



Photographic silver halide emulsions

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PHOTOGRAPHIC SILVER HALIDE EMULSIONS

This relates to silver halide emulsions

and more particularly to novel spectrally sensitized photographic silver halide emulsions containing azaindene stabilizers and certain sulfated polymeric addenda.

By incorporating a sulfated polyvinyl alcohol into a photographic silver halide emulsion which is spectrally sensitized with a cyanine dye and which also contains an azaindene stabilizer certain advantages are provided. It has been found that the presence of the sulfated polyvinyl alcohol in emulsions sensitized with cyanine dyes gives higher sensitivity both to the region of inherent sensitivity of the emulsion and to the region of absorption of the sensitizing dye used. In addition the sulfated polymer, when added to spectrally sensitized emulsions also containing an azaindene stabilizer, increases the absorption of the sensitizing dye in the region of the J-aggregate band. The sulfated polyvinyl alcohol does not alter the stabilizing benefit of the azaindene. Thus, the sulfated polyvinyl alcohol when added to the spectrally sensitized and azaindene-stabilized silver halide emulsion, counteracts the deaggregation-effect of the azaindene stabilizers without removing their benefits.

The term 'sulfated polyvinyl alcohol' as employed herein includes, for example, a polymer which is comprised of vinyl hydrogen sulfate and vinyl alcohol monomer units, along, or in combination with other monomers, eg, copoly (vinyl alcohol, vinyl hydrogen sulfate, vinyl 2-hydroxy-5-sulfophenyl carbonate). An especially preferred sulfated polyvinyl alcohol is one in which the polymer is comprised only of vinyl hydrogen sulfate and vinyl alcohol monomer units, viz, copoly(vinyl alcohol, vinyl hydrogen sulfate). Also preferred are the sulfated polyvinyl alcohols in which the sulfated bound monomeric unit recurring in the vinyl polymer chain constitutes from about 5 to about 75 mole percent of the total monomer units in the polymer. Normally the sulfated polyvinyl alcohols in the described compositions are employed in the form of salts, such as ammonium or alkali metal salts.

Examples of sulfated polyvinyl alcohols which can be used are disclosed in the patent to King et al, US 3,437,486 of April 8, 1969.

The silver halide emulsions used can comprise silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide or mixtures thereof. The emulsions may be coarse or fine grain and can be prepared by any of the well-known procedures, eg single

jet emulsions, double jet emulsions, such as Lippmann emulsions, ammonia-cal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al US Patent 2,222,264; Illingsworth US Patent 3,320,069; and McBride US Patent 3,271,157.

Surface image emulsions may be used or internal image emulsions such as those described in Davey et al US Patent 2,592,250; Porter et al US Patent 3,206,313; Berriman US Patent 3,367,778 and Bacon et al US Patent 3,447,927. If desired, mixtures of surface and internal image emulsions may be used as described in Luckey et al US Patent 2,996,382. Negative type emulsions may be used or direct positive emulsions such as those described in Leermakers US Patent 2,184,013; Berriman US Patent 3,367,778; Schouwenaars British Patent 723,019; Illingsworth et al French Patent 1,520,821; Ives US Patent 2,563,785; Knott et al US Patent 2,456,953 and Land US Patent 2,861,885. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, J. Phot. Sci., Vol. 12, No.5, Sept/Oct, 1964, pp 242-251.

The spectrally sensitized emulsions include orthochromatic, panchromatic and infrared sensitive emulsions, for example. The spectral sensitization of the emulsions can be accomplished in conventional manner, for example, by treating the emulsion with a solution of a cyanine sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al British Patent 1,154,781. For optimum results, the dye may either be added to the emulsion as a final step or at some earlier stage.

The term cyanine dye is used herein in its broad sense to include not only the simple cyanine dyes but also the carbocyanines, dicarbocyanines, tricarbocyanines and the like. Cyanine dyes useful in sensitizing emulsions of the present invention are described, for example, in Sprague US Patent 2,503,776; Van Lare US Patent 2,739,149; Rosenoff US Patent 3,177,210; Heseltine US Patent 2,734,900; Heseltine et al US Patent 2,666,761; Brooker et al US Patent 3,411,916, and in Mees et al, 'The Theory of the Photographic Process', The Macmillan Company, publishers, 3rd Edition, Chapter II, especially pages 201-216 and the references cited therein.

Dyes of the cyanine class may contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei may contain

alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and may be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes may be symmetrical or unsymmetrical and may contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

As previously mentioned, the sulfated polyvinyl alcohol compounds can be incorporated in spectrally sensitized silver halide emulsions that also contain an azaindene stabilizer. Such azaindenes (also known as azaindolizines) include triazaindenes, tetrazaindenes and pentazaindenes.

Typical suitable azaindenes are, for example, the 1-thia-3,5,7-triazaindenes of US Patent 2,772,164 and those azaindenes disclosed in US Patents Nos 2,444,605; 2,444,606; 2,444,607; 2,415,397; 2,444,609; 2,449,225; 2,713,541; 2,743,181; 2,716,062; 2,735,760; 2,756,147; 2,886,437 and Z. Wiss. Phot., Vol 47, 1952, pgs 2 to 28.

The concentration of the sulfated polyvinyl alcohol employed may vary over a wide range. However, suitable ranges include between about 1 and about 75 grams of the sulfated polyvinyl alcohol per mole silver, preferably between about 1 and about 25 grams per mole.

The increased speed effect resulting from the incorporation of the sulfated polyvinyl alcohol extends over a wide range of development times and is relatively independent of the sulfated polyvinyl alcohol level over the range of 1 to 10 grams per mole of silver halide. Also, the addenda do not alter the covering power of the developed silver.

The emulsions used may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al US Patent 1,623,499; Waller et al US Patent 2,399,083; McVeigh US Patent 3,297,447; and Dunn US Patent 3,297,446.

The emulsions include those designed for color photography, for example, emulsions containing color-forming couplers such as those described in Frohlich et al US Patent 2,376,679, Jelley et al US Patent 2,322,027; Fierke et al US Patent 2,801,171; Godowsky US Patent 2,698,794; Barr et al US Patent 3,227,554 and Graham

et al US Patent 3,046,129; or emulsions to be developed in solutions containing color-forming couplers such as those described in Mannes et al US Patent 2,252,718, Carroll et al US Patent 2,592,243 and Schwan et al US Patent 2,950,970; and in false-sensitized color materials such as those described in Hanson US Patent 2,763,549.

This may be used with elements designed for colloid transfer processes such as described in Yutzy et al US Patent 2,716,059; silver salt diffusion transfer processes such as described in Rott US Patent 2,352,014; Land US Patent 2,543,181; Yackel et al US Patent 3,020,155, and Land US Patent 2,861,885; color image transfer processes such as described in Rogers US Patents 3,087,817; 3,185,567; and 2,983,606; Weyerts et al US Patent 3,253,915; Whitmore et al US Patent 3,227,550; Barr et al US Patent 3,227,551; Whitmore US Patent 3,227,552; and Land US Patents 3,415,644; 3,415,645; 3,415,646; and imbibition transfer processes as described in Minsk US Patent 2,882,156.

The photographic emulsions and elements employed can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example, gelatin and gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed can also contain alone or in combination with hydrophilic, water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports.

The silver halide emulsions used may contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper US Patent 2,886,437; Dann et al US Patent 3,046,134; Carroll et al US Patent 2,944,900; and Goffe US Patent 3,294,540.

The silver halide emulsions used can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping by means of one or more antifoggants and stabilizers in addition to the azaindenes which have already been mentioned.

The photographic elements of this invention may contain incorporated developing agents such as hydroquinones, catechols, aminophenols 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines. Combinations of developing agents can be employed.

The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element.

The photographic and other hardenable layers used can be hardened by various organic or inorganic hardeners.

The photographic layers employed may contain surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen US Patent 2,600,831; amphoteric compounds such as those described in Ben-Ezra US Patent 3,133,816; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Patent 1,022,878.

Photographic elements prepared can be processed by various methods including processing in alkaline solutions containing conventional developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, phenylenediamines, ascorbic acid derivatives, hydroxylamines, hydrazines; reductones and the like; web processing such as described in Tregillus et al US Patent 3,179,517; stabilization processing as described in Russell et al 'Stabilization Processing of Films and Papers,' PSA Journal, Vol 16B, August 1950; monobath processing as described in Levy 'Combined Development and Fixation of Photographic Images with Monobaths,' Phot.Sci. and Eng., Vol 2, No 3, October 1958, and Barnes et al US Patent 3,392,019. If desired, the photographic elements can be processed in hardening developers such as those described in Allen et al US Patent 3,232,761; in roller transport processors such as those described in Russell et al US Patent 3,025,779; or by surface application processing as described in Example 3 of Kitze US Patent 3,418,132.

Example 1

Into a 500 ml three-neck flask, fitted with a mechanic stirring device, heating mantle, condenser and thermometer, is placed 22g (0.5 mole) of poly(vinyl alcohol), 36.4g (0.375 mole) of sulfamic

acid and 250 ml of N,N-dimethylformamide. This mixture is stirred and slowly heated to 90deg C at which time solution occurs and then from the dark amber solution separates a polymer mass. After precipitation occurs the temperature of the reaction mixture is slowly raised to 110deg C and then cooled to 90deg C. The N,N-dimethylformamide is decanted off and the soft cake is dissolved in 100 ml of distilled water, (pH 2.2).

The polymer solution is filtered by suction through filter paper covered by a layer of filteraid. The dope is poured into acetone to precipitate the polymer. The light tan precipitate is washed with acetone and is then dried overnight under reduced pressure over P₂O₅. The recovered product is a poly(vinyl alcohol, vinyl hydrogen sulfate).

The effect of incorporating sulfated polyvinyl alcohols in silver halide emulsions with other addenda is illustrated in Examples 2-9 which follow.

Examples 2-5

Four photoelements are prepared by coating silver chlorobromide emulsions containing the spreading agent, saponin, and the gelatin hardener, formalin, onto a film support.

Two of the coatings (Ex 4 and 5) are panchromatically sensitized with a mixture of 3,3'-diethyl-9-methylthiacarbocyanine bromide, 1,1'-diethyl-2,2'-cyanine iodide and 3,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide. A sulfated polyvinyl alcohol similar to that of Example 1 is incorporated into one of the nonspectrally sensitized coatings (Ex 2) and into one of the spectrally sensitized coatings (Ex 5).

Each of the coatings is exposed to an intensity modulating wedge and is developed for a period of 6 minutes in Kodak developer D-19.

Typical results of these tests for speed in regard to each of the coatings are given in the following table:

<u>Table A</u>		
<u>Example No</u>	<u>Addenda</u>	<u>Relative Speed</u>
2	---	100
3	sulfated polyvinyl alcohol	91
3	Panchromatic sensitizing dyes	776
5	Panchromatic sensitizing dyes; sulfated polyvinyl alcohol	1050

Examples 4 and 5 of Table A show that the relative speed of a silver halide emulsion which is spectrally sensitized

with a cyanine dye is greatly increased when a sulfated polyvinyl alcohol is incorporated therein. As shown by Examples 2 and 3, the addition of the sulfated polymer to the particular non-spectrally sensitized emulsion which these examples employ does not necessarily increase the relative speed, although the sulfated polymer does serve as a valuable non-migrating antifoggant for the emulsion, as reported in King et al US Patent 3,437,486.

Examples 6-7

Two coatings are formed in a manner identical to that of the spectrally sensitized coatings of Examples 4 and 5, respectively, with the exception that the azaindene stabilizer, 4-hydroxy-6-methyl-1,3,3a,7-tetraza-indene, is also included in each of the coatings.

These coatings are exposed and processed as before, and typical results of tests conducted on the coatings are as follows:

Table B

<u>Example No</u>	<u>Addenda</u>	<u>Relative Speed</u>
6	Panchromatic sensitizing dyes; azaindene stabilizer	1020
7	Panchromatic sensitizing dyes; azaindene stabilizer; sulfated polyvinyl alcohol	1320

The results shown in Table B indicate that the sensitivity of the stabilized, spectrally-sensitized coating is greatly increased by the addition of the sulfated polyvinyl alcohol.

Examples 8-9

A silver chlorobromide emulsion (Ex 8) which is panchromatically sensitized with the same mixture of cyanine dyes as in Examples 4 and 5 and which contains the spreading agent, saponin, the gelatin hardener, formalin, and the same azaindene stabilizer, is coated onto a film support. A similar emulsion (Ex 9) which contains, in addition, a sulfated polyvinyl alcohol, is coated onto an identical film support. The films are exposed on a spectrograph and processed in the developer employed in the foregoing examples. The sensitivities at various wave lengths of exposing lights are as follows:

The advantages of the addition of sulfated polyvinyl alcohol to the silver halide emulsions in other photographic systems are illustrated by Examples 10-15 which follow:

Examples 10-13

As a control (Ex 10) is prepared a photographic element for a multicolor diffusion transfer system, as described in Example 1 of the patent to Weyerts et al US 3,146,102, but consisting only of the support (layer 10), the cyan developer coating (layer 11), the gelatin silver bromiodide emulsion layer sensitized with a cyanine dye to the red region of the spectrum (layer 14) and the hydroquinone derivative layer (layer 19). For comparison a similar photoelement is prepared (Ex 11) except that it contains a sulfated polyvinyl alcohol in the silver halide emulsion layer. An azaindene stabilizer is added to other photographic elements (Ex 12 and 13) that are otherwise identical to those of Examples 10 and 11, respectively. The photoelements with the sulfated polyvinyl alcohol (Ex 11 and 13) result in a 0.1 to 0.15 log E speed increase over the control (Ex 10) which contains no sulfated polyvinyl alcohol. In Example 13 the sulfated polyvinyl alcohol regains the incubation speed lost in the coating containing azaindene stabilizer but no sulfated polymer (Ex 12).

Example 14

A sulfated polyvinyl alcohol is added in the amounts of 1 to 25 grams per mole of silver bromiodide to an infrared-sensitized aero film containing an azaindene stabilizer and sensitized with 3,3'-diethyl selenadicarbocyanine ethyl sulfate. This addition increases the blue and infrared speeds by 0.2 log E. Incubation speed stability is best at the 1 to 10 grams per mole levels.

Example 15

A sulfated polyvinyl alcohol is added in the amount of 2 grams per mole of silver bromiodide to a color-separation negative film spectrally sensitized as described in Examples 2-5. This addition increases the red gamma, while it also increases the red and green speeds by 0.14 to 0.20 log E. The incubation speed stability is excellent.

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Table C

<u>Example No</u>	<u>Sulfated Polyvinyl Alcohol</u>	<u>Relative Speed</u>			
		<u>400 mμ</u>	<u>520 mμ</u>	<u>573 mμ</u>	<u>650 mμ</u>
8	no	100	100	100	100
9	yes	141	132	191	155