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3,597,215

PHOTOGRAPHIC SILVER HALIDE AND A POLY (VINYL ALCOHOL) BINDING AGENT

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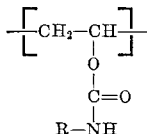
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9 Claims

ABSTRACT OF THE DISCLOSURE

Polymers comprising about 5 to about 30 mole percent of recurring units having the formula:



where R is hydrogen or methyl are particularly effective in improving the covering power and sensitometric properties of photographic silver halide materials.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photographic silver halide materials having a binding agent comprising a polymer as described hereinafter. In one aspect, this invention relates to light-sensitive compositions comprising a polymer which imparts improved characteristics to photographic silver halide emulsions. In another aspect, this invention relates to means for achieving said characteristics. In still another aspect, this invention relates to photographic elements comprising at least one layer having a binding agent comprising a hydrophilic colloid in combination with said polymer.

Description of the prior art

It is well known that by the addition of certain additives to light-sensitive compositions such as emulsions containing silver halide, for example, improved sensitometric characteristics can be attained. In particular, the characteristics of increased covering power and stable wet and dry density values are of special interest to those engaged in the photographic arts and more specifically those concerned with the manufacture of light-sensitive emulsions. The term covering power is generally understood to mean the ratio of the optical density of developed silver to the actual quantity of silver present in the photographic composition. The maximum optical density after exposure, processing, and drying depends only in part upon the concentration of free silver which results from the development process. It also depends upon the manner in which the silver is laid down in the photographic element during processing and the stresses to which it is subjected during drying.

Photographic silver halide emulsions possessing increased covering power are of considerable interest and are particularly desirable since their use results in an increase in gamma and very often an increase in speed while the silver content is maintained at the same level. While covering power, and therefore silver density, can be thus increased, it is also essential that variations in density between wet and dry states of the photographic compositions be minimized. For example, it is often the practice for purposes of expedience in the graphic arts to measure contrast and density of wet processed film. If unpredictable and substantial density changes occur in the film upon drying, the photographic technician cannot

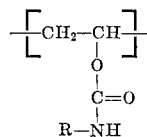
relay upon his initial measurements in order to control contrast and density of the photographic negatives and positives made therefrom. Further, a loss in density on drying represents a loss of covering power, i.e., a less efficient utilization of the concentration of silver present to achieve practical density. The ability to increase covering power, particularly in combination with an ability to inhibit density loss upon drying in photographic silver halide materials is very specific and few polymers have been found suitable. Furthermore, when such polymers are used in photographic silver halide emulsions comprising polymeric latexes, the beneficial effect of the covering power addenda very often is not realized or appreciably diminished.

As shown in U.S. Pat. 2,882,161 issued Apr. 14, 1959, vinyl polymers comprising carbamate appendages affixed to a polyvinyl alcohol chain have been employed as vehicles in photographic silver halide emulsions. However, there is no suggestion in this patent that polymers comprising vinyl carbamate or methyl-substituted vinyl carbamate groups will increase the covering power or inhibit the density loss upon drying of a photographic material. Furthermore, as pointed out in this patent, the vinyl carbamate containing polymers disclosed therein do not readily tolerate the use of the usual silver halide peptizing agents such as gelatin (see column 7, lines 52 et seq. of the patent).

SUMMARY OF THE INVENTION

In accordance with this invention, it has been found that the aforementioned deficiencies of the prior art can be overcome by using a particular class of vinyl carbamate polymers, as described hereinafter, in photographic materials.

Thus, this invention relates to photographic compositions and more particularly to light-sensitive compositions such as those comprising silver halides, for example, which exhibit improved properties. Said properties include increased covering power of developed silver, decreased density loss on drying, reduced drying time, decreased dimensional changes, and the like. Said improved properties are unexpectedly obtained by the presence of a minor concentration, for example, up to about 50 weight percent, based on the weight of the silver in the photographic composition, of a poly(vinyl alcohol) polymer comprising recurring units having the formula:



where R is hydrogen or methyl. Said units are present in said polymer in the range of about 5 to about 30 mole percent. The mole percent employed within the range will vary depending upon such things as the amount of silver halide employed and the particular binding agent utilized. Concentrations of polymer of about 10% to about 50%, and preferably about 30% to about 45%, by weight based on the weight of the silver present in the photographic composition are generally sufficient to provide increased covering power and reduced density loss on drying without marked emulsion softening.

Accordingly, it is an object of this invention to provide photographic materials exhibiting improved covering power, without undue softening of said materials, decreased drying time, after processing, and decreased dimensional change without adversely affecting desired sensitometric characteristics.

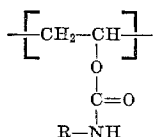
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It is another object to provide compositions, e.g., improved photographic silver halide emulsions and photographic elements, utilizing them.

Still other objects will become apparent from an examination of the specification and claims which follow.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with our invention, the above objects are attained with a photographic silver halide composition comprising a poly(vinyl alcohol) polymer having recurring units having the formula:



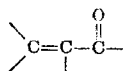
where R is hydrogen or methyl, said units being present in said polymer in a concentration of about 5 to about 30 mole percent. Said polymers are exemplified in one aspect by copoly(vinyl alcohol-vinyl carbamate). In another aspect, said polymers are exemplified by copoly(vinyl alcohol-vinyl N-methyl carbamate). While such polymers can be synthesized with higher than 30 mole percent of carbamate and methyl-substituted carbamate units, such an excess produces decreased solubility and general incompatibility with hydrophilic colloids such as gelatin with resultant failure to provide the improved characteristics set forth herein.

In still another embodiment of our invention, the described polymers contain about 15 to about 25 mole percent of said vinyl carbamate and methyl-substituted carbamate units with the remaining 75 to about 85 mole percent being comprised of substantially all vinyl alcohol units. It will be understood that where reference is generally made to vinyl carbamate units herein, it is intended to so include the N-methyl substituted carbamate polymeric unit.

Preparation of the vinyl carbamate polymers which are employed in practicing our invention can be by any of the methods known in the art such as, for example, by reacting highly polymerized alcohols such as poly(vinyl alcohol) with urea or its derivatives as shown in Chem. Abstracts, volume 25, p. 3782, describing German Patent 519,049 issued Feb. 8, 1930. A preferred method is set forth hereafter. A method of preparation for the N-methyl carbamate is set forth in Example 7.

The binding agent employed in the silver halide compositions of the invention can comprise any water-permeable hydrophilic colloid commonly employed. These include, for example, gelatin, colloidal albumin, polysaccharides, cellulose derivatives, synthetic resins such as polyvinyl compounds, including poly(vinyl alcohol) derivatives, acrylamide polymers, and the like.

The poly(vinyl alcohol) polymer additives employed in practicing this invention have also been found to be effective when the vehicle or binding agent contains, in addition to the water-permeable, hydrophilic colloids aforementioned, other colloids such as dispersed polymerized vinyl compounds, particularly those with increase the dimensional stability of photographic materials. Suitable polymers which can also be used in the binding agents according to this invention are acrylic copolymers, i.e., those copolymers prepared from polymerizable acrylic monomers containing the characteristic acrylic group,



Such polymers are conveniently prepared, for example, by the copolymerization of an acrylic monomer with at least one dissimilar monomer which can be another acrylic

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monomer or some other different polymerizable ethylenically unsaturated monomer. Preferably, such acrylic copolymers are compatible with hydrophilic colloids such as gelatin itself and have a Tg of less than about 20° C. as disclosed in "Techniques and Methods of Polymer Tg can be calculated by differential thermal analysis as disclosed in "Techniques and Methods of polymer Evaluation," volume 1, Marcel Dekker Inc., New York, 1966.) A similar increase in physical and photographic properties is not achieved when polymers having a Tg of above about 20° C. are employed in the emulsions of our invention. The term Tg is understood to be a time dependent, kinetic phenomenon represented by a transition temperature at which substantial segmental mobility of the copolymer structure is achieved. The temperature at which the thermodynamic characteristics are assumed by the copolymers particularly useful in our invention, within a given time, has been found to be not more than about 20° C.

In one embodiment, preferred copolymer binding agents 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 copolymers 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-sulfopropyl acrylate) and the like. In one preferred embodiment, the copolymer comprises up to about 30 percent, by weight, of acrylic acid, a sulfonic acid acrylate or the sulfoester acrylate; especially good results are obtained with latex alkyl acrylate copolymers having up to about 30 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. In addition to the products of a polymerization process, physical mixtures of the more soluble solution type polymers and the latex polymers can also be used effectively within the scope of this invention to achieve the desired emulsion characteristics.

In another preferred embodiment of this invention, the above-mentioned copolymeric binding agents 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 an active methylene group in a side chain such as, for example, in a malonic ester group, an acetoacetic ester group, a cyanoacetic ester group or 1,3-diketone groups as disclosed in Smith U.S. application Ser. No. 625,593 filed Mar. 24, 1967, now U.S. Patent 3,488,708. Typical polymers of this class include copoly(ethyl acrylate-acrylic acid - 2 - acetoacetoxyethyl methacrylate), copoly(butyl acrylatesodium acryloyloxypropanesulfonate - 2 - acetoacetoxyethyl methacrylate), copoly(methyl acrylate-sodium acryloyloxypropanesulfonate-2-acetoacetoxyethyl methacrylate), copoly(butyl acrylateacrylic 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 hydrochlorides, 2 - [2-methacryloyloxyethyl] isothiuronium methanesulfonate 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 emulsions of our invention comprise polymeric binding agents generally comprising at least 10 percent and up to about 99 percent, by weight, of the binder vehicle. In a preferred embodiment, the binder comprises from about 25 to about 75 percent of the acrylic copoly-

mer and from about 75 percent to about 25 percent, by weight, of gelatin. If desired, the emulsion can have less than 100 grams of gelatin per mole of silver halide in the emulsion in order to permit fast drying times of the developed emulsion.

The novel emulsions of the invention can be made in various manners. In a practical aspect, a light-sensitive silver halide or mixture of such halides is precipitated in an aqueous solution of a photographic binding agent such as gelatin. The light-sensitive silver halide utilized can be, for example, silver bromide, silver iodide, silver chloride, silver chlorobromide or silver bromiodide. To the precipitated silver halide emulsion, which can be washed in any known way, can be added other emulsion adjuvants, and the emulsion then digested. To the thus digested emulsion is added an aqueous solution of the modified poly(vinyl alcohol) polymer additive of the invention; when a uniform mixture has been obtained, the resulting emulsion can be coated onto a suitable support.

The photographic compositions of the invention can be coated on a wide variety of supports. Typical supports include polymeric films such as cellulose acetate film, polyvinyl acetate film, polystyrene film, polypropylene film and other polyolefin film, polycarbonate films, polyethylene terephthalate film and other polyester film as well as glass, paper, wood and the like. Supports such as paper, which are coated with alpha-olefin polymers, particularly polymers of alpha-olefins containing 2-10 carbon atoms as exemplified by polyethylene, polypropylene and ethylene-butene copolymers and the like, can also be employed.

The emulsions of this invention which contain the polymer additives disclosed 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 oxystarch, oxy plant gums, vinylsulfonyl ethers, and the like. The emulsions (containing the polymeric additives disclosed herein) 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. 2,839,405 of Jones issued June 17, 1958, the substituted triazaindolizines as disclosed in U.S. Patents 2,444,605 of Heimbach and Kelly issued July 6, 1948, and 2,444,607 of Heimbach issued July 6, 1948, speed-increasing materials, plasticizers and the like. In addition, these emulsions can be used in X-ray and other non-optically sensitized systems and in orthochromatic, panchromatic and infrared sensitive systems. The sensitizing addenda can be added to photographic systems before or after any sensitizing dyes which are used. Some 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. Patent 2,886,437 of Piper issued May 12, 1959, or with mercury compounds and nitrogen-containing compounds, as disclosed in U.S. Patent 2,751,299 of Carroll issued June 19, 1956.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

Preparation of copoly(vinyl alcohol-vinyl carbamate)

In a 500-ml. flask equipped with a reflux condenser, thermometer, and stirrer are placed 110 ml. of dimethylformamide and 22 g. (0.5 mole) of low viscosity poly

(vinyl alcohol) ["Elvanol" 70-05, a trademark of the E. I. du Pont de Nemours Company for a low viscosity poly(vinyl alcohol)]. The suspension is heated by an electric heating mantle with stirring to 150° C. to obtain a clear dope. Thirty grams (0.5 mole) of urea are added slowly over a ten-minute interval and the solution is then heated and stirred for one hour at reflux. The dope is allowed to cool with stirring over a one-hour period and poured into methanol to obtain a solid white rubbery product. After washing said solid several times in fresh changes of methanol, 160 ml. of water are added to dissolve the solid. The polymer is isolated again by precipitating in methanol and washed in methanol as before, followed by several acetone rinses to harden the polymer. The solid is dried under constantly applied vacuum at room temperature. Analysis indicates a nitrogen content of 3.5% which is equivalent to 12.3 mole percent of combined vinyl carbamate. The polymer is dissolved in water to give a dope of 15% solids content.

EXAMPLE 2

A medium speed silver bromiodide gelatin negative emulsion is prepared and coated (I) on a polyester support at 450 mg./ft.² silver and 1248 mg./ft.² gelatin. A second coating (II) is made from the same emulsion except for the addition before coating of 50 g./silver mole of copoly(vinyl alcohol-vinyl carbamate) in a 15% aqueous solution as prepared in Example 1. Samples of the two films are exposed in an Eastman 1B Sensitometer, developed for five minutes in Kodak DK-50 Developer, fixed, washed and dried. The densities of the sensitometric steps are measured both before and after drying. The density change on drying is measured at a wet density of 1.6.

TABLE A

Coating number	Addendum, g./Ag mole	Relative speed	γ	Fog	Density change
I.....	None.....	100	1.11	.01	-0.10
II.....	Copoly(vinyl alcohol-vinyl carbamate), 50 g.	105	1.17	.01	+0.02

From these results, it is apparent that copoly(vinyl alcohol-vinyl carbamate) has eliminated the wet-dry loss in density without adverse sensitometric effects.

EXAMPLE 3

A high speed silver bromiodide gelatin negative emulsion is prepared and coated (I) on acetate support at 459 mg./ft.² silver and 1040 mg./ft.² gelatin. A coating identified as II in Table B is prepared from the same emulsion to which has been added 30 g./silver mole of the copoly(vinyl alcohol-vinyl carbamate) of Example 1 as a 15% aqueous solution, while to the emulsion for a coating identified as III in Table B, 45 g./silver mole of copoly(vinyl alcohol-vinyl carbamate) is added. Samples of the three films are exposed in an Eastman 1B Sensitometer, developed for five minutes in Kodak DK-50 Developer, fixed, washed and dried. The sensitometric results of these coatings are shown in Table B.

TABLE B

Coating number	Addendum, g./Ag mole	Relative	γ	Fog	D _{max}
I.....	None.....	100	1.34	.20	2.44
II.....	Copoly(vinyl alcohol-vinyl carbamate), 30 g.	115	1.50	.18	2.74
III.....	Copoly(vinyl alcohol-vinyl carbamate), 45 g.	115	1.50	.18	2.74

The results shown in Table B show that the addition of 30 g./silver mole of copoly(vinyl alcohol-vinyl carbamate) gives a substantial increase in gamma which is accompanied by an increase in D_{max} covering power. Increasing the concentration of copoly(vinyl alcohol-vinyl carbamate) to 45 g./silver mole offers no appreciable additional covering power advantage.

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EXAMPLE 4

A latex of copoly(methyl acrylate-sodium-3-acryloyloxypropane-1-sulfonate) (95:5 weight percent) is prepared in the following manner: 375 ml. of distilled water is placed in a flask, heated to 95° C. and purged of oxygen by bubbling in nitrogen. To the water is added 4 ml. of Triton 770 (a 30% solution of a surfactant composition composed of a sodium alkylaryl polyether sulfate in aqueous isopropanol, manufactured by Rohm and Haas Co.), 1.0 g. of potassium persulfate and 0.1 g. of sodium bisulfite. The following monomer and solution are then added simultaneously under nitrogen with vigorous stirring over a period of 15 minutes: (1) 118.7 g. of methyl acrylate and (2) a solution of 6.3 g. of sodium 3-acryloyloxypropane-1-sulfonate, 0.23 g. of sodium bisulfite and 4 ml. of Triton 770 in 125 ml. of distilled water. After the polymerization mixture is stirred for an additional 30 minutes at 95° C., the resulting latex is chilled and raised to pH 5.0 with an aqueous sodium hydroxide solution.

EXAMPLE 5

A high speed silver bromoiodide gelatin negative emulsion is prepared and coated on an acetate support. The coating is identified in the table below as Coating No. I. Coatings of silver bromoiodide-gelatin emulsions on acetate supports are also prepared to which is added copoly(vinyl alcohol-vinyl carbamate) prepared by the method of Example 1, alone or in combination with copoly(methyl acrylate - 3 - acryloyloxypropane-1-sulfonic acid sodium salt), prepared by the method of Example 4. For purposes of further comparison, coatings are also prepared wherein water-soluble polyacrylamide is added to the emulsion. All of the samples are identified in the table below. The coated film samples are evaluated for density change on drying at original wet density of 1.6, drying time at room temperature and dimensional change. The results are reported in Table C below.

TABLE C

Coating No.	Gelatin, g./mole Ag.	Latex, g./mole Ag ¹	Addendum, g./mole Ag	Density change on drying at 1.6 orig. wet density	Drying time at room temp., minutes	Dimensional change ²
I.....	300	-0.10	35	0.0015
II.....	300	50, polyacrylamide.....	-0.04	34	0.0021
III.....	200	100 do.....	-0.10	28	0.0012
IV.....	300	50, copoly(vinyl alcohol-vinyl carbamate). do.....	+0.02	35½	0.0021
V.....	200	100 do.....	-0.03	30	0.0012

¹ Copoly(methyl acrylate-3-acryloyloxypropane-1-sulfonic acid, sodium salt).

² This figure represents the percent dimensional change per 1% change in relative humidity.

EXAMPLE 6

This demonstrates the effectiveness of poly(vinyl alcohol-vinyl carbamate) in all gelatin and gelatin-latex binders without causing marked mushiness or softness of the binder. Comparison is made with a known covering power agent, polyacrylamide.

(A) A medium speed silver bromoiodide gelatin negative emulsion is prepared and coated (Coating No. I) on a polyester support at 450 mg./ft.² silver and 1248 mg./ft.² gelatin. Additional coatings are made identically except that before the coating the following polymers are added:

Coating No. II—50 g./silver mole of polyacrylamide (a known covering power addendum)

Coating No. III—30 g./silver mole of copoly(vinyl alcohol-vinyl carbamate)

Samples of each of these films are exposed in a sensitometer and developed for five minutes in Kodak DK-50 Developer. Mushiness measurements are made on the wet coating. The values listed in Table D represent the weight load of a stylus under which each coating is subjected

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before the emulsion becomes ploughed. The hard coating, therefore, is indicated by the high figure.

TABLE D

Coating No.	Addendum	Mushiness in DK-50
I.....	37
II.....	Polyacrylamide.....	22
III.....	Copoly(vinyl alcohol-vinyl carbamate).....	34

(B) A gelatin-latex combination, using a medium speed silver bromoiodide gelatin negative emulsion containing a butyl acrylate-acrylic acid-sulfoester polymer (synthesized according to Example 9 of Smith U.S. application Ser. No. 625,593, now U.S. Pat. No. 3,488,708) is prepared and coated (Coating No. IV) on a polyester support at 450 mg./ft.² silver, 832 mg./ft.² gelatin and 415 mg./ft.² latex. Additional coatings are made identically except that before coating the following polymers are added:

Coating No. V—50 g./silver mole of polyacrylamide
Coating No. VI—50 g./silver mole of copoly(vinyl alcohol-vinyl carbamate)

Mushiness measurements on these coatings are made as described in Part A of this example.

TABLE E

Coating No.	Addendum	Mushiness in DK-50
IV.....	42
V.....	Polyacrylamide.....	24
VI.....	Copoly(vinyl alcohol-vinyl carbamate).....	38

EXAMPLE 7

Copoly(vinyl alcohol, vinyl N-methylcarbamate) is prepared by the following method.

A mixture of 44 g. (1 mole) of dried Elvanol (described supra) and 210 ml. of distilled hexamethylphosphoric triamide is heated and stirred in a flask until solution is

effected. After cooling to room temperature, 11.4 g. (0.2 mole) of methyl isocyanate is added over a period of 10 minutes with stirring. The reaction temperature is kept below 40° C. by external cooling. The reaction mixture is stirred and heated on a steam bath for four hours and then allowed to cool down to room temperature. The product is then precipitated in acetone, washed with several portions of fresh acetone, and dried at room temperature under vacuum. There is obtained 43.5 g. of very light yellow copoly(vinyl alcohol, vinyl N-methylcarbamate). This is identified as Coating Material No. VII hereafter (Tables F and G).

This procedure is repeated except that only 5.7 g. (0.1 mole) of methyl isocyanate is used and the isolated polymer is dried at 30–35° C. in a vacuum oven. This yield is 42.5 g. (Coating Material No. VIII in Table G).

EXAMPLE 8

A solution of Coating Material VII containing 10% solid polymer by weight is tested photographically in the following manner. A sample of this solution equivalent to 30 g. of dry polymer per mole of silver and a sample of polyacrylamide equivalent to 30 g. per mole of silver

are added to separate portions of a medium speed silver bromiodide gelatin-latex negative emulsion and coated on a polyester support at 450 mg. silver per square foot, 832 mg. gelatin per square foot, and 416 mg. per square foot of the butyl acrylate-sulfoalkylacrylate-acetoacetyl-methacrylate polymer of the type described in Smith U.S. application Ser. No. 625,593 filed Mar. 24, 1967, now U.S. Pat. 3,488,708. The photographic results and mushiness values recorded hereafter are the results of testing described in preceding Examples 3 and 6 and are recorded in Table F.

EXAMPLE 9

The above coating materials VII and VIII are used in solution form having 10% solid polymer therein by weight. Samples of each solution are added to separate portions of a medium speed silver bromiodide gelatin emulsion to yield concentrations of 30 g. and 45 g. of dry polymer per mole of silver. Each emulsion sample is coated onto a polyethylene terephthalate film support at a coverage of 450 mg. of silver and 1248 mg. of gelatin per square foot. A sample of each film coating is exposed and processed as described hereinabove. The values recorded in Table G are the results obtained from sensitometric testing and mushiness measurements performed as described in Examples 3 and 6, part A, respectively.

TABLE F

Coating material	Concentration (g./mole Ag)	Fresh		1 week incubation at 125° F. and 50% relative humidity		Density change	Mushiness in DK-50
		Relative speed	γ	Relative speed	γ		
No. VII.....	30	107	1.04	105	0.90	-0.08	30
Polyacrylamide.....	30	112	1.18	115	1.07	-0.13	17
Control.....		100	0.98	105	0.98	-0.14	35

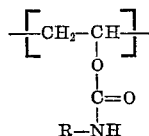
TABLE G

Coating material	Concentration (g./mole Ag)	Fresh		1 week incubation at 125° F. and 50% relative humidity		Density change	Mushiness in DK-50
		Relative speed	γ	Relative speed	γ		
No. VII.....	30	110	1.50	85	1.23	-0.03	30
No. VII.....	45	102	1.43	80	1.22	-----	-----
No. VIII.....	30	105	1.43	82	1.20	-0.03	25
No. VIII.....	45	107	1.43	78	1.18	-----	-----
Control.....		100	1.38	73	1.18	-0.10	33

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic silver halide composition having a binding agent comprising a poly(vinyl alcohol) polymer wherein about 5 to about 30 mole percent of the recurring units in said polymer have the formula:



where R is hydrogen or methyl, said polymer being present in a concentration of about 10 to about 50%, by weight, based on silver present in said composition.

2. The composition of claim 1 in which R is hydrogen.

3. The composition according to claim 1 in which the polymer is copoly(vinyl alcohol-vinyl carbamate).

4. The composition of claim 1 in which said binding agent therein in addition includes a hydrophilic colloid.

5. The composition of claim 4 in which said binding agent therein in addition includes gelatin in a concentration of about 75 to about 25 percent, by weight, and about 25 to about 75 percent, by weight, of an acrylic copolymer.

6. The composition of claim 4 in which said colloid is gelatin.

7. The composition according to claim 1 in which said polymer is present in a concentration in the range of about 30 to about 45 percent, by weight, based on silver.

8. A photographic element comprising a support bearing the composition of claim 1.

9. The composition according to claim 1 in which the polymer is copoly(vinyl alcohol-vinyl N-methylcarbamate).

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