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3,533,800

GELATIN HARDENED WITH A DIALDEHYDE-CONTAINING POLYMER-OXIDATION PRODUCT OF POLYDEXTROSE

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ABSTRACT OF THE DISCLOSURE

Photographic elements comprising a support having thereon a gelatin layer hardened by a dialdehyde-containing polymer-oxidation products of polydextrose are disclosed.

This invention relates to gelatin compositions containing as a hardening agent therein the dialdehyde of polydextrose.

The hardening of gelatin compounds with aldehyde-type hardeners such as formaldehyde and the like is well known. However, in many instances these hardeners are unsuitable for use in photographic materials containing color couplers in that discoloration, e.g., a yellow strain, results from the combination of a color coupler and the aldehyde hardener particularly in the case of pyrazolone couplers.

One object of our invention is to provide compositions for use in photographic products comprising gelatin and the dialdehyde of polydextrose. Another object of our invention is to provide improved hardening agents for gelatin in incorporated coupler photographic materials. Other objects of our invention will appear herein.

We have achieved these objects by using the dialdehyde of polydextrose as the hardening agent in gelatin compositions employed for photographic purposes. These objects are particularly in evidence when these hardeners are used in gelatin compositions containing or in contact with color couplers especially pyrazolone couplers.

The term polydextrose, as used herein, means a synthetic polymer of dextrose which can be prepared using any convenient method, e.g., by polymerizing dextrose by the procedure of P. Mora and J. Wood, Jour. Am. Chem. Soc., 80, 685 (1958). The dialdehyde of this material is obtained by oxidizing the polydextrose such as with periodic acid or a periodate salt which is described in U.S. Pat. 3,034,894 issued May 15, 1962. For photographic purposes this hardener is conveniently employed in aqueous solution.

The hardener in accordance with our invention has varied advantages, for instance being synthetic it avoids uncertain composition and other difficulties encountered with materials with natural origin. The hardener of the invention functions actively in incorporated coupler photographic materials without entry into stain-forming reaction with said couplers. Another advantage is its substantial freedom from toxicity. A still further advantage is that in addition to its ability to harden gelatin the aldehyde of polydextrose displays considerable antifogging activity. A still further advantage of this hardener is the irreversible nature of the hardening action on gelatin thereby preventing migration of the hardener to other layers in multilayer photographic products. The feature of avoiding stain with color couplers is obtained not only in cases where the couplers are incorporated in the photographic emulsion in which the hardeners of our invention are used but is also noted in those cases where coupler is in solution in the processing baths with which the photographic products are contacted.

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It is to be understood that where the term gelatin is used herein it refers not only to gelatin per se but also to derivatives of gelatin such as where gelatin is reacted upon with phthalic anhydride as described in U.S. Pat. 2,525,753 or benzene sulfonyl chloride or other reactants such as described in U.S. Pat. 2,614,928.

Ordinarily the use of the dialdehyde of dextrose as a hardener involves incorporating a solution of this material in an aqueous solution of gelatin such as a composition to be used in making photographic products or a gelatin-silver halide photographic emulsion. Although we have noted that just about any proportion of this hardener has a hardening effect on gelatin, it may be conveniently used by incorporating in the gelatin composition in a proportion of about 0.1–1.0 part by weight of active aldehyde per 100 parts by weight of gelatin. We prefer to use about 0.4–0.6 part by weight of active aldehyde per 100 parts by weight of gelatin. For higher processing temperatures, it is desirable to use a larger amount of hardener.

The term poly(dialdehyde-dextrose) as used in this specification describes the product resulting from the oxidation of poly(dextrose), wherein the bond between adjacent carbon atoms carrying hydroxyl groups on the sugar residue is ruptured with the formation of two aldehyde groups, and includes both the homopolymer in which all of the dextrose units have been oxidized to the dialdehyde and also interpolymer compositions comprising oxidized and unoxidized units.

The hardener of our invention has been found to be effective as a gelatin hardener not only in hardening gelatin per se but also in hardening gelatin derivatives and in hardening physical mixtures of gelatin and gelatin derivatives or with other colloids as for example mixtures of gelatin with compatible synthetic polymers such as ethyl acrylate-acrylic acid copolymer or butyl acrylate-acrylic acid copolymer. The hardener in accordance with our invention has been found to be useful for hardening amine containing polymers such as polyvinyl amine.

The following is given as an example of the preparation of a dextrose polymer.

(A) POLYDEXTROSE

Into a 300 ml., 3-neck flask fitted with a mechanical stirrer, an addition funnel, an oil bath at 142° C., and a variable reflux still head attached to a vacuum pump through a Dry Ice-acetone trap, was placed 54 g. (0.3 mole) of dextrose and 150 ml. (dry volume) of dimethyl sulfone (M.P., 109°; B.P., 238° C.) or 150 ml. (liquid volume) of tetramethyl sulfone (B.P., 285° C.). This mixture was stirred vigorously and heated at 142° C. as vacuum was applied. A homogeneous melt resulted at a vacuum of 0.7 mm. Hg. The reaction solution refluxed slowly at 120° C./0.7 mm. Hg. To this, 8.9 g. of 85 percent phosphoric acid was rapidly added and sulfone-water azeotrope was slowly distilled off. The polymer came out of solution slowly until stirring was no longer possible. Distillation was continued for 45 min. at which time the sulfone was decanted from the polymer mass. The polymeric mass was dissolved in 100 ml., of distilled water and isolated by pouring into mechanically stirred acetone. The precipitate was washed in fresh acetone, filtered out on a Büchner funnel with suction, and dried at reduced pressure at 40° C. for 18 hours. Yield, 48.6 g. Inherent viscosity in water at 0.25 g./100 ml., 0.03.

The following example illustrates the preparation of a compound which is a hardener in accordance with our invention.

(B) POLY(DIALDEHYDE-DEXTROSE)

Into a 200 ml., 3-neck flask, fitted with a magnetic stirrer, a thermometer, and a cold water bath (at 5° C.)

were placed 100 ml., of distilled water and 47.7 g., of periodic acid ($2\text{H}_2\text{O}$) (0.21 mole). This mixture was stirred to a homogeneous solution and cooled to 20°C . at which time 36 g. (0.2 mole) of poly-dextrose was added and stirred to a homogeneous solution. The reaction solution temperature rose to 35°C . then decreased to 20°C . at which time external cooling was removed and the reaction allowed to proceed at ambient temperature for 23 hours with stirring.

The resulting reaction mixture was poured, with mechanical stirring, into 2.5 liter of acetone. The precipitate was filtered out on a Buchner funnel with suction and washed repeatedly with methanol until free of iodic acid. The washed product was dried at reduced pressure at 40°C . for 18 hours. Yield, 13.3 g.

The 13 g., of the dried oxidized poly-dextrose was dissolved in 56 g., of distilled water, with magnetic stirring, at $80\text{--}95^\circ\text{C}$. The hot solution was filtered and stored in the refrigerator until used. Yield, 51.8 g.; solids, 12.8 percent; aldehyde content, 2.2 percent; 44.5 percent oxidized.

The following examples illustrate the use of hardeners in accordance with our invention for the hardening of gelatin layers in photographic products.

EXAMPLE 1

Poly(dialdehyde-dextrose) was added to separate portions of a high speed negative type gelatin-silver bromide emulsion which had been panchromatically sensitized by the addition of cyanine dye. The emulsion used contained 245 grams of gelatin per mole of silver. A control sample was also employed consisting of the above emulsion but with no hardener therein. Each sample was coated on suitably subbed cellulose acetate support at a coverage of 459 mg., of silver and 1040 mg., of gelatin per square foot. A sample of each coating was exposed on an Eastman 1B sensitometer, processed for 5 minutes in Kodak developer DK-50, fixed, washed and dried. The following results were obtained:

Solution	Poly(dialdehyde dextrose), g. ¹	Rel. speed	Gamma	Fog	Percent swell ²
Control	-----	100	1.33	0.11	730
A	0.82	82	1.07	0.09	350
B	1.64	76	1.02	0.09	300

¹ Grams active polymer per 100 grams of gelatin.

² The percent swell was determined by comparing the thickness of the samples as measured after processing and before drying with the thickness of the photographic element before exposure and processing.

The hardener in accordance with our invention is particularly useful in color photography especially in photographic emulsions in which a color coupler such as a pyrazolone coupler has been incorporated because of the freedom from stain when using these hardeners. The following example illustrates the use of the hardener of the invention in color photography.

EXAMPLE 2

Coatings of the following structure were applied to a cellulose acetate film support in the order given. As a comparison, formaldehyde was also used as a typical aldehyde hardener.

Layer 6—Gelatin.

Layer 5—Blue-sensitive silver chlorobromide gelatin emulsion consisting of 98 mole percent bromide and an acyl acetanilide yellow coupler of the type described in U.S. Pat. 2,875,057.

Layer 4—Gelatin.

Layer 3—Green-sensitive silver chlorobromide gelatin emulsion consisting of 80 mole percent chloride and a pyrazolone magenta coupler of the type described in U.S. Pat. 2,600,788.

Layer 2—Gelatin layer.

Layer 1—Red-sensitive silver chlorobromide gelatin emulsions consisting of 90 mole percent bromide and a phenolic cyan coupler of the type described in U.S. Pat. 2,423,730.

Each hardener was employed in all six layers at a concentration of 0.5 gram per 100 grams of gelatin. The layers were coated on the support in the order given, layer 1 being immediately adjacent to the support. Each sample was exposed and processed in the Kodak E-2 Ektra-chrome process. A visual examination of the processed strips revealed the absence of unwanted yellow stain in the sample containing poly (dialdehyde-dextrose) whereas such stain was present in the sample in which formaldehyde was used.

Photographic emulsions containing the hardening agents of our invention may be sensitized using any of the techniques well known in emulsion making, for example, by digesting with naturally active gelatin or various sulfur compounds and/or gold compounds. The emulsions may be sensitized with salts of noble metals of Group VIII of the Periodic Table which have an atomic weight greater than 100.

Silver halide emulsions containing the hardeners of the invention may be of the surface-sensitive or internally sensitive type.

The emulsions may also contain speed-increasing addenda such as quaternary ammonium salts, polyethylene glycols, or thioether sensitizers.

The hardeners of the invention may be used in gelatin layers containing conventional addenda such as gelatin plasticizers, antifoggants and coating aids. These hardeners may be useful in X-ray and other emulsions not spectrally sensitized. They may also be used in orthochromatic, panchromatic and infrared-sensitive emulsions. The addenda may be added to the emulsion before or after sensitizing dyes, if any, are used. Various silver salts may be used as the sensitive salt, such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromiodide. The hardeners of the invention may be used in photographic elements intended for color photography, and which may contain color-forming couplers, or which may be intended to be developed by solutions containing the couplers or other color-generating materials.

The hardeners of this invention are very useful in photographic elements intended for color photography since they are compatible with high-boiling solvents generally used to dissolve color-forming couplers, such as the solvents disclosed in Mannes et al., U.S. Pat. 2,304,939, issued Dec. 15, 1942, Jelley et al., U.S. Pat. 2,322,027, issued June 15, 1943, etc. These hardeners are also compatible with low-boiling or water-soluble organic solvents used with or in place of the high-boiling solvents, such as those disclosed in Vittum et al., U.S. Pat. 2,801,170 and Fierke et al., U.S. Pat. 2,949,360, issued Aug. 16, 1960.

In addition, the hardeners of this invention are compatible with mixtures of gelatin and dispersed vinyl polymers which are often employed in photographic silver halide emulsions. Suitable compounds of this type include polymeric latexes of the type described, for example, in U.S. Pats. 2,272,166, 2,729,137, 2,768,080 and 3,142,568. The hardeners of this invention may also be used with emulsions of the mixed-packet type, as described in U.S. Pat. 2,698,794, or in emulsions of the mixed grain type such as described in U.S. Pat. 2,592,243.

Emulsions obtained in accordance with our invention may be used in diffusion transfer materials. In one common form of diffusion transfer process, the undeveloped silver halide in non-image areas of the negative is complexed to form a water soluble compound which is permitted to diffuse to a receiving layer where it is precipitated out as a metallic silver positive image. In other diffusion transfer processes the final image is produced by diffusion of developer, oxidized developer, coupler or dye, from an exposed and developed light-sensitive layer to a second layer in close proximity.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations

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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 composition of matter comprising gelatin containing a hardening amount of a dialdehyde-containing polymer-oxidation product of polydextrose.

2. A composition in accordance with claim 1 in which the gelatin is a carrier for silver halide.

3. A composition in accordance with claim 1 in which the gelatin is of a modified type.

4. A composition in accordance with claim 1 in which the gelatin is mixed with synthetic water-soluble polymers.

5. A composition in accordance with claim 1 in which pyrazolone coupler is also present therein.

6. A photographic element comprising silver halide and a support having therein at least one gelatin layer containing a dialdehyde-containing polymer-oxidation product of polydextrose in a concentration of from about 0.1 to about 1.0 weight percent of active aldehyde to gelatin.

7. The photographic element of claim 6 in which one of the layers thereon is a gelatin-silver halide emulsion containing a dialdehyde-containing polymer-oxidation product of polydextrose in a concentration of from about 0.1 to about 1.0 weight percent of active aldehyde to gelatin.

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8. The photographic element of claim 6 in which at least one layer thereof contains a pyrazolone coupler.

9. A composition of matter as defined in claim 1 further comprising a synthetic polymeric latex in combination with said gelatin and dialdehyde of polydextrose.

10. The photographic element of claim 6 in which said gelatin layer comprises in addition to gelatin, a colloid other than gelatin.

11. The photographic element of claim 6 in which said gelatin layer comprises a dispersed vinyl polymer.

References Cited

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