

United States Patent

Jones

[15] 3,644,119

[45] Feb. 22, 1972

[54] **PHOTOGRAPHIC MATERIALS AND ELEMENTS**

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[22] Filed: May 18, 1970

[21] Appl. No.: 38,495

[52] U.S. Cl.: 96/108, 96/101, 96/84

[51] Int. Cl.: G03c 1/28, G03c 1/36, G03c 1/84

[58] Field of Search: 96/101, 131, 84, 108, 106

[56] **References Cited**

UNITED STATES PATENTS

2,503,776	8/1950	Spague	96/131
3,501,305	3/1970	Illingsworth	96/101

3,488,708	1/1970	Smith	96/84
3,501,306	3/1970	Illingsworth	96/101
3,501,307	3/1970	Illingsworth	96/101

FOREIGN PATENTS OR APPLICATIONS

723,019 2/1955 Great Britain

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[57] **ABSTRACT**

Direct positive emulsions fogged with a reducing agent and a compound of a metal more electropositive than silver contain a dinitro-substituted thiacyanine dye as electron acceptor. Preferably, the emulsions contain a synthetic polymeric latex and the dye contains a sulfoalkyl substituent.

12 Claims, No Drawings

PHOTOGRAPHIC MATERIALS AND ELEMENTS

This invention relates to novel photographic materials, and more particularly to new and improved direct positive photographic silver halide emulsions and photographic elements prepared with these new emulsions.

Direct positive photographic silver halide emulsions fogged with the combination of a reducing agent and a compound of a metal more electropositive than silver, and containing as electron acceptor or "desensitizer" 3,3'-dimethyl-6,6'-dinitrothiacarbocyanine p-toluenesulfonate are described in British Pat. No. 723,019 published Feb. 2, 1955. Such emulsions provide direct positive images which have low fog in the areas of high exposure. However, it would be desirable to modify such emulsions to increase the maximum density of images obtained therewith. In addition, emulsions of this type have heretofore not exhibited as high a degree of dimensional stability as would be desired for certain uses, for example in making reproductions of radiographic images. Moreover, the images obtained with the emulsions should be substantially free from stain, such as any stain which might be caused by residual electron acceptor being retained in the emulsion subsequent to processing.

It is, therefore, one object of this invention to provide direct positive photographic silver halide emulsions and photographic elements prepared therewith.

Another object of this invention is to provide direct positive photographic silver halide emulsions which produce photographic images having low fog in areas of high exposure and high maximum density in areas which receive little or no exposure.

A further object of this invention is to provide direct positive photographic silver halide emulsions which exhibit good dimensional stability when coated on a support.

Still another object of this invention is to provide photographic emulsions which are substantially free from stain after processing.

Other objects of this invention will become apparent from this disclosure and the appended claims.

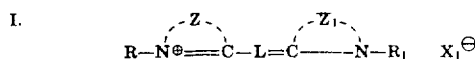
In accordance with one embodiment of this invention, direct positive photographic emulsions are provided comprising light-sensitive silver halide grains fogged with the combination of a reducing agent and a compound of a metal more electropositive than silver, said emulsion containing as electron acceptor a simple cyanine dye comprising first and second nuclei selected from the group consisting of a nitrobenzothiazole nucleus and a nitronaphthothiazole nucleus, said nuclei being joined, by the two carbon atoms thereof, to a monomethine linkage. It has been found that direct positive photographic emulsions of this type exhibit high density in areas of low exposure and low minimum density in areas of high exposure.

In another embodiment of this invention, photographic emulsions which exhibit good dimensional stability are provided which comprise a direct positive photographic silver halide emulsion fogged with the combination of a reducing agent and a compound of a metal more electropositive than silver, said emulsion containing as electron acceptor a simple cyanine dye comprising first and second nuclei selected from the group consisting of a nitrobenzothiazole nucleus and a nitronaphthothiazole nucleus, said nuclei being joined through the two carbon atoms thereof to a monomethine linkage, at least one of said nuclei having a sulfoalkyl group attached to the heterocyclic nitrogen atom thereof; and, the binder for said photographic silver halide emulsion comprising a synthetic polymeric latex. Photographic silver halide emulsions in accordance with this embodiment of the invention can be coated on supports to provide photographic elements of excellent dimensional stability, and can be processed to provide substantially stain-free photographic records. The electron acceptors employed in this invention are compatible with synthetic polymeric latices, whereas many known electron acceptors are not compatible with synthetic polymeric latices.

In accordance with another embodiment of this invention, photographic elements are provided having a support coated with a direct positive emulsion of the type described herein.

As used herein and in the appended claims, the term "nitrobenzothiazole" means that at least one hydrogen atom of the benzene ring of the benzothiazole nucleus is replaced with a nitro group. Similarly, the term "nitronaphthothiazole" means that at least one hydrogen atom of the naphthylene ring of the naphthothiazole nucleus is replaced with a nitro group.

The preferred cyanine dyes of this invention include those having the following formula:



wherein L represents a methine linkage, e.g., $-\text{CH}=\text{}$, $-\text{C}(\text{CH}_3)=$, $-\text{C}(\text{C}_2\text{H}_5)=$, $-\text{C}(\text{C}_6\text{H}_5)=$, etc.; R and R₁ each represents the same or different alkyl group, including substituted alkyl, (advantageously a lower alkyl containing from one to four carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., and substituted alkyl groups (preferably a substituted lower alkyl containing from one to four carbon atoms), such as a hydroxyalkyl group, e.g., β -hydroxyethyl, ω -hydroxybutyl, etc., an alkoxyalkyl group, e.g., β -methoxyethyl, ω -butoxybutyl, etc., a carboxyalkyl group, e.g., β -carboxyethyl, ω -carboxybutyl, etc.; an acyloxyalkyl group, e.g., β -acetoxyethyl, γ -acetoxypropyl, ω -butyryloxybutyl, etc., an alkoxycarbonylalkyl group, e.g., β -methoxycarbonyl-ethyl, ω -ethoxycarbonylbutyl, etc., a dialkylaminoalkyl group, e.g., diethylaminoethyl, etc., benzyl, phenethyl, and preferably at least one of R and R₁ represents a sulfoalkyl group such as sulfomethyl, 2-sulfopropyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, or higher sulfoalkyl groups such as 6-sulfohexyl, and 12-sulfododecyl; X represents an acid anion, e.g., chloride, bromide, iodide, perchlorate, sulfamate, p-toluenesulfonate, methyl sulfate, etc., and can be included in R or R₁, for example, when R or R₁ represents a sulfoalkyl group or a carboxyalkyl group; and Z and Z₁ each represents a nitrosubstituted nucleus selected from the group consisting of: a nitrobenzothiazole nucleus, e.g., 5-nitrobenzothiazole, 6-nitrobenzothiazole, 5-chloro-6-nitrobenzothiazole, 5,6-dinitrobenzothiazole, nitronaphthothiazole nucleus, e.g., 5-nitronaphtho[2,3-d]thiazole, 6-nitronaphtho[1,2-d]thiazole, a 5,6-dinitronaphtho[2,3-d]thiazole, a 4,5-dinitronaphtho[1,2-d]thiazole, a 7,8-dinitronaphtho[2,1-d]thiazole, 8-nitronaphtho[2,1-d]thiazole, etc. The simple cyanine nitrobenzothiazole dyes wherein R and R₁ in each instance represents a sulfoalkyl group of one to four carbon atoms are especially useful in this invention and are preferred. The above defined cyanine dyes can be prepared, for example, by the general procedures described in Sprague U.S. Pat. No. 2,503,776, issued Apr. 11, 1950, by replacing intermediates disclosed therein with appropriate intermediates containing nitro groups.

Typical nitrosubstituted thiacyanine dyes useful in the practice of this invention include the following:

Anhydro-6,6'-dinitro-3,3'-di(3-sulfopropyl)thiacyanine hydroxide, sodium salt
3,3'-Diethyl-6,6'-dinitrothiacyanine chloride
3,3'-Diethyl-6,6'-dinitro-6,7,6',7'-dibenzothiacyanine iodide
Anhydro-3-methyl-5',6'-dinitro-3'-(3-sulfobutyl)-4,5-benzothiacyanine hydroxide
Anhydro-3-ethyl-8,8'-dinitro-3'-(3-sulfopropyl)-4,5,4',5'-dibenzothiacyanine hydroxide
Anhydro-6,6'-dinitro-3,3'-di(3-sulfopropyl)thiacyanine hydroxide, sodium salt

The direct positive emulsions of this invention can comprise various alkali-permeable colloids and combinations thereof as vehicles or binding agents. Suitable alkali-permeable colloid materials include substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like.

Preferably, the binder comprises a synthetic polymeric latex. Synthetic polymeric latices increase the dimensional stability of emulsions in which they are incorporated.

The concentration of alkali-permeable colloid can vary over a wide range. Typical useful concentrations are from about 20 to 500 grams of the alkali-permeable colloid per mole of silver halide. The most useful concentration is from about 50 to 200 grams alkali-permeable colloid per mole of silver halide.

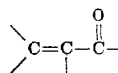
The alkali-permeable colloid binder can consist solely of the synthetic polymeric latices referred to herein. If desired, a hydrophilic colloid, such as gelatin, can be employed together with the synthetic polymeric latex. The proportions of synthetic polymeric latex to hydrophilic colloid can vary over a wide range, such as from 10 to 90 percent, and preferably about 25 to 75 percent, by weight of the colloid being synthetic polymeric latex. The synthetic polymeric latex should be employed in a concentration sufficient to impart dimensional stability to photographic elements prepared with the emulsion.

Generally the emulsion comprises up to about 150 grams of gelatin and up to 125 grams synthetic polymeric latex per mole of silver halide in the emulsion to permit fast drying times of the developed emulsion. Preferably the emulsion comprises about 100 to 130 grams of gelatin and about 70 to 95 grams synthetic polymeric latex per mole of silver halide.

The synthetic polymeric latex materials referred to herein are generally polymeric materials which are relatively insoluble in water compared to water-soluble polymers, but have sufficient water solubility to form colloidal suspensions of small polymeric micelles. Typical latex polymeric materials can be made by rapid copolymerization with vigorous agitation in a liquid carrier, such as the common bonfire polymerization, of at least one monomer which would form a hydrophobic homopolymer and at least one monomer which would form a hydrophilic homopolymer. In certain preferred embodiments, from about 1 to about 30 percent, by weight, of units of monomer containing the water-solubilizing group is present in the copolymer product. Copolymers prepared by this method and analogous methods provide discrete micelles of the copolymer which have low viscosities in aqueous suspensions. Typical useful copolymers include interpolymers of acrylic esters and sulfoesters as disclosed in Dykstra, U.S. Pat. No. 3,411,911 issued Nov. 19, 1968, interpolymers of acrylic esters and sulfobetaines as described in Dykstra and Whiteley, U.S. Pat. No. 3,411,912 issued Nov. 19, 1968, interpolymers of alkyl acrylates and acrylic acids as disclosed in Ream and Fowler, U.S. Pat. No. 3,287,289 issued Nov. 22, 1966, interpolymers of vinyl acetate, alkyl acrylates and acrylic acids as disclosed in Corey, U.S. Pat. No. 3,296,169, and interpolymers as disclosed in Smith, U.S. Pat. No. 3,488,708 issued Jan. 6, 1970. Polymeric latex materials can also be made by rapid polymerization with vigorous agitation of hydrophobic polymers when polymerized in the presence of high concentrations of surfactants which contain water-solubilizing groups. The surfactants are apparently entrained in the micelle and the solubilizing group of the surfactant provides sufficient compatibility with aqueous liquids to provide a dispersion very much like a soap. Generally good latex materials are also disclosed in Nottorf, U.S. Pat. No. 3,142,568 issued July 28, 1964; White, U.S. Pat. No. 3,193,386 issued July 6, 1965; Houck et al., U.S. Pat. No. 3,062,674 issued Nov. 6, 1962; and Houck et al., U.S. Pat. No. 3,220,844 issued Nov. 30, 1965.

The synthetic polymeric latex materials are generally polymerized in a manner to produce micelles of about 1.0 micron average diameter or smaller to be highly useful in photographic emulsions and preferably the discrete micelles are less than 0.3 micron in average diameter. Generally, the micelles can be observed by photomicrographs when incorporated in gelatin emulsions; however, it is understood that some coalescing can occur when the emulsions are coated and dried.

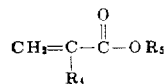
In one embodiment, the latex polymers which can be used according to this invention are acrylic interpolymers, i.e., those interpolymers prepared from polymerizable acrylic monomers containing the characteristic acrylic group



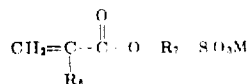
Such polymers are conveniently prepared by the interpolymerization of an acrylic monomer with at least one dissimilar monomer which can be another acrylic monomer or some other different polymerizable ethylenically unsaturated monomer. It is, of course, understood that the acrylic interpolymers employed in the practice of this invention are compatible with gelatin and have a Tg of less than 20° C. (Tg can be calculated by differential thermal analysis as disclosed in "Techniques and Methods of Polymer Evaluation," Vol. 1, Marcel Dekker, Inc., N.Y., 1966).

In one embodiment, preferred interpolymers which can be used in this invention comprise units of an alkyl acrylate such as, for example, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylates (e.g., n-butyl or t-butyl acrylates), amyl acrylates, hexyl acrylates and the like. Acrylic interpolymers containing units of acrylic acid or a sulfoester acrylate are especially useful in the process. Typical polymers of this type are copoly(butyl acrylate-acrylic acid), copoly(methyl acrylate-acrylic acid), copoly(ethyl acrylate-acrylic acid), copoly(butyl acrylate-sulfoethyl acrylate) and the like. In a preferred embodiment, the copolymer comprises up to about 30 percent, by weight, of acrylic acid or the sulfoester acrylate; especially good results being obtained with latex alkyl acrylate copolymers having up to about 20 percent, by weight, of the acrylic acid or the sulfoester acrylate. High ratios of solubilizing groups, such as the acrylic acid groups or the sulfoester groups produce a more soluble solution-type polymer with respect to water carrier solvents and therefore preferably concentrations of about 5 to about 25 percent by weight are utilized to provide the better latex polymers, depending on the molecular weight of the monomer unit. Mixtures of the more soluble solution-type polymers and the latex polymers can also be used within the scope of this invention to achieve the desired emulsion characteristics.

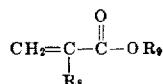
In another preferred embodiment of this invention, the above-mentioned copolymers contain units of a third monomer. Exceptionally good results are obtained in the process of this invention when the synthetic polymers comprise units of (1) alkyl acrylates, (2) acrylic acid or sulfoester acrylates and (3) an acrylic monomer unit having active methylene groups in side chains such as in malonic ester groups, acetoacetic ester groups, cyanoacetic ester groups of 1,3-diketone groups such as disclosed in Smith, U.S. Pat. No. 3,488,708 issued Jan. 6, 1970. Polymers which are especially useful in this invention, and which are described in the Smith patent just mentioned, are interpolymers of (a) about 50 to about 90 percent, by weight, of a monomer (1) having the formula:



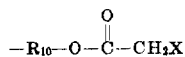
where R₁ is hydrogen or methyl and R₂ is alkyl, desirably containing up to about 10 carbon atoms, as exemplified by methyl, propyl, isobutyl, octyl, decyl and the like; (b) about 3 to about 20 percent, by weight, of a sulfoester monomer (2) having the formula:



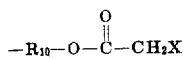
where R_6 is hydrogen or alkyl, desirably containing up to about 12 carbon atoms, often one to eight carbon atoms, as exemplified by methyl, pentyl, octyl, dodecyl and the like. R_7 represents a divalent hydrocarbon radical or a divalent aliphatic hydrocarbon radical in which a chain of carbon atoms joining the oxygen and sulfur atoms in the above formula is interrupted by an —O— and/or —S— atom and M is a cation such as an alkali metal, e.g., sodium or potassium, an ammonium salt or an organic amine such as triethylamine or diethanolamine and (C) about 2 to about 20 percent, by weight, of a monomer (3) having the formula:



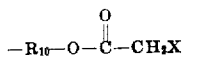
where R_8 is hydrogen, alkyl, desirably containing up to 12 carbon atoms as exemplified by methyl, n-butyl, octyl, dodecyl and the like, or



where R_{10} is alkylene, desirably containing up to 10, preferably one to eight carbon atoms, as exemplified by ethylene, tetramethylene, 1,3-isobutylene, octamethylene and the like and X is aliphatic acyl containing up to about eight carbon atoms, such as alkyl carbonyl groups exemplified by acetyl, butyryl, caprylyl and the like, and R_9 is alkyl, desirably containing up to about 10 carbon atoms, as exemplified by methyl, butyl, octyl, decyl and the like, cycloalkyl, desirably containing up to about 10 carbon atoms, as exemplified by cyclopentyl, cyclobutyl, cyclohexyl and the like, aryl, desirably containing up to about 12 carbon atoms as exemplified by phenyl and the like or



where R_{10} and X are as defined hereinabove for this radical, provided that one and only one of R_8 and R_9 is always



where R_7 in the sulfoester monomer (2) above is hydrocarbon, it can be any aliphatic, cycloaliphatic or aromatic radical and will generally contain up to about 12 carbon atoms. Preferred hydrocarbon R_7 radicals are alkylene radicals, generally those containing two to four carbons. R_3 can also be a divalent aliphatic hydrocarbon radical in which there is an —O— and/or —S— radical and generally contains up to 12 carbon atoms. Such R_3 radicals can, therefore, be saturated or unsaturated, although saturated divalent alkylene groups in which the carbon chain is interrupted by oxygen and sulfur atoms are preferred. Suitable R_7 radicals include, for example, ethylene, 1,3-propylene, 1,2-propylene, tetramethylene, 1,3-isobutylene, pentamethylene, hexamethylene, octamethylene, phenylene, bisphenylene, naphthylene, cyclopentylene, cyclohexylene, 2-butylene, butynylene, 2-oxatrimethylene, 3-tripentamethylene and the like.

Typical specific polymers useful herein include copoly(ethyl acrylate-acrylic acid-2-acetoacetoxy-ethyl methacrylate), copoly(butyl acrylate-sodium acryloxy propane sulfonate-2-acetoacetoxyethyl methacrylate), copoly(methyl acrylate-sodium acryloyloxypropane sulfonate-2-acetoacetoxyethyl methacrylate), copoly(butyl acrylate-acrylic acid-2-cyanoacetoxyethyl methacrylate) and the like and mixtures thereof. The copolymers of (1) alkyl acrylates and (2) acrylic acid or the sulfoester can also contain units of 3) sulfobetaines, N-methacryloyl-N'-glycylhydrazine hydrate, 2-[2-methacryloyloxyethyl]isothiuronium methane sulfonate and the like. Typical copolymers having

sulfobetaine units include copoly-(butyl acrylate-acrylic acid-4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate) and the like.

The direct positive silver halide emulsions hereof are fogged by the combination of a reducing agent such as thiourea dioxide and a compound of a metal more electropositive than silver, such as a gold salt, for example, potassium chloroaurate, as described in British Pat. No. 723,019 (1955).

Typical reducing agents that are useful in providing such emulsions include stannous salts, e.g., stannous chloride, hydrazine, sulfur compounds such as thiourea dioxide, phosphonium salts such as tetra(hydroxymethyl) phosphonium chloride, and the like. Typical useful metal compounds that are more electropositive than silver include gold, rhodium, platinum, palladium, iridium, etc., preferably in the form of soluble salts thereof, e.g., potassium chloroaurate, auric chloride, $(\text{NH}_4)_2\text{PdCl}_6$ and the like.

Useful concentrations of reducing agent and metal compound (e.g., metal salt) can be varied over a considerable range. As a general guideline, good results are obtained using about 0.05 to 40 mg. reducing agent per mole of silver halide, and 0.5 to 15.0 mg. metal compound per mole of silver halide. Best results are obtained at lower concentration levels of both reducing agent and metal compound.

The concentration of added dye can vary widely, e.g., from about 50 to 2,000 mg. and preferably from about 400 to 800 mg. per mole of silver halide.

As used herein, and in the appended claims, "fogged" refers to emulsions containing silver halide grains which produce a density of at least 0.5 when developed, without exposure, for 5 minutes at 68° F. in developer Kodak DK-50 having the composition set forth below, when the emulsion is coated at a silver coverage of 50 mg. to 500 mg. per square foot.

Developer	
N-methyl-p-aminophenol sulfate	2.5 g
Sodium sulfite (anhydrous)	30.0 g
Hydroquinone	2.5 g
Sodium metaborate	10.0 g
Potassium bromide	0.5 g
Water to make	1.0 l.

The dyes of this invention are highly useful electron acceptors in high speed direct positive emulsions comprising fogged silver halide grains and a compound which accepts electrons, as described and claimed in Illingsworth U.S. Pat. No. 3,501,307 issued Mar. 17, 1970. The fogged silver halide grains of such emulsions are such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about one upon processing for 6 minutes at about 68° F. in Kodak DK-50 developer, has a maximum density which is at least about 30 percent greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

potassium cyanide	50 mg.
acetic acid (glacial)	3.47 cc.
sodium acetate	11.49 g.
potassium bromide	119 mg.
water to	1 liter

The grains of such emulsions will lose at least about 25 percent and generally at least about 40 percent of their fog when bleached for 10 minutes at 68° F. in a potassium cyanide bleach composition as described herein. This fog loss can be illustrated by coating the silver halide grains as a photographic silver halide emulsion on a support to give a maximum density of at least 1.0 upon processing for 6 minutes at about 68° F. in Kodak DK-50 developer and comparing the density of such a coating with an identical coating which is processed for 6 minutes at 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at 68° F. in the potassium cyanide bleach composition. As already indicated, the maximum

density of the unbleached coating will be at least 30 percent greater, generally at least 60 percent greater, than the maximum density of the bleached coating.

The silver halides employed in the preparation of the photographic emulsions useful herein include any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride, silver chlorobromide, silver bromiodide, silver chlorobromide, and the like. Silver halide grains having an average grain size less than about 1 micron, preferably less than about 0.5 micron, give particularly good results. The silver halide grains can be regular and can be any suitable shape such as cubic or octahedral, as described and claimed in Illingsworth, U.S. Pat. No. 3,501,306 issued Mar. 17, 1970. Such grains advantageously have a rather uniform diameter frequency distribution, as described and claimed in Illingsworth U.S. Pat. No. 3,501,305 issued Mar. 17, 1970. For example, at least 95 percent, by weight, of the photographic silver halide grains can have a diameter which is within about 40 percent, preferably within about 30 percent of the mean grain diameter. Mean grain diameter, i.e., average grain size, can be determined using conventional methods, e.g., as shown in an article by Trivelli and Smith entitled "Empirical Relations Between Sensitometric and Size-Frequency Characteristics in Photographic Emulsion Series" in *The Photographic Journal*, Vol. LXXIX, 1949, pages 330-338. The fogged silver halide grains in these direct positive photographic emulsions of this invention produce a density of at least 0.5 when developed without exposure for 5 minutes at 68° F. in Kodak DK-50 developer when such an emulsion is coated at a coverage of 50 to about 500 mg. of silver per square foot of support. The preferred photographic silver halide emulsions comprise at least 50 mole percent bromide, the most preferred emulsions being silver bromiodide emulsions, particularly those containing less than about 10 mole percent iodide. The photographic silver halides can be coated at silver coverages in the range of about 50 to about 500 milligrams of silver per square foot of support.

In the preparation of the above photographic emulsions, the dyes and other mentioned addenda of the invention are advantageously incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating dye and other addenda in emulsions are relatively simple and well known to those skilled in the art of emulsion making. For example, it is convenient to add them from solutions for latexes in appropriate solvents, in which case the solvent selected should be completely free from any deleterious effect on the ultimate light-sensitive materials. Methanol, isopropanol, pyridine, water, etc., alone or in admixture, have proven satisfactory as solvents for this purpose. The type of silver halide emulsions that can be sensitized with the new dyes include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides, for example, emulsions comprising natural materials such as gelatin, albumin, agar-agar, gum arabic, alginic acid, etc., and hydrophilic synthetic resins such as polyvinyl alcohol polyvinylpyrrolidone, cellulose ethers, partially hydrolyzed cellulose acetate, and the like.

The silver halide emulsions spectrally sensitized with the dyes of this invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed, e.g., by the procedures described in Hewitson et al., U.S. Pat. No. 2,618,556; Yutzky et al., U.S. Pat. No. 2,614,928; Yackel U.S. Pat. No. 2,565,418; Hart et al., U.S. Pat. No. 3,241,969; and Waller et al., U.S. Pat. No. 2,489,341.

The dyes employed in this invention can be used alone or in combination with other dyes, such as symmetrical or unsymmetrical dyes having a nitrosubstituted selenazole nucleus, e.g., 3,3'-dimethyl-6,6'-dinitroselenathiacyanine p-toluenesulfonate, 3,3'-dimethyl-6,6'-dinitroselenacarbocyanine p-toluenesulfonate, 1,3-diallyl-3'-methyl-6'-nitroimidazo[4,5-

b]-quinoxalinoselenacarboxyanine p-toluenesulfonate, 1,3,3,3'-tetramethyl-5,6'-dinitroindoselenacarbocyanine-p-toluenesulfonate, 3,3'-dimethyl-6,6'-dinitroselenathiacyanine p-toluenesulfonate, 2-p-dimethylaminostyryl-3-methyl-6-nitrobenzoselenazolium-p-toluenesulfonate, 1,3'-dimethyl-6'-nitro-2-phenyl-3-indoloselenacarbocyanine p-toluenesulfonate and 2-[2-(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-methyl-6-nitrobenzoselenazolium-p-toluenesulfonate. Such dyes are also independently useful as electron acceptors and spectral sensitizers in fogged direct positive silver halide emulsions.

Silver halide emulsions of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers, which can be used alone or in combination, include the thiazolium salts described in Staud U.S. Pat. No. 2,131,038 and Allen U.S. Pat. No. 2,694,716; the azaindenes described in Piper U.S. Pat. No. 2,886,437 and Heimbach U.S. Pat. No. 2,444,605; the mercury salts described in Allen U.S. Pat. No. 2,728,663; the urazoles described in Anderson U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard U.S. Pat. No. 3,236,652; the oximes described in Carroll et al., British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al., U.S. Pat. No. 2,403,927; Kennard et al., U.S. Pat. No. 3,266,897 and Luckey et al., U.S. Pat. No. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405; the thiuronium salts described in Hertz U.S. Pat. No. 3,220,839; and the palladium, platinum and gold salts described in Trivelli U.S. Pat. No. 2,566,263 and Damschroder U.S. Pat. No. 2,597,915.

Photographic elements including emulsions spectrally sensitized in accordance with this invention can contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines, or combinations of developing agents. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agent can be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. No. 2,592,368 and Dunn et al., French Pat. No. 1,505,778.

Silver halide spectrally sensitized in accordance with the invention can be dispersed in colloids that can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters sulfonyl halides and vinyl sulfones, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde starch, oxyguargum, etc.

Emulsions spectrally sensitized in accordance with this invention can be used in photographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. Nos. 2,861,056 and 3,206,312 or insoluble inorganic salts such as those described in Trevoy U.S. Pat. No. 3,428,451.

Photographic emulsions of the invention can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous material, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing two to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

Spectrally sensitized emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton U.S. Pat. No.

2,960,404; fatty acids or esters such as those described in Robijns U.S. Pat. No. 2,588,765 and Duane U.S. Pat. No. 3,121,060; and silicone resins such as those described in Dupont British Pat. No. 955,061.

The photographic emulsions spectrally sensitized as described herein can contain surfactants such as saponin, anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831 and amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816.

Photographic elements containing emulsion layers sensitized as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica polymeric beads including beads of the type described in Jelley et al., U.S. Pat. No. 2,992,101 and Lynn U.S. Pat. No. 2,701,245.

Spectrally sensitized emulsions of the invention can be utilized in photographic elements which contain brightening agents including stilbene, triazine, oxazole and coumarin brightening agents. Water soluble brightening agents can be used such as those described in Albers et al., German Pat. No. 972,067 and McFall et al., U.S. Pat. No. 2,933,390 or dispersions of brighteners can be used such as those described in Jansen German Pat. No. 1,150,274 and Oetiker et al., U.S. Pat. No. 3,406,070.

Light sensitive photographic emulsion layers spectrally sensitized with the subject dye combinations can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. No. 3,253,921; Gaspar U.S. Pat. No. 2,274,782; Carroll et al., U.S. Pat. No. 2,527,583 and VanCampen U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and Jones U.S. Pat. No. 3,282,699.

Photographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell U.S. Pat. No. 2,761,791 and Wynn British Pat. No. 837,095.

Direct positive emulsions spectrally sensitized as described herein are useful in color image transfer processes such as described in Whitmore et al., U.S. Pat. Nos. 3,227,550; 3,227,551 and 3,227,552.

Exposed photographic emulsions of this invention 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 and the like; web processing such as described in Tregillus et al., U.S. Pat. No. 3,179,517; stabilization processing as described in Yackel et al., "Stabilization Processing of Films and Papers," *PSA Journal*, Vol. 16B, Aug., 1950; monobath processing as described in Levy "Combined Development and Fixation of Photographic Images with Monobaths," *Phot. Sci. and Eng.*, Vol. 2, No. 3, Oct. 1958, and Barnes et al., U.S. Pat. No. 3,392,019. If desired, the photographic emulsions of this invention can be processed in hardening developers such as those described in Allen et al., U.S. Pat. No. 3,232,761; in roller transport processors such as

those described in Russell U.S. Pat. No. 3,025,779; or by surface application processing as described in Example 3 of Kitze U.S. Pat. No. 3,418,132.

The silver halide emulsions spectrally sensitized in accordance with this invention can be used for making lithographic printing plates such as by the colloid transfer of undeveloped and unhardened areas of an exposed and developed emulsion to a suitable support as described in Clark et al., U.S. Pat. No. 2,763,553; to provide a relief image as described in Woodward U.S. Pat. No. 3,402,045 of Spencer U.S. Pat. No. 3,053,658; or, to prepare a relief printing plate as described in Baxter et al., U.S. Pat. No. 3,271,150.

The dyes, polymeric latices, reducing agents and metal compounds of the invention can be used with emulsions prepared with any of the light-sensitive silver halide salts including silver chloride, silver bromide, silver chlorobromide, silver bromiodide, silver chlorobromiodide, etc. Particularly useful for direct positive fogged emulsions in which the silver salt is a silver bromohalide comprising more than 50 mole percent bromide.

The novel emulsions of this invention may be coated on any suitable photographic support, such as glass, film base such as cellulose acetate, cellulose acetate butyrate, polyesters such as polyethylene terephthalate, paper, baryta coated paper, polyolefin coated paper, e.g., polyethylene or polypropylene coated paper, which may be electron bombarded to promote emulsion adhesion to produce the novel photographic elements of invention.

The following example is included for a further understanding of the invention.

EXAMPLE

A gelatin silver bromiodide emulsion (2.5 mole percent of the halide being iodide) and having an average grain size of about 0.2 micron is prepared by adding an aqueous solution of potassium bromide and potassium iodide, and an aqueous solution of silver nitrate, simultaneously to a rapidly agitated aqueous gelatin solution at a temperature of 70° C., over a period of about 35 minutes. The emulsion is chill-set, shredded and washed by leaching with cold water in the conventional manner. The emulsion is reduction-gold fogged by first adding 0.2 mg. of thiourea dioxide per mole of silver and heating for 60 minutes at 65° C. and then adding 4.0 mg. of potassium chloroaurate per mole of silver and heating for 60 minutes at 65° C. The emulsion is split into portions and prepared for coating, varying by addition of the dyes and binding agents as described in the following Table 1. Each sample is then coated on a cellulose acetate support at 300 mg. of silver and 330 mg. of gelatin per square foot. Samples of the coated support are then exposed using a mercury vapor lamp for a 365 nm. emission modulated by a continuous wedge, processed for 2 minutes and 4 minutes at 20° C. in Kodak D-11 developer which has the following composition:

N-methyl-p-aminophenol sulfate	1.0 g.
Sodium sulfite (anhydrous)	75.0 g.
Hydroquinone	9.0 g.
Sodium carbonate (monohydrate)	30.0 g.
Potassium bromide	5.0 g.
Water to make	1.0 liter

then fixed, washed and dried. The results are listed in Table 1 below.

TABLE 1

Dye and concentration (mg./mole silver)		Binder (g./ mole silver)		Development					
				2 minutes			4 minutes		
				Relative reversal speed	Density ² Max.	Min.	Relative reversal speed	Density ² Max.	Min.
Sample No. ¹									Stain
(a) Control ³ Dye I, 611	119	None	100	1.08	.18	95	2.21	.30	Very slight.
(b) Dye A, 611	119	None	229	2.33	.06	186	4.62	.06	None.
(c) Control Dye I, 611	119	85	295	.66	.08	282	1.31	.10	Slight.
(d) Dye A, 611	119	85	148	2.81	.06	155	4.52	.06	None.

¹ The polymer is copoly(methylacrylate-2-sulfoxypropylacrylate-2-acetoxyethyl methacrylate) in the proportions of approximately 80%, 6% and 5%, by weight, respectively, of methylacrylate, 2-sulfoxypropylacrylate and 2-acetoxyethylmethacrylate.

² Density values: max. is for maximum density in unexposed areas and min. is for minimum density in exposed areas.

³ Control contains 611 mg./mole silver halide of a comparison Dye I which is 3,3'-diethyl-5,5'-dinitrothiacarbocyanine chloride (see Gevaert British Patent 723,019, Example 2).

NOTE.—Dye A is anhydro-6,6'-dinitro-3,3'-di(3-sulfoxypropyl)thiacyanine hydroxide, sodium salt.

The above Table illustrates the unexpectedly higher maximum density obtained with the nitrosubstituted thiacyanine of this invention (coatings *b* and *d*) as compared to the control coatings containing the prior art nitrosubstituted thiacyanines (coatings *a* and *c*). In addition, less stain was present in the emulsions containing the preferred combination of synthetic polymeric latex and nitrosubstituted sulfoalkylthiacyanine of the invention (coating *d*) compared to control (coating *c*) containing the prior art nitrosubstituted thiacyanine dyes. Coatings (*c*) and (*d*), containing synthetic polymeric latex, exhibit better dimensional stability than coatings consisting essentially of hydrophilic colloids such as gelatin, and which are free from synthetic polymeric latex. When coating (*d*) is repeated, except using 611 mg. per mole of a nonsulfoalkyl nitrosubstituted thiacyanine dye, i.e., 3,3'-diethyl-6,6'-dinitrothiacyanine chloride, similar results are obtained except that this dye leaves a yellow stain. Further improvement in dimensional stability is achieved when the support employed is poly(ethylene terephthalate) or glass.

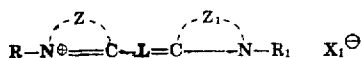
It will be apparent from all of the foregoing that other electron accepting and spectral sensitizing dyes defined by Formula I above in combination with a hydrophilic colloid such as gelatin and a suitable synthetic polymeric latex such as defined above will likewise provide still other new and improved fogged direct positive photographic silver halide emulsions of the invention which give generally similar dimensionally stable photographic elements that are stain free after processing.

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 invention.

I claim:

1. In a direct positive photographic silver halide emulsion comprising silver halide grains fogged with the combination of a reducing agent and a compound of a metal more electropositive than silver: the improvement wherein said emulsion contains, as electron acceptor, a simple cyanine dye comprising first and second nuclei selected from the group consisting of a nitrobenzothiazole nucleus and nitronaphthothiazole nucleus, said nuclei being joined through the two carbon atoms thereof to a monomethine linkage.

2. In a direct positive photographic silver halide emulsion comprising silver halide grains fogged with a combination of a reducing agent and a compound of a metal selected from the group consisting of gold, rhodium, platinum, palladium and iridium: the improvement wherein said emulsion contains, as electron acceptor, a dye having the following formula:



wherein R and R₁ each represents an alkyl group or an aryl group; L represents a monomethine linkage; Z and Z₁ each represents the atoms necessary to complete a nitrosubstituted nucleus selected from the group consisting of a nitrobenzothiazole nucleus and a nitronaphthothiazole nucleus; and, X₁ represents an acid anion.

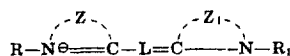
3. In a direct positive photographic silver halide gelatin emulsion comprising silver bromoiodide grains in which about 2.5 mole percent of the halide is iodide, said grains being fogged with a combination of thiourea dioxide and potassium chloroaurate: the improvement wherein said emulsion contains, as electron acceptor, about 600 milligrams per mole of silver of 3,3'-diethyl-6,6'-dinitrothiacyanine chloride.

4. In a direct positive photographic emulsion comprising silver halide grains fogged with a combination of a reducing agent and a compound of a metal more electropositive than silver, said grains being dispersed in an alkali-permeable colloid: the improvement wherein said emulsion contains, as electron acceptor, a simple cyanine dye comprising first and second nuclei selected from the group consisting of a nitrobenzothiazole nucleus and a nitronaphthothiazole

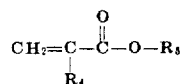
nucleus, said nuclei being joined through the two carbon atoms thereof to a monomethine linkage, at least one of said nuclei having a sulfoalkyl group attached to the heterocyclic nitrogen atom thereof; and, said alkali-permeable colloid comprises a synthetic polymeric latex.

5. A photographic silver halide emulsion as defined in claim 4 wherein said synthetic polymeric latex is an interpolymer comprising units of (1) an alkyl acrylate, (2) acrylic acid or sulfoester acrylates, and (3) an acrylic monomer having active methylene groups in side chains.

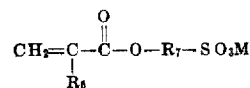
6. In a photographic emulsion comprising silver halide grains fogged with the combination of a reducing agent and a compound of a metal selected from the group consisting of gold, rhodium, platinum, palladium and iridium, said grains being dispersed in an alkali-permeable colloid; the improvement wherein said emulsion contains, as electron acceptor, a dye having the following formula:



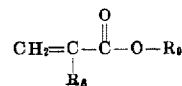
wherein R and R₁ each represents an alkyl group or an aryl group, at least one of R and R₁ representing a sulfoalkyl group; L represents a monomethine linkage; Z and Z₁ each represents the atoms necessary to complete a nitrosubstituted nucleus selected from group consisting of a nitrobenzothiazole nucleus and a nitronaphthothiazole nucleus; and, said alkali-permeable colloid comprises a synthetic polymeric latex, the polymer being an interpolymer of (a) about 50 to 90 percent, by weight, of a monomer having the formula:



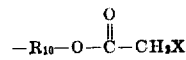
wherein R₄ represents hydrogen or methyl and R₅ represents alkyl, (b) about 3 to 20 percent, by weight, of a sulfoester of a monomer having the following formula:



wherein R₆ represents hydrogen or alkyl and R₇ represents a divalent hydrocarbon radical or a divalent aliphatic hydrocarbon radical in which the chain of carbon atoms is interrupted by an oxygen or sulfur atom, and M is a cation, and (c) about 2 to 20 percent, by weight, of a monomer having the following formula:



wherein R₈ and R₉ are selected from the group consisting of hydrogen, alkyl and an aliphatic acyl or cyano containing group of the formula:



wherein R₁₀ represents alkylene and X represents aliphatic acyl or cyano, one and only one of R₈ and R₉ representing said aliphatic acyl or cyano containing group.

7. In a direct positive photographic silver bromoiodide emulsion in which the halide is about 2.5 mole percent iodide, said silver halide being fogged with a combination of thiourea dioxide and potassium chloroaurate, and said grains being dispersed in an alkali-permeable colloid: the improvement wherein said emulsion contains, as electron acceptor, about 600 milligrams per mole of silver of the dye anhydro-6,6'-

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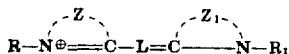
dinitro-3,3'-di(3-sulfopropyl) thiocyanine hydroxide, sodium salt; and, said binder comprises about 120 milligrams gelatin per mole of silver and about 85 milligrams per mole of silver of copoly(methylacrylate-2-sulfo-propylacrylate-2-acetoxyethyl methacrylate).

8. A photographic element comprising a support having coated thereon a direct positive photographic silver halide emulsion as defined in claim 1.

9. In a photographic element comprising a support having coated thereon a direct positive photographic emulsion comprising silver halide grains fogged with the combination of a reducing agent and a compound of a metal more electropositive than silver, said grains being dispersed in an alkali-permeable colloid: the improvement wherein said emulsion contains, as electron acceptor, a simple cyanine dye comprising first and second nuclei selected from the group consisting of a nitrobenzothiazole nucleus and a nitronaphthothiazole nucleus, said nuclei being jointed through the two carbon atoms thereof to a monomethine linkage, at least one of said nuclei having a sulfoalkyl group attached to the heterocyclic nitrogen atom thereof; and, said alkali-permeable colloid comprises a synthetic polymeric latex.

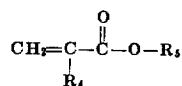
10. A photographic element comprising a support having coated thereon a direct positive photographic silver halide emulsion as defined in claim 9 wherein said synthetic polymeric latex is an interpolymer comprising units of (1) an alkyl acrylate, (2) acrylic acid or sulfoester acrylates, and (3) an acrylic monomer having active methylene groups in side chains.

11. In a photographic element comprising a support having coated thereon a photographic emulsion comprising silver halide grains fogged with the combination of a reducing agent and a compound of a metal selected from the group consisting of gold, rhodium, platinum, palladium and iridium, said grains being dispersed in an alkali-permeable colloid: the improvement wherein said emulsion contains, as electron acceptor, a dye having the following formula:

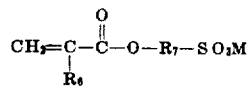


wherein R and R₁ each represents an alkyl group or an aryl group at least one of R and R₁ represents a sulfoalkyl group; L represents a monomethine linkage; Z and Z₁ each represents the atoms necessary to complete a nitrosubstituted nucleus selected from the group consisting of a nitrobenzothiazole nucleus and a nitronaphthothiazole nucleus; and said alkali-permeable colloid comprises a synthetic polymeric latex, the polymer being an interpolymer of (a) about 50 to 90 percent, by weight, of a monomer having the formula:

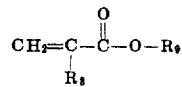
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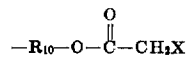
wherein R₄ represents hydrogen or methyl and R₅ represents alkyl, (b) about 3 to 20 percent, by weight, of a sulfoester of a monomer having the following formula:



wherein R₆ represents hydrogen or alkyl and R₇ represents a divalent hydrocarbon radical or a divalent aliphatic hydrocarbon radical in which the chain of carbon atoms is interrupted by an oxygen or sulfur atom, and M is a cation, and (c) about 2 to 20 percent, by weight, of a monomer having the following formula:



wherein R₈ and R₉ are selected from the group consisting of hydrogen, alkyl and an aliphatic acyl or cyano containing group of the formula:



wherein R₁₀ represents alkylene and X represents aliphatic acyl or cyano, one and only one of R₈ and R₉ representing said aliphatic acyl or cyano containing group.

12. In a photographic element comprising a support having coated thereon a direct positive photographic silver bromoiodide emulsion in which the halide is about 2.5 mole percent iodide, said silver halide being fogged with a combination of thiourea dioxide and potassium chloroaurate, and said grains being dispersed in an alkali-permeable colloid: the improvement wherein said emulsion contains, as electron acceptor, about 600 milligrams per mole of silver of the dye anhydro-6,6'-dinitro-3,3'-di(3-sulfopropyl) thiocyanine hydroxide, sodium salt; and, said binder comprises about 120 milligrams gelatin per mole of silver and about 85 milligrams per mole of silver of copoly(methylacrylate-2-sulfo-propylacrylate-2-acetoxyethyl methacrylate).

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