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3,536,491 PHOTOGRAPHIC MATERIALS CONTAINING POLYMERS

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16 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to new silver halide photographic elements comprising (A) a water-insoluble interpolpolymer of (1) units of an alkyl acrylate, (2) units of a vinyl sulfoester and (3) from 0 to 20% of units of at least one other ethylenically unsaturated polymerizable monomer that is different from (1) and (2); (B) gelatin; and (C) at least one other hydrophilic colloid. In one preferred embodiment, this invention relates to silver halide emulsions comprising said water-insoluble interpolpolymer, gelatin and at least one other hydrophilic colloid. In one aspect, photographic elements of this invention have improved sensitivity and reduced desensitization due to kink marks.

This invention relates to photographic materials, their preparation and use. In one of its aspects, this invention relates to a means for both reducing desensitization due to kink marking and improving the sensitivity of photographic emulsions and elements. In another of its aspects, this invention relates to improved photographic silver halide emulsions and elements containing a unique combination of at least two hydrophilic colloids and at least one water insoluble vinyl polymer.

The desensitization, i.e., reducing the sensitivity to subsequent exposure, of certain film coatings by improper handling of the coatings so as to produce kink marking is well known. This problem is particularly troublesome in high speed negative silver bromide emulsions of the type used in radiography. Antikink agents have been added to photographic materials to reduce kink marking. However, such materials often reduce the photographic speed, i.e., the sensitivity, of the emulsion to which they are added. It is, of course, desirable to obtain photographic emulsions and elements, particularly those suited for use in radiography which exhibit improved antikink as well as increased photographic speed, i.e., sensitivity. It is evident that a means for reducing susceptibility of photographic materials to kink mark desensitization while also increasing photographic speed would greatly enhance the art.

Accordingly, it is an object of this invention to provide photographic emulsions and elements exhibiting improved properties.

Another object of this invention is to provide a means for obtaining improved antikink and photographic speed in photographic materials.

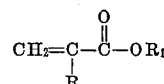
Still another object of this invention is to provide gelatin, photographic silver halide emulsions and elements which contain a unique combination of polymers and which have improved antikink and sensitivity.

Other objects of this invention will become apparent from an examination of the specification and claims which follow.

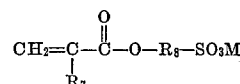
In accordance with this invention, it has been found that the use of the combination of gelatin, another hydrophilic colloid in addition to gelatin, and a water insoluble interpolpolymer, as described herein, in photographic materials, not only reduces kink mark desensitization but also improves sensitivity, i.e., photographic speed.

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One embodiment of this invention relates to a gelatin photographic silver halide emulsion exhibiting improved antikink and sensitivity comprising a hydrophilic colloid other than gelatin and a water insoluble interpolpolymer of (1) at least about 65%, by weight, of a monomer having the formula:

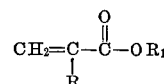


where R is a member selected from the group consisting of hydrogen and methyl and R₁ is alkyl, (2) up to about 20%, by weight, of a monomer having the formula:

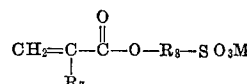


where R₇ is a member selected from the group consisting of hydrogen and alkyl, R₈ has its valence bonds represented in the above formula on different carbon atoms and is a member selected from the group consisting of divalent hydrocarbon radicals and divalent aliphatic hydrocarbon radicals in which a chain of carbon atoms joining the oxygen and sulfur atoms of the above formula is interrupted by an atom from Group VI-A of the Periodic Table having an atomic weight less than about 33 and M is a cation and (3) 0 to about 20%, by weight, of a polymerizable ethylenically unsaturated monomer that is different from (1) and (2).

Another embodiment of this invention relates to a photographic element exhibiting improved antikink and sensitivity comprising a support, at least one gelatin, photographic silver halide emulsion layer containing a hydrophilic colloid other than gelatin, and incorporated in at least one layer which is no farther from said support than said emulsion layer, water insoluble interpolpolymer of (1) at least about 65%, by weight, of a monomer having the formula:



where R is a member selected from the group consisting of hydrogen and methyl and R₁ is alkyl, (2) up to about 20%, by weight, of a monomer having the formula:

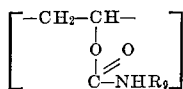


where R₇ is a member selected from the group consisting of hydrogen and alkyl, R₈ has its valence bonds represented in the above formula on different carbon atoms and is a member selected from the group consisting of divalent hydrocarbon radicals and divalent aliphatic hydrocarbon radicals in which a chain of carbon atoms joining the oxygen and sulfur atoms of the above formula is interrupted by an atom from Group VI-A of the Periodic Table having an atomic weight less than about 33 and M is a cation and (3) 0 to about 20%, by weight, of a polymerizable ethylenically unsaturated monomer that is different from (1) and (2).

It is a significant feature of this invention that neither the gelatin-hydrophilic colloid nor the gelatin-water insoluble polymer combination alone give both the increased sensitivity and improved antikink exhibited by the photographic materials described herein. Although hydrophilic colloids such as water soluble polyacrylamides have been used to improve antikink, e.g., as shown in Jones and Damschroder U.S. Pat. 2,759,821, issued Aug. 21, 1956, it could not have been expected that such materials could be used in combination with the water in-

soluble interpolymers described herein to obtain both reduced kink marking and increased speed, as shown by the working examples that follow.

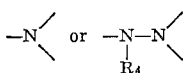
The binding material or vehicle employed in the emulsions and elements described herein is gelatin, a hydrophilic colloid. A portion of the gelatin is replaced by at least one different hydrophilic colloid such as water soluble polyacrylamide. While particularly efficacious results are obtained with water soluble polyacrylamide, other hydrophilic colloids can be used in combination with the polyacrylamide or in lieu thereof. Such other hydrophilic colloids which can be employed with gelatin, and with or in place of the preferred polyacrylamide, include any of the hydrophilic water permeable colloids, particularly the materials generally employed in the preparation of photographic silver halide emulsion as binding materials or vehicles, as exemplified by colloidal albumin, cellulose derivatives, synthetic resins, particularly polyvinyl compounds and the like. Specific examples include water soluble polymers such as polysaccharides, e.g., dextran, as disclosed in U.S. Pat. 3,063,838, issued Nov. 13, 1962, vinyl polymers, e.g., poly-N-vinyl pyrrolidones, as disclosed in U.S. Pat. 3,043,697, issued July 10, 1962, polyvinyl alcohol derivatives, e.g., acid derivatives such as succinoylated polyvinyl alcohol, as disclosed in Minsk and Abel U.S. Pat. 3,165,412, issued Jan. 12, 1965, proteins, protein derivatives, as described in U.S. Pat. 2,852,382, issued Sept. 16, 1958 or U.S. Pat. 3,011,890, issued Dec. 5, 1961, cellulose derivatives, e.g., hydroxyethyl cellulose, as disclosed in Illingsworth and Minsk U.S. Pat. 3,003,878, issued Oct. 10, 1961, and like compounds. Additional hydrophilic colloids that can be used in the practice of this invention are polymers containing repeating units having the following formula:



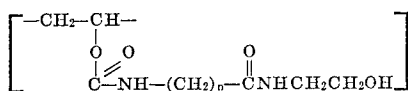
where R_9 is a carbon chain of 1 to 5 carbon atoms substituted with 1-3 substituents having the formula



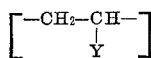
X being



R_4 being hydrogen or lower alkyl, and R_2 and R_3 each being hydrogen or alkyl groups containing up to 5 carbon atoms, alkoxy substituted alkyl groups containing up to 5 carbon atoms or hydroxy substituted alkyl groups containing up to 5 carbon atoms. Preferred polymers of this type contain repeating units having the following formula:



where n is an integer from 1 to 5. Polymers of this type can also include monomeric units such as vinyl alcohol or other vinyl monomeric units including those represented by the formula:



where Y is a photographically inert group such as hydroxy, an ester group such as acetoxy, an amide group such as N-alkylamido where the alkyl group contains up to 5 carbon atoms, carbamate groups such as



where R_5 and R_6 are each carbon chains, preferably alkylene, containing up to 5 carbon atoms. These additional polymers and copolymers can be prepared by any

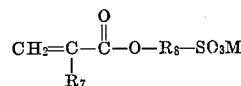
convenient method suitable for this purpose. For example, they can be prepared by treating the reaction product of poly(vinyl alcohol) and an ester of isocyanato mono- or polybasic fatty acid with an amine. The reaction of the isocyanato compound with the poly(vinyl alcohol) may be partial or complete, as may be the reaction of the amine with the initial reaction product. A polymer of this type which can be employed in the practice of this invention is one which contains, in combined form, monomeric units of vinyl alcohol, vinyl carboxymethyl carbamate and vinyl-N-β-hydroxyethylcarbamyl methylcarbamate. The concentration of hydrophilic colloid (not including gelatin) employed in the practice of this invention is subject to wide variation. However, the most suitable concentrations are generally in the range of about 5 to about 80, preferably about 10 to about 60 percent, by weight, based on gelatin. In practicing the invention, the hydrophilic colloid is employed in a gelatin photographic silver halide emulsion or in at least one gelatin photographic silver halide emulsion layer of a photographic element.

As already indicated, the water soluble polyacrylamides are the preferred hydrophilic colloids employed with gelatin and the water insoluble interpolymers in practicing this invention. Water soluble polyacrylamides can be obtained by polymerizing monomeric acrylamide using any procedure found suitable for this purpose. Typical methods for preparing water soluble polyacrylamides are described in Minsk et al. U.S. Pat. 2,486,191, issued Oct. 25, 1959, Lowe et al. U.S. Pat. 2,541,474, issued Feb. 13, 1951, U.S. Pat. 2,533,166, issued Dec. 5, 1950, and Allentoff et al. Belgian Pat. 651,507, issued Aug. 31, 1964. These water soluble polyacrylamides are characterized by a temperature below which their solutions in water precipitate polyacrylamide. Therefore, to get solubility, some of these compounds must be dissolved in water at elevated temperatures. In general, however, 10 grams of water soluble polyacrylamide will dissolve in one liter of water at 100° F. Furthermore, the polyacrylamides can contain, in combined form, not only acrylamide groups but also acrylic acid or acrylimide groups, depending upon their process of preparation. The inherent viscosity of the water insoluble polyacrylamides employed in the practice of this invention is subject to variation but is preferably in the range of about 0.1 to about 0.6, as determined at 25° C. in water. As used herein, the term "inherent viscosity" is determined by the formula:

$$\eta_1 = \frac{2.30 \log \eta_r}{c}$$

wherein η_1 is the inherent viscosity, η_r is the relative viscosity of water solution of the polymer divided by the viscosity of the water in the same units and at the same temperature and c is the concentration in grams (0.25) for a polymer per 100 cc. of solution.

The interpolymers employed in the practice of this invention are not hydrophilic colloids. They are water insoluble interpolymers which can be prepared by interpolymers of at least two monomers, one of which is a sulfoester of an α-methylene carboxylic acid. The sulfoesters employed in the preparation of these interpolymers include one or more of the sulfoesters having the formula:

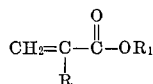


where R_7 , R_8 and M are each as defined hereinbefore. Suitable R_7 groups include hydrogen or any of the alkyl radicals, preferably alkyl radicals containing up to about 12 carbon atoms, often 1-8 carbon atoms, as exemplified by methyl, ethyl, propyl, pentyl, octyl, dodecyl, and the like. R_8 has its valence bonds represented in the above formula on different carbon atoms and can be a hydrocarbon radical or it can be an aliphatic hydrocarbon radical in which a chain of carbon atoms joining the oxy-

gen and sulfur atoms in the formula shown above is interrupted by an atom from Group VI-A of the Periodic Table having an atomic weight less than about 33, i.e., at least one —O— and/or —S— radical interrupts the carbon chain. Where R_8 is hydrocarbon, it can be any aliphatic, cycloaliphatic or aromatic radical and will generally contain up to about 12 carbon atoms. Preferred hydrocarbon R_8 radicals are alkylene radicals, generally those containing 2-4 carbons. R_8 can also be a divalent aliphatic hydrocarbon radical in which there is a —O— and/or —S— radical and generally contains up to 12 carbon atoms. Such R_8 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_8 radicals include, for example, ethylene, 1,3-propylene, 1,2-propylene, tetramethylene, 1,3-isobutylene, pentamethylene, hexamethylene, octamethylene, phenylene, bisphenylene, naphthylene, cyclopentylene, cyclohexylene, 2-butenylene, butynylene, 2-oxatrimethylene, 3-thiapentamethylene, and the like. M is a cation, as exemplified by hydrogen, an alkali metal such as sodium or potassium, ammonium, the cation of an organic amine such as triethyl amine, diethanol amine and the like.

The sulfoesters can be prepared using any method known to be suitable for this purpose. For example, in U.S. Pat. 2,923,734, issued Feb. 2, 1960, it is disclosed that an α -methylene carboxylic acid and an aliphatic hydroxy sulfonic acid in the free form are interacted by heating together, optionally while dispersed in an inert liquid medium capable of forming an azeotrope with water and while azeotropically distilling water out of the reaction mixture to form the corresponding carboxylate ester. The reaction is generally carried out at a temperature between 50° and 200° C. In U.S. Pat. 3,024,221, issued Mar. 6, 1962, there is disclosed a method for preparing the sulfoesters by reacting the appropriate acyl halide with the salt of the hydroxy sulfonic acid, generally at a temperature in the range of about 0° to about 200° C., although the particular temperature employed depends upon the nature of the specific reactants. Examples of hydroxy sulfonic acids (and their salts) that can be employed to form the sulfoesters are 2-hydroxyethane sulfonic acid, 2-hydroxy-1-propane sulfonic acid, 1-hydroxy-2-butane sulfonic acid, 2-hydroxycyclohexane sulfonic acid, *p*-phenolsulfonic acid, 2-(2-hydroxyethoxy) ethane-1-sulfonic acid, 2-(2-hydroxyethylthio)ethane-1-sulfonic acid, 4-hydroxy-2-butene-1-sulfonic acid, 4-hydroxy-2-butyne-1-sulfonic acid and the like. α -Methylene carboxylic acids or acyl halides include acrylic acid, methacrylic acid, α -butylacrylic acid, acryloyl chloride, methacryloyl bromide, α -hexylacryloyl chloride and the like.

The solid interpolymers employed in the practice of this invention are prepared by copolymerizing at least one sulfoester monomer, as described above, with at least one ethylenically unsaturated acrylic ester having the formula:



where R is hydrogen or methyl and R_1 is an alkyl radical, desirably containing 1-12 carbon atoms and preferably 1-4 carbon atoms. Suitable alkyl radicals include, for example, ethyl, methyl, propyl, pentyl, dodecyl and the like. Suitable monomers include, for example, ethyl acrylate, methyl acrylate, butyl acrylate, ethyl methacrylate, octyl methacrylate, and the like. The interpolymers employed in practicing this invention are water insoluble and contain, in polymerized form, at least about 65%, preferably about 85 to about 95%, by weight, of polymerized acrylic ester of the above formula with up to about 20%, preferably about 5 to about 15%, by weight, of sulfoester. If desired, the interpolymers can

also contain no more than about 20%, preferably no more than about 10%, by weight, of additional ethylenically unsaturated monomer. Monomeric units of this latter type include those derived from one or more different monomers which are copolymerizable with the acrylates, methacrylates and sulfoesters set forth hereinbefore, i.e., different unsaturated, polymerizable compounds containing one or more —CH=C< groups or more particularly, one or more $\text{CH}_2=\text{C}<$ groups. Useful water insoluble polymers are, therefore, interpolymers of the acrylates, methacrylates and sulfoesters as described above, with other ethylenically unsaturated polymerizable monomers which form water insoluble addition polymers such as vinyl esters, amide, nitriles, ketones, halides, ethers, α,β -unsaturated acids or esters thereof, olefins, diolefins and the like, as exemplified by acrylonitrile, methacrylonitrile, styrene, α -methylstyrene, vinyl chloride, vinylidene chloride, methyl vinyl ketone, vinyl acetate, fumaric, maleic and itaconic esters, 2-chloroethyl vinyl ether, methylenemalonitrile, acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate, N-vinylsuccinimide, N-vinylphthalimide, N-vinylpyrrolidone, butadiene, isoprene, vinylidene cyanide and the like. It is obvious that the nature of the different polymerizable, ethylenically unsaturated compound which is copolymerized with the acrylates, methacrylates and sulfoesters is subject to wide variation. However, as already indicated, the interpolymers employed can contain 0 to about 20%, by weight, of such additional monomer, in polymerized form. Generally, the interpolymers employed in the practice of this invention have a molecular weight in the range of about 5000 to about 500,000 or more.

The temperature at which the water insoluble interpolymers employed in practicing this invention are prepared is subject to wide variation since this temperature depends upon such variable features as the specific monomers used, the duration of heating, pressure employed, and like considerations. However, the polymerization temperature generally does not exceed about 100° C., and most often, is in the range of about 50° to about 90° C. The polymerization can be carried out in suitable solvents or diluents, for example, water or mixtures of water with water miscible solvents, as exemplified by methanol, ethanol, propanol, isopropyl alcohol, butyl alcohol, and the like. The pressure employed in the polymerization, if any, is usually only sufficient to maintain the reaction mixture in liquid form, although either superatmospheric or subatmospheric pressures can be used. The concentration of polymerizable monomer in the polymerization mixture can be varied widely with concentrations up to about 40 percent, by weight, and preferably about 20 to about 40 percent, by weight, based on the weight of vehicle being satisfactory. Suitable catalyst for the polymerization reaction include, for example, the free radical catalysts, such as hydrogen peroxide, cumene hydroperoxide, water soluble azo type initiators and the like. In redox polymerization systems the usual ingredients can be employed. If desired, the polymer can be isolated from the reaction vehicle by freezing, salting out, coagulation or by using other separation procedures suitable for this purpose. Interpolymers of the type employed in the practice of this invention and a process of preparation are described in U.S. Pat. 2,914,499, issued Nov. 24, 1959.

The water insoluble interpolymers described herein can be incorporated in the photographic emulsions and elements using any of the means usually employed in the photographic field for this purpose. For example, the polymers can be conveniently added from solvent solutions prior to coating. The polymers can also be conveniently incorporated in the photographic elements by dispersion in gelatin, in some other hydrophilic colloid or in water rather than by means of solvents. Any of the polymers employed in practicing this invention can be added to the photographic emulsions at any time during manufacture of the emulsions, although the polymers are

most conveniently added just prior to coating. The water insoluble interpolymers are generally employed in photographic emulsions at concentrations in the range of about 5 to about 100 grams, preferably about 20 to about 60 grams per mole of silver halide. When employed in a layer which is between the emulsion layer and the support in photographic elements, for example, in a contiguous or adjacent layer, the water insoluble interpolymers are generally employed in concentrations of about 25 to about 300 mg. per foot square of support. This generally corresponds to a concentration of about 10 to about 150%, by weight, of the binding agent, preferably gelatin, employed in the layer. Gelatin is generally coated in layers between the emulsion layer and the support at concentrations in the range of about 0.25 to about 1 g. per square foot of support. In the emulsion layer, gelatin is generally coated at a concentration of about 50 to about 200 grams per mole of silver halide.

Any of the gelatin photographic silver halide emulsions can be employed in practicing this invention, including, for example, photographic silver halide emulsions used in X-ray and camera films and the like. Suitable photographic emulsions contain silver halides such as silver chloride, silver bromide, silver bromiodide, silver chloriodide, silver chlorobromide and the like. Photographic emulsions which form latent images predominantly within the silver halide grains can be usefully employed in the practice of this invention. Such internal latent image emulsions are disclosed in Davey and Knott U.S. Pat. 2,592,250, issued Apr. 8, 1952. The photographic silver halide emulsions are generally coated in the photographic element at concentrations in the range of about 250 to about 1,000 mg. of silver per square foot of support. Particularly good results are obtained with elements containing high speed X-ray sensitive emulsion layers which are generally coated at coverages of at least 250 mg. of silver per square foot of support, preferably polyester film support.

The photographic compositions described herein can be coated on a wide variety of supports in preparing photographic elements. The photographic silver halide emulsions can be coated on one or both sides of the support which is preferably transparent and/or flexible. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetyl film, polystyrene film, polyethylene terephthalate film and other polyester film as well as glass, paper, metal, wood and the like. Supports such as paper which are coated with α -olefin polymers, particularly polymers of α -olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers, and the like, give good results.

The photographic emulsions described herein can be chemically sensitized with compounds of the sulfur group, noble metal salts such as gold salts, reduction sensitized with reducing agents, and combinations of these. Furthermore, emulsion layers and other layers present in photographic elements made according to this invention can be hardened with any suitable hardener such as aldehyde hardeners, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxy-starch, oxy plant gums, and the like.

The photographic silver halide emulsions can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including for example, stabilizers or antifoggants, particularly the water soluble inorganic acid salts of cadmium, cobalt, manganese and zinc as disclosed in U.S. Pat. 2,829,404, the substituted triazaindolizines as disclosed in U.S. Pats. 2,444,605 and 2,444,607, speed increasing materials, plasticizers, absorbing dyes, and the like. Sensitizers which give particularly good results in the photographic compositions disclosed herein are the alkylene oxide polymers which can be employed alone or in combination with other materials, such as quaternary ammonium salts, as disclosed in U.S. Pat. 2,886,437 or with mercury com-

pounds and nitrogen containing compounds, as disclosed in U.S. Pat. 2,751,299.

The invention described herein can be used with various kinds of photographic emulsions. For example, it can be used with X-ray sensitive photographic silver halide emulsions and other nonspectrally sensitized emulsions as well as orthochromatic, panchromatic and infrared sensitive emulsions, particularly those sensitized with merocyanine dyes, cyanine dyes, carbocyanine dyes and the like. Furthermore, this invention can be used with 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. In addition, the invention can be used with emulsions intended for use in diffusion transfer processes which utilize the nondeveloped silver halide in the non-image 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. Pat. 2,352,014, Land U.S. Pat. 2,543,181, and Yackel et al. U.S. Pat. 3,020,155. The invention described herein can also be used with 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 transfer processes of this type are described in Yutzy U.S. Pat. 2,856,142, Land et al. U.S. Pat. 2,983,606, Whitmore et al. British Pats. 904,364 and 840,731 and Whitmore et al. U.S. application Ser. No. 392,471, now Pat. No. 3,227,552. Silver halide emulsions containing the polymers can be processed in monobath processes such as described in Haist et al. U.S. Pat. 2,875,048 or in stabilization type processes.

In most cases the effect of kink desensitization is readily visible in the fresh film coating, but in many cases the effect is most pronounced only after the film has been aged prior to kinking. The antikink marking effect can be observed by means of a triangle or sensitometric bend test. The triangle test involves compressing a sample of a film coating between two plates, one of which has a raised triangle and the other of which has a triangle of about three times the area of the first cut in it. The raised triangle is an isosceles triangle, the longer sides being about $\frac{3}{16}$ inch in length, the shorter side being about $\frac{7}{16}$ inch in length. The offset of the raised triangle is about $\frac{1}{16}$ inch and the proportions of the depressed triangle are the same as those of the raised triangle. For testing purposes, a three kilogram weight is applied to the top of the raised triangle. The sensitometric bend test involves bending a strip of film through an angle of about 90° (the radius of curvature being about $\frac{3}{4}$ inch in most instances), the radius of curvature being great enough so that the film strip is not creased. The film, after kinking, is then given either a uniform flash or is exposed to an Eastman IB sensitometer and developed, fixed, washed and dried in the usual manner. The spectral distribution of the light source is adjusted by means of a filter to be almost identical with that emitted by a standard fluorescent screen such as is customarily employed in X-ray photography. Of course, when using the sensitometric bend test the bending is done longitudinally so that each step in the exposure by the simulated X-ray screen is crossed by the line of kinking. The results of the triangle and sensitometric bend tests parallel each other generally. In all instances reported in the following tables the film is aged at 120° F. at 45% relative humidity for three days before kinking. The results of the sensitometric bend tests are given in the tables below in the columns headed "AD aged 3 days at 120° F., 50% R.H."

The effectiveness of the addenda can be observed by visual comparison between the densities of the unaffected and kinked portions of the film, or by making density measurements therefrom. The densities reported in the following tables are obtained from sensitometric steps,

the densities of which are 0.40 and 0.90 above gross fog. The difference in density between the normal density of these steps and the density in the kinked portion is measured and is designated as ΔD in the following tables. The effects of the triangle bend test are observed visually. The effects are rated on the basis of 0 for no kinking, 1 for very slight kinking, 2 for slight kinking, 3 for moderate improvement and 4 for no improvement. Photographic speed as reported in the following tables is indicated as a function of the exposure necessary to give a density of 0.20 above background fog and is relative with respect to the control in each case.

This invention can be further illustrated by the following examples of preferred embodiments thereof although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLE 1

The gelatin, hydrophilic colloid, water insoluble interpolymer combination described herein improves antikink and sensitivity of photographic silver halide emulsions. To illustrate, an ordinary coarse grain gelatino-silver bromoiodide emulsion of the type normally used in radiography which is chemically ripened to optimum sensitivity is divided into several portions. One portion of the emulsion is untreated and serves as a Control while water insoluble copoly (methyl acrylate-sodium-4-acryloyloxybutane-sulfonate) (95:5 weight percent) referred to in the following table simply as "copolymer" and water soluble poly-

As shown by the above table, the use of water soluble polyacrylamide as a second hydrophilic colloid with gelatin and the water soluble interpolymer significantly increases photographic speed over the gelatin coating alone as well as over the coatings in which gelatin is combined with either the water soluble polyacrylamide or water insoluble polymer in the binding material. Furthermore, this speed increase is combined with good antikink protection.

Similar results are obtained when the above procedure is repeated with other water insoluble interpolymers such as copoly(methyl methacrylate-sodium 3-acryloyloxypropane-1-sulfonate), copoly(methyl acrylate-sodium 3-acryloyloxypropane-1-sulfonate), copoly(methyl acrylate-acrylic acid-sodium 3-acryloyloxypropane-1-sulfonate) and copoly(methyl acrylate-glycidyl methacrylate-sodium 3-acryloyloxypropane-1-sulfonate).

EXAMPLE 2

As already indicated, the water insoluble interpolymers described herein can be incorporated in a layer coated between the silver halide emulsion layer and the support, preferably an adjacent gelatin layer. To illustrate, the procedure of Example 1 is repeated except that the portions of emulsion are coated over a gelatin layer containing 200 mg. of gelatin per square foot of support and the copoly(methyl acrylate-sodium-4-acryloyloxybutane-sulfonate) and polyacrylamide are incorporated in this gelatin layer in the concentrations listed in the following table. Upon testing as described in Example 1 the results are as follows:

TABLE 2

Coating	Grams of polymer addenda per mole of silver halide	Speed	Gamma	Fog	ΔD after 3 days, 120° F., 50% R.H.	
					0.40	0.90
Control.....		126	2.80	.13	-.02	-.02
Control over gelatin layer (200 mg. gelatin/ft. ²).....		132	2.90	.13	-.04	-.06
Control, plus copolymer.....	25	148	2.90	.13	-.04	-.05
Do.....	50	155	3.00	.14	-.04	-.04
Do.....	75	159	2.85	.14	-.02	-.03
Do.....	100	162	2.85	.14	+ .01	0.0
Control, plus:						
Copolymer.....	100	200	3.05	.16	0.0	-.03
Polyacrylamide.....	45					

acrylamide (inherent viscosity of 0.30 in water at 25° C.) are incorporated into another portion of the gelatin, silver halide photographic emulsion at the concentrations listed in the following table. Each of the portions of the photographic emulsion are coated on an ordinary polyester film support at a silver coverage of 484 mg./ft.² and a gelatin coverage of 535 mg./ft.². The coated samples are exposed on an Eastman IB sensitometer and developed for 6 minutes in an ordinary MQ developer such as Kodak developer D-19. After development the samples are fixed, washed and dried in the usual manner. The kink mark desensitization is determined by the sensitometric bend test described above and the results given in Table 1 are obtained. The speed, gamma, and fog of the emulsion are also determined and the results listed in the following table.

TABLE 1

Coating	Grams of polymer addenda per mole of silver halide	Speed	Gamma	Fog	ΔD after 3 days, 120° F., 50% R.H.	
					0.40	0.90
Control.....		123	3.00	.12	-.06	-.11
Control, plus copolymer.....	20	155	2.85	.14	-.03	-.03
Do.....	60	174	2.45	.21		
Control, plus polyacrylamide.....	45	159	3.25	.14	-.01	-.05
Control, plus:						
Copolymer.....	20					
Polyacrylamide.....	45	195	2.90	.19	-.03	-.06
Copolymer.....	60					
Polyacrylamide.....	45	214	2.65	.24	-.02	-.04

As previously pointed out, water soluble polyacrylamides are the preferred hydrophilic colloids to be used in combination with gelatin and the water insoluble interpolymers when practicing this invention. However, other hydrophilic colloids with gelatin and water soluble interpolymer give both an increase in speed and anti-kink protection. To illustrate, succinoylated polyvinyl alcohol, as described in Minsk and Abel U.S. Pat. 3,165,412, issued Jan. 12, 1965, is added to one portion of an ordinary coarse grain gelatino-silver bromoiodide emulsion containing 200 g. of gelatin per mole of silver halide and 100 g. of copoly(methyl acrylate-sulfopropyl acrylate) (95:5 weight percent). One portion of the emulsion is untreated and serves as the control. Each portion of the emulsion is coated on an ordinary polyethylene terephthalate film support at a silver coverage of 450 mg./ft.². The coated

samples are exposed on an Eastman IB sensitometer and developed for 5 minutes in Kodak DK-50 developer. After development, the samples are fixed, washed and dried in the usual manner. The antikink marking effect is determined using the triangles bend test described hereinabove. The speed, gamma and fog are determined. The untreated portion is designated Coating A in the following table while the treated portion is designated Coating B. The results achieved are as follows:

TABLE 3

Coating:	Grams of polymer per mole AgX	Speed	Gamma	Fog	Kink
A-----	100	1.03	.03	4	
B-----	50	129	1.30	.01	2

In addition to reduced kink-mark desensitization, the coatings obtained using the above procedure also exhibit increased $D_{\max}$ in areas unaffected by kink.

EXAMPLE 4

The procedure of Example 3 is repeated with a coarse grain gelatino-silver bromiodide emulsion using dextran (Coating B), as described in U.S. Pat. 3,063,838, issued Nov. 13, 1962, and poly-N-vinyl-2-pyrrolidone (Coating C). Coating A is the untreated control. After testing as in Example 3 the following results are obtained:

TABLE 4

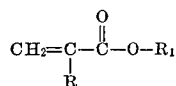
Coating:	Grams of polymer per mole AgX	Speed	Gamma	Fog	Kink
A-----	100	1.05	.01	4	
B-----	50	186	1.25	.02	2
C-----	50	115	1.30	.01	1

Thus, by the practice of this invention there is provided photographic emulsions and elements exhibiting improved anti-kink and sensitivity. This is achieved by using, in photographic silver halide emulsions and elements, a unique combination of gelatin, a second hydrophilic colloid and water insoluble polymer as described herein. The novel combination is particularly useful in emulsions intended for use in radiography but the combination is also useful in any coated film where a tendency toward desensitization as a result of kinking is exhibited and where an increase in speed is desired.

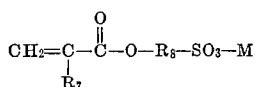
Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic silver halide emulsion comprising (A) a water-insoluble interpolymers of (1) at least about 65%, by weight, of units of a monomer having the formula:



wherein R is a hydrogen atom or a methyl group and R_1 is alkyl, (2) units of a monomer having the formula:

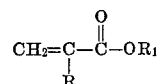


in a concentration of up to about 20%, by weight, wherein R_7 is a hydrogen atom or an alkyl, R_8 has its valence bonds represented in the above formula on different carbon atoms and is a divalent hydrocarbon radical or a divalent aliphatic hydrocarbon radical in which the chain of carbon atoms joining the oxygen and sulfur atoms in the above formula is interrupted by an oxygen or sulfur

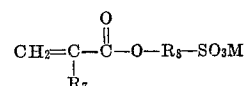
atom, and M is a cation, and (3) 0 to about 20%, by weight, of units of ethylenically unsaturated monomer that is copolymerizable with and different from (1) and (2); (B) gelatin; and (C) at least one other hydrophilic colloid.

2. A photographic element comprising a support and at least one layer of the photographic silver halide emulsion according to claim 1.

3. A photographic silver halide emulsion comprising (A) about 5 to about 100 grams per mole of silver halide of a water-insoluble interpolymers of (1) about 85 to about 95%, by weight, of units of a monomer having the formula:

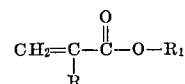


where R is a hydrogen atom or a methyl group and R_1 is alkyl, (2) about 5 to about 15%, by weight, of units of a monomer having the formula:

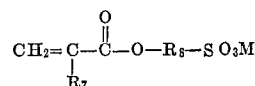


where R_7 is a hydrogen atom or an alkyl, R_8 has its valence represented in the above formula on different carbon atoms and is a divalent hydrocarbon radical or a divalent aliphatic hydrocarbon radical in which a chain of carbon atoms joining the oxygen and sulfur atoms of the above formula is interrupted by an oxygen or sulfur atom and M is a cation and (3) 0 to about 10%, by weight, of ethylenically unsaturated monomer that is copolymerizable with and different from (1) and (2); (B) gelatin; and (C) about 5 to about 80%, by weight, based on said gelatin of at least one other hydrophilic colloid.

4. A photographic element comprising (A) a support; (B) at least one gelatin, photographic silver halide emulsion layer containing at least one other hydrophilic colloid; and (C) incorporated in at least one layer, which is contiguous to or in close proximity to the said silver halide emulsion layer, a water-insoluble interpolymers of (1) at least about 65%, by weight, of units of a monomer having the formula:



wherein R is a hydrogen atom or a methyl group and R_1 is alkyl, (2) units of a monomer having the formula:



in a concentration of up to about 20%, by weight, wherein R_7 is a hydrogen atom or an alkyl, R_8 has its valence bonds represented in the above formula on different carbon atoms and is a divalent hydrocarbon radical or a divalent aliphatic hydrocarbon radical in which the chain of carbon atoms joining the oxygen and sulfur atoms in the above formula is interrupted by an oxygen or sulfur atom, and M is a cation, and (3) 0 to about 20%, by weight, of units of ethylenically unsaturated monomer that is copolymerizable with and different from (1) and (2).

5. A photographic element according to claim 4 wherein said silver halide emulsion layer comprises about 5 to about 80%, by weight, based on said gelatin of said other hydrophilic colloid.

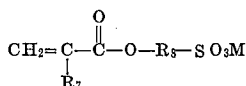
6. A photographic element according to claim 4 comprising from about 5 to about 100 grams per mole of silver halide in said element of said water-insoluble polymer.

7. The photographic element of claim 4 in which said water-insoluble interpolymers is in a gelatin layer contiguous to said emulsion layer.

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8. The photographic element of claim 4 in which the support is a flexible support, said other hydrophilic colloid is water-soluble polyacrylamide having an inherent viscosity in the range of about 0.1 to about 0.6 and said water-insoluble interpolymers has a molecular weight in the range of about 5,000 to about 50,000.

9. The photographic element of claim 4 in which said water-insoluble interpolymers is a water-insoluble interpolymers of (1) about 85 to about 95%, by weight, of units of an alkyl acrylate and (2) about 5 to about 15%, by weight, of units of a monomer having the formula:

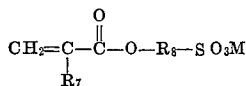


10. The photographic element of claim 4 in which the water-insoluble is a water-insoluble interpolymers of (1) about 85 to about 95%, by weight, of methyl acrylate and (2) about 15 to about 5%, by weight, of sodium-3-acryloyloxybutane-1-sulfonate.

11. The photographic element of claim 4 in which said other hydrophilic colloid is succinoylated polyvinyl alcohol.

12. The photographic element of claim 4 in which said other hydrophilic colloid is poly-N-vinylpyrrolidone.

13. A photographic element comprising a polyester film support, an X-ray sensitive gelatin photographic silver halide emulsion layer on each side of said support containing about 5 to about 80%, by weight, based on the gelatin, of water-soluble polyacrylamide, and incorporated in at least one layer, which is no farther from said support than said emulsion layer, a water-insoluble interpolymers of about 85 to about 95%, by weight, of (1) units of an alkyl acrylate and (2) about 5 to about 15%, by weight, of units of a monomer having the formula:



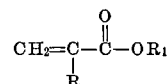
where R_7 is hydrogen, R_8 has its valence bonds represented in the above formula on different carbon atoms and is a divalent hydrocarbon radical and M is an alkali metal.

14. A photographic element of claim 13 in which said polyester support is polyethylene terephthalate.

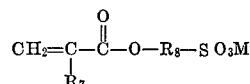
15. A photographic element comprising a support, at least one gelatin photographic silver halide emulsion layer containing about 5 to about 80%, by weight, based on

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the gelatin, of a water-soluble polyacrylamide having an inherent viscosity in the range of about 0.1 to about 0.6 and incorporated in at least one layer, which is contiguous to or in close proximity to the said emulsion layer, about 5 to about 100 grams per mole of silver halide of a water-insoluble interpolymers of (1) about 85 to about 95% by weight, of units of a monomer having the formula:



where R is a hydrogen atom or a methyl group and R_1 is alkyl, (2) about 5 to about 15%, by weight, of units of a monomer having the formula:



where R_7 is a hydrogen atom or an alkyl group, R_8 has its valence bonds represented in the above formula on different carbon atoms and is a divalent hydrocarbon radical or divalent aliphatic hydrocarbon radical in which a chain of carbon atoms joining the oxygen and sulfur atoms of the above formula is interrupted by an oxygen or sulfur atom and M is a cation and (3) 0 to about 10%, by weight, of ethylenically unsaturated monomers that is copolymerizable with and different from (1) and (2).

16. A photographic element comprising a flexible support, at least one gelatin, photographic silver halide emulsion layer containing about 5 to about 80%, by weight, based on the gelatin, of a water-insoluble polyacrylamide which has an inherent viscosity in the range of about 0.1 to about 0.6, and incorporated in at least one layer, which is contiguous to or in close proximity to the said emulsion layer, a water-insoluble interpolymers of (1) about 85 to about 95%, by weight, of methyl acrylate and (2) about 15 to about 5%, by weight, of sodium-3-acryloyloxypropane sulfonate.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96-114