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3,068,102

PHOTOGRAPHIC EMULSIONS SENSITIZED WITH SULFITE ESTER POLYMERS

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This invention concerns photographic silver halide emulsions, and more particularly, photographic silver halide emulsions containing a novel polymeric sensitizing material.

It is well known in the photographic art that silver halide emulsions can be chemically sensitized with a variety of materials in order to increase the speed thereof. Certain chemical sensitizers are believed to react with the silver halide to form on the surface of the silver halide minute amounts of silver sulfide, silver, or other noble metals. In addition, other classes of compounds can be utilized to increase the sensitivity of photographic silver halide emulsions that apparently do not enter into chemical combination with the silver halide. Such sensitization reaches a limit beyond which further addition of sensitizer merely increases the fog of the photographic emulsion with constant or decreasing speed.

It is an object of this invention to provide novel photographic silver halide emulsions that have increased sensitivity.

It is another object of this invention to provide new photographic silver halide emulsions having increased sensitivity without concomitant undesirable increases in fog.

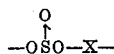
It is another object of this invention to provide a new class of photographic addenda that can provide additional sensitivity to photographic silver halide emulsions already sensitized with known chemical sensitizers.

It is still another object of this invention to provide novel photographic silver halide emulsions sensitized with a polymeric composition.

It is also an object of this invention to provide novel photographic silver halide-gelatin emulsions sensitized with a novel polymeric material containing polyalkylene oxide moieties having average molecular weights of less than about 300.

These and other objects of the invention are attained by employing in photographic silver halide emulsions sensitizing amounts of certain sulfite ester polymers as described hereinafter.

The polymeric sulfite ester sensitizers of the invention consist essentially of the recurring structural unit



wherein the substituent "X" is a polyoxyethylene radical having the structure

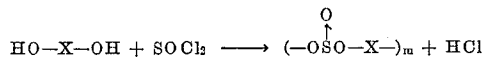


wherein the substituent "R" is an alkylene radical having 2 to 4 carbon atoms including ethylene, propylene and butylene radicals and mixtures thereof. The average molecular weight of the subject polymeric sulfite ester sensitizers suitably ranges from about 400 to about 3000 and preferably from about 400 to about 2000. The polyoxyalkylene moieties comprising the subject sensitizers have average molecular weights of less than about 300.

The polymeric sensitizers of the invention can be

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prepared by reacting polyalkylene glycols, $\text{HO}(\text{RO})_n\text{H}$, with thionyl chloride. The resulting reaction can be represented by the following Equation:



wherein the substituent "X" is a polyoxyalkylene radical as described above. Typically this reaction is carried out by slowly adding substantially equal molar proportions of thionyl chloride to a polyalkylene glycol in a suitable inert organic solvent such as benzene and thereafter refluxing the resulting reaction mixture for a few minutes. The resulting polymeric sensitizer can then be readily separated from the reaction mixture by distilling off the solvent. Further purification of the polymer can be effected, if desired, by conventional methods. Polyalkylene glycols are well-known compositions of commerce and can be prepared from alkylene oxides such as ethylene oxide, 1,2-propylene oxide, 1,3-butylene oxide and the like which have in turn been prepared from the corresponding unsaturated hydrocarbon. Typical polyalkylene glycols that can be employed to prepare the present sulfite ester polymers include:

- (a) Diethylene glycol, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$
- (b) Triethylene glycol, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$
- (c) Tetraethylene glycol, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_4\text{H}$
- (d) Tripropylene glycol, $\text{HO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_3\text{H}$
- (e) Dibutylene Glycol, $\text{HO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{H}$,

and the like.

The polymeric addenda of the invention can be added to photographic silver halide emulsions for the purpose of increasing the sensitivity thereof.

The preparation of photographic silver halide emulsions involves three separate operations: (1) emulsification and digestion of 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 sensitizers of our invention can be added to the emulsion before the final digestion or after-ripening, or they can be added immediately prior to the coating. Our new photographic sensitizers are unique in that no special final digestion or after-ripening are required in order to obtain optimum sensitization.

The particular quantity of the present sulfite ester sensitizers used in a given emulsion can vary, depending upon the effects desired, degree of ripening, silver content of the emulsion, etc. The amount used is also dependent upon the particular stage at which the sensitizer is added during the preparation of the emulsion. We have found that generally from about .1 to 10 grams per mole of silver halide are quite adequate to accomplish the desired sensitization. Exposure of the treated emulsion in conventional photographic testing apparatus, such as an intensity scale sensitometer, will reveal the most advantageous concentrations for the present polymeric sensitizers in that particular emulsion. Such techniques are well understood by those skilled in the art.

The sensitizer addenda of the invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, the subject sensitizers can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming

compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. The solvent should be selected so that it has no harmful effect upon the emulsion in accordance with usual practice, and generally solvents or diluents which are miscible with water are to be preferred. Water alone is a dispersing medium for some of the sensitizers of the invention. In other cases, the subject sensitizers can be dissolved in solvents, such as ethanol, acetone, pyridine, N,N-dimethylformamide, etc., and added to the emulsion in this form.

The emulsions of the invention can be chemically sensitized by any of the other well-known procedures. The sensitizers of the invention functions additively to customary sensitizers and can thus be used in combination therewith. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added, such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, and Sheppard et al. 1,623,499, issued April 5, 1927, and Sheppard and Brigham U.S. Patent 2,410,689, issued November 5, 1946. The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum. Representative compounds are ammonium chloropalladate, potassium chloropalladate, and sodium chloropalladate, 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, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, issued August 28, 1951. The emulsions can also contain sensitizing amounts of gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or stabilizing amounts of gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurate, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride. The emulsions can also contain sensitizing amounts of reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β -aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes as indicated above, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950; and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950 and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; VanLare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers, and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; and triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605, and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents

2,444,607, issued July 6, 1948, and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955 and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2-28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938; the bis-quaternary salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene bis-benzothiazolium perchlorate, etc.), and the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958.

The emulsions can also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955.

The emulsions can contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. Patent 2,960,404, issued November 15, 1960; an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. Patent 2,904,434, issued September 15, 1959; bis(ethoxy diethylene glycol) succinate as described in Gray U.S. Patent 2,940,854, issued June 14, 1960, or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. Patent 2,852,386 issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion can be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll U.S. Patents 2,725,294 and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonyl)ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxy-methylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2-3 carbon atoms, such as β -methylglutaraldehyde bis-sodium bisulfite; a bisaziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. Patent 2,950,197, issued August 23, 1960; or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959.

The emulsions can contain a coating aid such as saponin; a lauryl or oleoyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and

Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxy)pentaoxy)glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Stenberg, U.S. patent application Serial No. 691,125, filed October 21, 1957.

The polymeric sensitizer addenda which have been described can be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions they can also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They can be added to the emulsion before or after any sensitizing dyes which are used. 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 bromiodide. The subject addenda can be used in emulsions intended for 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 Godowsky U.S. Patent 2,698,794, issued January 4, 1955, or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243 issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

The subject addenda can also be used in emulsion intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,608,236, issued December 28, 1954 and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. patent application Serial No. 586,705, filed May 23, 1956. They can also be used in color transfer processes which utilize the 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. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957, and 554,935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, issued July 24, 1956 and Whitmore and Mader U.S. patent application Serial No. 734,141, filed May 9, 1958.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there can be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound, although gelatin is preferred. Some colloids which can be used

are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19-26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30-60% and a specific viscosity of 0.25-1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in Illingsworth, Dann and Gates U.S. Patent 2,852,382, issued September 19, 1958. If desired, compatible mixtures of two or more of these colloids can be employed for dispersing the silver halide in its preparation.

The above-described emulsions can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of resinous materials, as well as glass, paper, metals and others.

The molecular weights of the sulfite ester polymers of the invention described herein are average molecular weights of the respective polymeric compositions and were determined by the boiling point elevation method.

The invention is further illustrated by the following examples of preferred embodiments thereof.

EXAMPLE 1

A solution of 150 g. (1.0 mole) of triethylene glycol in 250 ml. of benzene was heated to boiling on a steam bath. The heat was then shut off and 119 g. (1.0 mole) of thionyl chloride was added dropwise at a rate sufficient to keep the benzene solution refluxing. After completion of the addition of the thionyl chloride, the resulting solution was refluxed for about 5 more minutes, after which the volatile constituents were stripped off with a water aspirator. The remaining syrupy residue was dissolved in ethyl acetate, boiled with charcoal, filtered, and the solvent evaporated in vacuo. The remaining sulfite ester polymer was a light amber syrup having an average molecular weight of about 1540. Similarly, other polymeric compositions of the invention were prepared by substituting other polyalkylene glycols or by employing other proportions of benzene solvent to reactants. The details of the preparation of several polymeric compositions of the invention are summarized by the data set out in Table A below.

Table A

Glycol	Moles of glycol	Moles of SOCl ₂	Ml. of benzene solvent	Average molecular weight of product
(1) Diethylene glycol.....	0.5	0.5	125	1200
(2) Triethylene glycol.....	1.0	1.0	250	1540
(3) Triethylene glycol.....	0.5	0.5	125	1290
(4) Triethylene glycol.....	0.2	0.2	3000	455
(5) Tetraethylene glycol.....	0.5	0.5	150	490
(6) A polyethylene glycol ¹ ...	1.0	1.0	250	1200
(7) Tripropylene glycol.....	0.5	0.5	150	705

¹ "Carbowax 200," a polyethylene glycol having an average molecular weight of about 200.

In a similar manner polybutylene derivatives can be prepared by substituting a polybutylene glycol such as dibutylene or tributylene glycol for the described alkylene glycols.

EXAMPLE 2

The sulfite ester polymers prepared as described in Example 1, when incorporated in a high speed silver bromoiodide-gelatin photographic emulsion at levels of 0.3, 0.9 and 3.0 grams per mole of silver bromoiodide, and coated on a cellulose acetate film support, significantly improve the relative speed of the emulsion. The emulsion was optically sensitized with a cyanine dye. Such photographic elements were exposed in the form of film strips in the usual manner in an Eastman Type Ib Sensitometer and then developed for 5 minutes at 68° F. in a photographic developer having the following formula:

	Grams
N-methyl-p-aminophenol sulfite	2.5
Hydroquinone	2.5
Sodium sulfite (anhydrous)	30.0
Sodium borate	10.0
Potassium bromide	0.5
Water to make 1 liter.	

The results of the sensitometric tests are summarized by the data set out in Table B below wherein the speed, gamma and fog for several of the emulsions containing the polymeric sensitizers of the invention are compared with emulsions not containing the polymeric sulfite ester sensitizers of the invention.

Table B

Polymeric addenda ¹	Amount of addenda (g./mole AgX)	Relative speed	Gamma	Fog
Control		100	1.43	.13
1	0.3	107	1.53	.13
1	0.9	115	1.45	.14
1	3.0	141	1.33	.15
2	0.3	105	1.42	.14
2	0.9	126	1.57	.15
2	3.0	148	1.47	.16
4	0.9	120	1.88	.14
6	0.3	118	1.45	.14
6	0.9	135	1.40	.16
6	3.0	166	1.18	.16

¹ The polymeric addenda correspond in number to the sulfite ester polymers identified in Table A of Example 1.

EXAMPLE 3

Several emulsions were prepared and coated on a film support as described in Example 2 but were developed for 15 minutes at 68° F. after exposure in the sensitometer with a color developer containing the coupler, H-acid. The developer contained 10 g./liter of the H-acid. The color developer composition had the following composition:

Benzyl alcohol	cc	10
Sodium hexametaphosphate	g	2.0
Sodium sulfite	g	2.0
Sodium hydroxide	g	3.4
H-acid	g	10.0
4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamido-ethyl) aniline sulfate	g	8.0
Sodium carbonate monohydrate	g	40.0
Sodium bromide	g	1.5
Sodium thiocyanate	g	0.2
Benzotriazole	g	.03
Water to make 1 liter.		

The results of the sensitometric tests are summarized by the data set out in Table C below wherein the speed, gamma and fog for several of the emulsions containing the polymeric sulfite ester sensitizers of the invention are compared with emulsions not containing the sensitizers of the invention.

Table C

Polymeric addenda ¹	Amount of addenda (g./mole AgX)	Relative speed	Gamma	Fog
Control		100	1.13	.15
1	0.3	102	1.28	.15
1	0.7	107	1.25	.15
1	3.0	118	1.38	.16
2	0.3	105	1.23	.16
2	0.9	112	1.43	.16
2	3.0	132	1.42	.18
4	0.3	105	1.28	.16
4	0.9	107	1.38	.15
6	0.3	112	1.38	.16
6	0.9	126	1.40	.18
6	3.0	145	1.50	.18

¹ The polymeric addenda correspond in number to the polymeric addenda identified in Table A of Example 1.

EXAMPLE 4

The sulfite ester polymeric addendum of the invention prepared from triethylene glycol and thionyl chloride and described in Example 1, Table A, compound 2, was incorporated at various levels in several high-speed bromoiodide emulsions optically sensitized to a particular region of the spectrum and containing color couplers. One emulsion containing no optical sensitizer and sensitive in the blue range contained dispersed therein an open-chain coupler having a reactive methylene group suitable for forming a yellow image with oxidized color developer, e.g. couplers Nos. I to V of McCrossen et al. U.S. Patent 2,875,057 in dibutyl phthalate. A second emulsion containing a carbo-cyanine dye optical sensitizer sensitive in the green range (ca. 500-600 mμ) contained dispersed therein a pyrazolone coupler suitable for forming a magenta image with oxidized color developer, e.g. couplers Nos. 7 etc. of Fierke et al. U.S. Patent 2,801,171 (column 2) a third emulsion containing a carbo-cyanine dye optical sensitizer and sensitive in the red range (ca. 600-700 mμ) contained dispersed therein a phenolic coupler suitable for forming a cyan image with oxidized color developer, e.g. couplers Nos. 1 to 6 of Fierke et al. U.S. Patent 2,801,171 (column 2) in a solvent such as tri-o-cresylphosphate. Emulsions containing none of the sulfite ester polymeric addenda were also prepared. The emulsions were then coated on a transparent cellulose acetate film support dried, then exposed in an Eastman Ib Sensitometer and thereafter processed in a reversal color process as follows:

The exposed film was developed in a developer having the following composition:

Sodium hexametaphosphate	g	2.0
N-methyl-p-aminophenol sulfite	g	6.0
Sodium sulfite, anhydrous	g	50.0
Hydroquinone	g	6.0
Sodium carbonate monohydrate	g	35.0
Potassium bromide	g	2.0
Sodium thiocyanate	g	1.5
0.5% solution of 6-nitrobenzimidazole nitrate	cc	12.0
0.1% solution of potassium iodide	cc	10.0
Water to make 1 liter.		

The element was then thoroughly washed with water and treated in a hardening bath having the following composition:

Potassium chrome alum crystals	g	30.0
Water to make 1 liter.		

The element was then thoroughly washed with water and treated for 30 seconds in a solution having the following composition:

Sodium borohydride	g	0.25
Sodium hydroxide	g	4.0
Water to make 1 liter.		

The element was then treated in a color developer having the following composition:

Benzyl alcohol-----cc--	6.0
Sodium hexametaphosphate-----g--	2.0
Sodium sulfite, anhydrous-----g--	5.0
Trisodium phosphate-----g--	40.0
Potassium bromide-----g--	0.25
0.1% solution of potassium iodide-----cc--	10.0
Sodium hydroxide-----g--	6.5
Color developer ¹ -----g--	11.33
Ethylenediamine sulfate-----g--	7.8
Citrazinic acid-----g--	1.5
Water to make 1 liter.	

¹ 4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.

The element was then thoroughly washed with water and treated in a clearing and fixing bath having the following composition:

	G.
Sodium thiosulfate-----	150.0
Sodium bisulfite-----	20.0
Water to make 1 liter.	

The elements was then treated in a bleach bath having the following composition:

	G.
Potassium dichromate-----	5.0
Potassium ferricyanide-----	70.0
Potassium bromide-----	20.0
Water to make 1 liter.	

The element was again washed and treated once again with the clearing and fixing bath identified above. The element was again washed and treated in a stabilizing bath having the following composition:

Formaldehyde (37% by weight)-----cc--	7.0
Dispersing agent ¹ -----g--	0.5
Water to make 1 liter.	

¹ Such as Triton-X 100, i.e., an alkylaryl polyether alcohol (octylphenoxy polyethoxy ethanol).

The increases in speed resulting from adding the sulfite ester polymers to the various emulsions are summarized by the data set out in Table D below.

Table D

Amount of sulfite ester polymer addenda (g./mole AgX)	Optical Sensitization range	Color image formed	Relative speed
(a) Control-----	blue-----	yellow-----	100
1-----	do-----	do-----	159
3-----	do-----	do-----	200
(b) Control-----	green-----	magenta-----	100
1-----	do-----	do-----	126
1.5-----	do-----	do-----	145
(c) Control-----	red-----	cyan-----	100
1-----	do-----	do-----	159
2-----	do-----	do-----	186

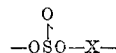
Thus, the present invention describes new and useful photographic silver halide emulsions.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the inven-

tion as described hereinabove and as defined in the appended claims.

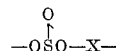
We claim:

1. A photographic silver halide emulsion containing a sensitizing amount of a sulfite ester polymer consisting essentially of the recurring structural unit



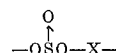
- 10 wherein X is a polyoxyalkylene radical having alkylene moieties with 2 to 4 carbon atoms and an average molecular weight of less than about 300.

2. A photographic silver halide-gelatin emulsion containing a sensitizing amount of a sulfite ester polymer having an average molecular weight in the range of about 400 to 3000 and consisting essentially of the recurring structural unit



- 20 wherein X is a polyoxyalkylene radical having alkylene moieties with 2 to 4 carbon atoms and an average molecular weight of less than about 300.

3. A photographic silver halide-gelatin emulsion containing .1 to 10 grams per mole of silver halide of a sulfite ester polymer having an average molecular weight in the range of about 400 to 2000 and consisting essentially of the recurring structural unit



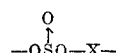
- 30 wherein X is a polyoxyethylene radical having an average molecular weight of less than about 300.

4. A photographic silver halide-gelatin emulsion as described in claim 3 wherein the polyoxyethylene radical has an average molecular weight of about 200.

5. A photographic silver halide-gelatin emulsion as described in claim 3 wherein X is a radical having the structure $-(\text{CH}_2\text{CH}_2\text{O})_3-$.

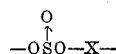
6. A photographic silver halide-gelatin emulsion as described in claim 3 wherein X is a radical having the structure $-(\text{CH}_2\text{CH}_2\text{O})_2-$.

7. A photographic silver bromoiodide-gelatin emulsion containing .1 to 10 grams per mole of silver bromoiodide of a sulfite ester polymer having an average molecular weight in the range of about 400 to 2000 and consisting essentially of the recurring structural unit



- 50 wherein X is a polyoxyethylene radical having an average molecular weight of less than about 300.

8. A photographic element comprising a support and a light-sensitive silver halide-gelatin emulsion layer containing .1 to 10 grams per mole of silver bromoiodide of a sulfite ester polymer having an average molecular weight in the range of about 400 to 3000 and consisting essentially of the recurring structural unit



- 60 wherein X is a polyoxyethylene radical having an average molecular weight of less than about 300.

No references cited.