams of gelatin per mole of silver halide was prepared for coating by adding coating aid thereto. The material was divided into 3 parts as follows:

(*a*) No further additions.
(*b*) 900 ccs. of a 10% solution of gelatin per mole of silver halide was added.
(*c*) 920 ccs. of a 9.8% solution of carboxymethyl casein per mole of silver halide was added.

Suitable hardener was added to each and these parts were coated onto cellulose acetate supports at a coverage of 300 square feet per mole of silver halide. The coatings were tested in the manner described in Example 14 with development in Kodak DK–50 developer for 5 minutes. The results obtained are as follows:

Part	D-max.	γ
(a)	1.89	2.26
(b)	2.03	2.40
(c)	2.51	2.80

Example 20

An emulsion similar to that used in Example 14 was prepared for coating and divided into 3 parts as follows:

(*a*) 1440 ccs. of a 10% solution of gelatin per mole of silver halide were added.
(*b*) 1080 ccs. of a 10% solution of gelatin and 360 ccs. of a 10% solution of carboxymethyl gelatin as prepared in Example 10 were added per mole of silver halide.
(*c*) 360 ccs. of a 10% solution of gelatin and 1080 ccs. of a 10% solution of carboxymethyl gelatin as prepared in Example 10 were added per mole of silver halide.

These parts were coated onto cellulose acetate film support and tested in the manner described in Examples 14 and 15. The results obtained were as follows:

Part	g. Ag per sq. ft.	D-max. Dry	D Dry, g. Ag ft.^{2}	Relative Speed	γ
(a)	.576	1.81	3.14	100	1.98
(b)	.613	1.92	3.13	121	2.22
(c)	.559	2.06	3.68	126	2.48

Example 21

An emulsion similar to that used in Example 14 was prepared for coating and divided into 5 parts as follows:

(*a*) 1440 ccs. of a 10% solution of gelatin per mole of silver halide were added.
(*b*) 360 ccs. of a 10% solution of gelatin and 1080 ccs. of carboxymethyl gelatin as described in Example 10 were added per mole of silver halide.
(*c*) Like *b* only the carboxymethyl gelatin added was that as prepared by the procedure of Example 11.
(*d*) Like *b* only the carboxymethyl gelatin added was that as prepared in Example 12.
(*e*) Like *b* only the carboxymethyl gelatin added was that as prepared in Example 13.

These parts were coated and strips thereof were tested as the manner described in Example 14. The results obtained were as follows:

Part	Relative Speed	γ	Fog	D-max. Dry
(a)	100	1.90	.06	1.72
(b)	132	2.08	.06	1.75
(c)	123	1.94	.06	1.75
(d)	121	2.10	.06	1.78
(e)	121	1.80	.06	1.65

The emulsions in accordance with our invention may, if desired, be chemically sensitized by any of the accepted procedures. For instance, these emulsions can be digested with naturally active gelatin, or sensitized sulphur compounds can be added such as those described in Sheppard U.S. Patent Nos. 1,574,944 and 1,623,499, and in Sheppard and Brigham 2,410,489.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, all of which belong to group VIII of the periodic table of elements and have an atomic weight greater than 100. Representative compounds are ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions can also be chemically sensitized with gold salts as described in Waller and Dodd U.S. Patent 2,399,083 or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856 and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850), polyamines such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925) or bis-(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926).

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, Carroll and Murray U.S. Patent 2,728,664, and Leubner and Murray U.S. Patent 2,728,665, the tetrazaindenes of Carroll U.S. Patent 2,716,062, and the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, Carroll and Allen U.S. Patent 2,288,226, and Carroll and Spence U.S. Patent 2,334,864, and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162.

We claim:

1. A photosensitive silver halide emulsion comprising silver halide carried by a protective colloid essentially consisting of protein material, 10–50% of which is photographically inert carboxymethylated protein substantially the remainder of the protein material being gelatin.

2. A photosensitive silver halide emulsion comprising silver halide carried by a protective colloid essentially consisting of a mixture of gelatin and photographically inert carboxymethylated gelatin, the latter being 10–50% of the mixture.

3. A photosensitive silver halide emulsion comprising

silver halide carried by a mixture essentially consisting of gelatin and photographically inert carboxymethylated oxidized casein, the latter being 10–50% of the mixture.

4. A photosensitive silver halide emulsion comprising silver halide carried by a protective colloid essentially consisting of a mixture of gelatin and photographically inert carboxymethylated soy protein, the latter being 10–50% of the mixture.

5. A photosensitive silver halide emulsion comprising silver halide carried by a mixture of gelatin and photographically inert carboxymethylated blood albumin, the latter being 10–50% of the mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,652,345	Jones	Sept. 15, 1953
2,691,582	Lowe et al.	Oct. 12, 1954
2,788,336	Uhring	Apr. 9, 1957
2,865,753	Griffin et al.	Dec. 23, 1958