United States Patent

[11] 3,619,236

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[54] METHOD FOR COATING LAYERS OF GELATIN AND A CARBOXYL-CONTAINING POLYMER ON A SUPPORT

7 Claims, No Drawings

[52] **U.S. Cl.** **117/34,**
96/111, 117/124 E, 117/132 C, 117/138.8 E, 117/155 UA, 117/156, 117/161 UC, 117/164, 260/8
[51] **Int. Cl.** **G03c 1/30**
[50] **Field of Search** 96/111; 117/34, 164, 124, 132, 138.8, 155, 156, 161; 260/8

[56] **References Cited**

UNITED STATES PATENTS

3,135,748	6/1964	Sheeham	260/566
3,178,296	4/1965	Minsk et al.	260/8
3,236,882	2/1966	Wilson	96/111
3,316,095	4/1967	Van Campen et al	96/111
3,321,313	5/1967	Burness et al.	96/111
3,396,029	8/1968	Himmelmann et al.	96/111

Primary Examiner—William D. Martin
Assistant Examiner—Bernard D. Pianalto
Attorney—Larson, Taylor & Hinds

ABSTRACT: A hardened coating such as a photographic emulsion, containing gelatin and a water soluble carboxyl-containing polymer, is provided on a support by first blending the gelatin with a carbodiimide or isoxazolium slat hardener and subsequently blending that mixture with the carboxyl-containing polymer to provide a coating material which hardens sufficiently slowly to provide uniform coating.

METHOD FOR COATING LAYERS OF GELATIN AND A CARBOXYL-CONTAINING POLYMER ON A SUPPORT

BACKGROUND OF THE INVENTION

This invention relates to a technique for coating a mixture of a water soluble synthetic polymer, gelatin and certain hardeners which involves mixing the carboxyl-containing polymer into a preformed mixture of gelatin and the hardener.

Most of the hardeners available for the hardening of water soluble carboxyl-containing polymers are either aziridines or bis (epoxides) and it is well known that these materials are relatively slow-reacting hardeners which afterharden severely. It has also been known for some time that certain hardeners, such as isoxazolium salts, react with mixtures of carboxyl-containing polymers and gelatin to give rapid hardening. Thus far, however, this reaction has not been controllable to the extent that the coating operation can be performed before the mixture cross-links. Attempts to coat layers containing the isoxazolium salt by mix melting it into the emulsion containing the carboxyl polymer just prior to coating have been unsatisfactory because the mixture cross-links before it can be coated.

SUMMARY OF THE INVENTION

According to the present invention, it has been found that mixtures of water soluble synthetic polymers and gelatin can be coated successfully with carbodiimide or isoxazolium salt hardeners by mixing the solution polymer in which a preformed gelatin-hardener mixture prior to coating. We have further found that hardener levels of 6–10 percent isoxazolium salt, based on the total vehicle, can be coated successfully by this technique. Coatings made in this manner have improved physical properties over similar coatings hardened in the conventional manner.

Similarly, we have found that polymer-gelatin mixtures containing carbodiimide hardeners can be coated in the same manner. By this technique, hardened coatings of the polymer-gelatin mixture may be provided on supports to provide, e.g. photographic materials of improved dimensional stability.

DETAILED DESCRIPTION OF THE INVENTION

The properties of gelatin are modified by the incorporation therein of water soluble synthetic polymers, or solution polymers, and such mixtures are particularly suited to photographic purposes as the vehicle for silver halide or as a layer between a photographic support and a light sensitive gelatin-silver halide emulsion. Several distinct advantages are obtained when a solution polymer, such as a water soluble carboxyl-containing alkyl acrylateH-acrylic acid polymer of the type disclosed in Houck et al. U.S. Pat. No. 3,220, 844,is mixed with gelatin. For example, in preparing photosensitive paper from emulsions containing the polymer as a considerable portion of the vehicle, the following advantages accrue:

1. When emulsions containing the polymer are coated on unsized paper support, the aqueous emulsion tends to remain on top of the paper stock, with little tendency to strike through the base thereby eliminating undesirable cockle of the paper;

2. incorporating the polymer in silver halide gelatin emulsions decreases the tendency of layers thereof to curl while wet in the coating machine or after drying;

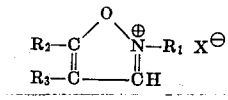
3. the addition of polymer gives high-coatability because it is possible to coat lower amounts of emulsion per unit area and thereby give thinner coatings than is possible when gelatin only is used as the vehicle, which property is particularly beneficial at high-coating speeds;

4. silver halide gelatin emulsions containing polymer exhibit a much greater hypoelimination rate than emulsions in which only gelatin is employed as the vehicle;

5. the presence of the polymer results in a decrease of tackiness or stickiness; and

6. silver halide emulsions containing the polymer when coated on light-weight papers have considerably more physical strength than similar coatings in which only gelatin is used.

It has been known for some time that isoxazolium salts are effective in hardening mixtures of gelatin and water soluble carboxyl-containing polymers, as illustrated by Burness et al., U.S. Pat. No. 3,321,313. The isoxazolium salts useful in this respect have the formula:



wherein R_1 is a monovalent organic residue containing from one to five carbon atoms, and R_2 and R_3 are each hydrogen or a monovalent organic residue having from one to 18 carbon atoms, or together form an alicyclic ring, and X is an anion when sulfonate anion does not form a part of R_1, R_2 or R_3. Preferably, R_1 is an aliphatic hydrocarbon group of one to four carbon atoms either with or without a sulfonate anion, R_2 and R_3 are each one of the following: hydrogen, unsubstituted alkyl, unsubstituted aryl, alkyl or aryl substituted with halogen, hydroxyl, alkyl, alkoxy and/or sulfonate anion, a simple heterocyclic ring such as furyl, or R_2 and R_3 together form an alicyclic ring, and X is an anion which contributes to the water solubility of the compound such as perchlorate, paratoluenesulfonate or the like, unless sulfonate anion is already present, attached to R_1, R_2 or R_3.

According to the present invention, it has been discovered that gelatin layers containing the carboxyl polymers and the isoxazolium hardeners can be effectively coated by mixing the polymer with a preformed mixture of the gelatin and hardener. It has also been found that carbodiimides behave similarly to the isoxazolium salts in that they give rapid hardening with mixtures of gelatin and carboxyl-containing polymers. This rapid hardening reaction can be delayed by adding the carbodiimide to the gelatin and holding this mixture for a specified length of time before the carboxyl-containing polymer is added. The carbodiimides preferably have the formula:

$$R_4\text{–N C N–}R_5,$$

wherein R_4 and R_5 are each monovalent organic residues containing from one to twenty carbon atoms. The carbodiimides include the symmetrical diaryl carbodiimides, the asymmetrical diaryl carbodiimides, the symmetrical dialiphatic carbodiimides, the asymmetrical dialiphatic carbodiimides, and the mixed arylaliphatic carbodiimides. The aliphatic and aryl groups may be unsubstituted or substituted with, for example, one or more of the following groups: halogen, cyano, nitro, amine, alkyl amine, alkoxy, alkyl carbonyl oxy, alkoxy carbonyl, etc. The compounds are conveniently prepared by the methods disclosed in U.S. Pat. No. 2,938,892 and No. 3,135,748.

The carboxyl-containing polymer is a solution polymer and preferably a water soluble salt of a polymer containing repeating units derived from acrylic acid as disclosed in Houck et al. U.S. Pat. No. 3,220,844, which may contain from 10 to 90 mole percent of acrylic acid units and 90 to 10 mole percent alkyl acrylate units. These polymers may also contain up to 40 mole percent of units derived from an ethylenically unsaturated copolymerizable monomer such as styrene, alkylmethacrylates, etc. in which case the polymer contains 6 to 54 mole percent acrylic acid units and, correspondingly, 54 to 6 percent of alkyl acrylate units. The polymer salt comprises from 20 to 80 and preferably from 35 to 65 percent, by weight, of the gelatin-resin vehicle employed in the aqueous solutions applied according to the invention which vehicle may serve as a carrier for a light sensitive silver salt such as a silver halide. The alkyl substituent of the alkyl acrylates preferably contains from one to 10 carbon atoms and when the alkyl substituent is from hexyl to decyl it is preferred that relatively more of the acid units are included in the polymer to enhance water solubility. The polymers are conveniently prepared as disclosed in U.S. Pat. No. 3,220,844.

The amount of hardener can vary widely but is preferably present in an amount of from 0.5 percent to 10 percent by weight based on the amount of gelatin and polymer, and more preferably in an amount of 1 to 6 percent by weight.

The coatings are provided according to the invention by adding the carboxyl polymer to a preformed mixture of gelatin and the hardener. The ultimate blend is conveniently prepared in the mixing apparatus disclosed in U.S. Pat. No. 2,912,343. In a typical process, a solution of gelatin and the hardener and a separate solution of the polymer are preferably compounded to have approximately equal viscosities at the coating temperature. The a mixing chamber of the type described in U.S. Pat. No. 2,912,343, wherein the solutions are subjected to the mixing, shearing, forces of the device. The mixed solution is then passed to the coating head and continuously coated on a substrate in conventional coating equipment. The coating can be set by heat without chilling.

The following examples illustrate the invention:

EXAMPLES 1–8

A coarse grain bromoiodide emulsion (example 1) was prepared and coated on a polyester support (polyethylene terephthalate) at a coating weight of 473 mg. Ag/ft.^{2}; 298 mg. gelatin/ft.^{2}; 298 mg. copoly (ethylacrylate-acrylic acid sodium salt)/ft.^{2}; with 0.13 formaldehyde hardener, based on the vehicle weight, by conventional coating methods. The copolymer contained approximately 80 mole percent ethyl acrylate and 20 mole percent acrylic acid units. A second coating (example 2) identical to example 1, but containing 298 mg. copoly (methylacrylate-acrylic acid sodium salt) /ft.^{2} in place of ethyl acrylate acrylic acid copolymer was also provided on the polyester base by conventional methods. Three coatings (examples 3, 4 and 5) identical to example 1, were provided on the polyester except that the formaldehyde hardener was replaced by 2, 5-dimethylisoxazolium p-toluenesulfonate hardener in an amount, respectively, of 2, 3, and 4 percent based on the total weight of gelatin and polymer. Three additional coatings (examples 6, 7, and 8) were similarly prepared identical to example 2, but containing 2, 3 and 4 of the isoxazolium hardener. The six coatings including the isoxazolium hardener were provided by blending an aqueous solution of the polymer with an aqueous solution of the gelatin and hardener in a mix-melting apparatus of the type disclosed in U.S. Pat. No. 2,912,343.

The coatings were rated for adhesion and mushiness after development for 25 seconds, after fixing for 15 seconds, and after washing for 40 seconds at 104° F. and sensitometric evaluation was made before and after incubation for one week at 120° F. 50 percent relative humidity, as shown in the following table:

TABLE 1

	Fresh			Incubated			Adhesion			Mushiness		
Ex.	Rel. speed	γ	Fog	Rel. speed	γ	Fog	Dev.	Fix	Wash	Dev.	Fix	Wash
1	100	2.00	.14	112	1.68	.15	2	2+	3−	24	53	80
2	100	2.36	.17	123	1.97	.22	2	2−	1	21	50	60
3	123	0.90	.17	135	0.85	.17	2	1	1−	24	58	60
4	107	0.85	.17	112	0.83	.17	3−	2+	2+	32	61	73
5	97	0.80	.16	118	0.8	.16	3−	2+	2+	50	100	102
6	112	1.31	.14	118	1.24	.16	2+	2	1+	31	72	83
7	107	1.15	.14	89	1.16	.16	3−	3	2+	42	72	84
8	100	1.05	.14	107	1.08	.16	3−	2+	2+	46	96	107

The adhesion ratings were as follows:

0—Coating floats off support.

1—Coating rubs off with ease.

1—Coating comes off only by scratching with fingernail.

4—Coating comes off only by scratching with steel blade.

The mushiness values for the coatings were determined by running a weighted stylus across the emulsion after immersion in developer, fixer, and water as indicated above; the weight in grams required to break through the emulsion is the value for mushiness in the table; therefore, a higher value represents a harder coating. Sensitomeric evaluation was made after exposure and processing in developer, fixed and water at 140°F.

Results in table 1 show the improved physical properties of coatings containing carboxyl polymers which have been hardened with an isoxazolium salt, i.e. improved mushiness and adhesion to the polyester support. The data in table 1 also shown the improved incubation stability of the coatings hardened with 2,5-dimethylisoxazolium p-toluenesulfonate.

EXAMPLE 9

An aqueous solution containing 3 percent by weight of gelatin was mixed with an equal amount of an aqueous solution containing 3 by weight (80:20) copoly(ethylacrylate-acrylic acid) ammonium salt and with 1percent by weight, based on the amount of gelatin and polymer, of 2,5-dimethylisoxazolium p-toluenesulfonate. The coated mixture set up in 45 seconds after mixing.

EXAMPLE 10

A mixture was made up as in example 9 except that the hardener was first mixed with the gelatin and the polymer subsequently added to the gelatin-hardener mixture. The coated mixture requires more than one hour to set up after mixing.

EXAMPLES 11–12

Two coatings were prepared as in example 10 except that the amount of hardener was 6 percent by weight. The first coating was heated at 98° F. and set up in 98 seconds. The second coating was heated to 130° F. and set up in 50 seconds.

The foregoing examples illustrate that the gelatin-polymer layers can be readily coated without setting up and that they can be conveniently set by heating if desired. It is preferred to heat the coatings to a temperature of up to 150° F., and preferably from 100° to 140° F., in order to rapidly set same.

EXAMPLE 13

Carbodiimide hardeners, such as diisopropyl-carbodiimide behave similarly to the isoxazolium hardeners in that conventional mixtures of the hardener with gelatin and the carboxyl polymer rapidly set up. Mixtures of equal parts of (80:20) copoly (methylacrylate-acrylic acid) sodium salt and gelatin containing 1, 3, and 5 percent of the hardener diisopropyl-carbodiimide were found to set up in, respectively, 55, 25 and 20 seconds. The up time is delayed by adding the hardener to the gelatin and subsequently adding the polymer thereto. It is preferred to hold the gelatin-hardener mixture for a short time prior to addition of the polymer to increase the time required to set up the coating. While the minimum amount of hold time sufficient to appropriately delay setup time will vary depending on the concentration of the hardener, a period of 30 seconds to 10 minutes or longer is generally sufficient. The maximum hold time can vary widely and is conveniently an hour or two.

A mixture as above containing 3 percent of the carbodiimide hardener but made by the first holding the gelatin-

hardener composition for 1 hour, requires more than 15 minutes to set up whereas the mixture made with zero hold time sets up in 25 seconds.

The support upon which the coating can be provided can vary widely and can, in fact, be in general any support upon which gelatin containing layers are conventionally provided including metal, and nonmetal such as glass, paper, ceramic, textiles, plastics, etc. The invention is particularly suited to the provision of photographic layers as described herein and, for instance, in U.S. Pat. No. 3,321,313, in which case the gelatin includes a light sensitive material such as a silver salt. The invention is also suited to providing hardened layers of carboxyl polymer and gelatin in general for protective, decorative, uses and the like and various fillers, pigments, dyes, etc. can be employed as will be apparent to those of ordinary skill in the art.

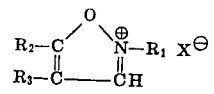
The carboxyl-containing polymers to which the invention is suited are solution polymers such as those disclosed in Houck et al. U.S. Pat. No. 3,220,844. In addition to the specific polymers mentioned above, the following have proven particularly suitable:

a. methylacrylate-acrylic acid (10:90)
b. methylacrylate-acrylic acid (50:50)
c. ethylacrylate-acrylic acid (50:50)
d. ethylacrylate-acrylic acid (60:40)
e. ethylacrylate-acrylic acid (70:30)
f. butylacrylate-acrylic acid (80:20)
g. butylacrylate-styrene-acrylic acid (60:20)
h. butylacrylate-methylmethacrylate-acrylic acid (60:20:20)

We claim:

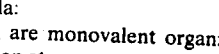
1. A method of providing a hardened coating of a mixture of gelatin and a water soluble synthetic polymer on a support comprising: providing an aqueous mixture comprising gelatin and a hardener selected from the group consisting of isoxazolium salts and carbodiimides; subsequently mixing a water soluble synthetic polymer containing from 90 to 10 mole percent of alkyl acrylate units, from 90 to 10 mole percent of acrylic acid units and from 0 to 40 mole percent of units derived from an ethylenically unsaturated copolymerizable monomer with the gelatin-hardener mixture; coating the mixture of gelatin, hardener, and water soluble synthetic polymer on the support whereby the setting time of said coating is substantially longer than that which would be obtained if said gelatin, hardener and polymer were simultaneously mixed; and drying and coating.

2. A method according to claim 1 wherein said hardener is an isoxazolium salt having the formula:



wherein R_1 is a monovalent organic residue containing from one to five carbon atoms, R_2 and R_3 are each hydrogen or monovalent organic residues having from one to 18 carbon atoms or together form an alicyclic ring, and X is an anion when sulfonate anion does not form a part of R_1, R_2 and R_3.

3. A method according to claim 2 wherein said carbodiimide has the formula:



wherein R_4 and R_5 are monovalent organic residues having from one to 20 carbon atoms.

4. A method according to claim 1 wherein said hardener comprises a carbodiimide and wherein the mixture of carbodiimide and gelatin is held for at least 30 prior to admixture with said polymer.

5. A method according to claim 1 wherein the aqueous gelatin solution includes silver halide.

6. A method of providing a hardened coating of a mixture of gelatin and a water soluble synthetic polymer on a support comprising: providing an aqueous mixture comprising gelatin and 2,5-dimethylisoxazolium p-toluenesulfonate hardener; subsequently mixing a water soluble synthetic polymer containing from 90 to 10 mole percent of alkyl acrylate units, from 90 to 10 mole percent of acrylic acid units and from 0 to 40 mole percent of units derived from an ethylenically unsaturated copolymerizable monomer with the gelatin-hardener mixture; coating the mixture of gelatin, hardener, and water soluble synthetic polymer on the support whereby the setting time of said coating is substantially longer than that which would be obtained if said gelatin, hardener and polymer were simultaneously mixed; and drying the coating.

7. A method of providing a hardened coating of a mixture of gelatin and a water soluble synthetic polymer on a support comprising: providing an aqueous mixture comprising gelatin and diisopropyl-carbodiimide hardener; subsequently mixing a water soluble synthetic polymer containing from 90 to 10 mole percent of alkyl acrylate units, from 90 to 10 mole percent of acrylic acid units and from 0 to 40 mole of units derived from an ethylenically unsaturated copolymerizable monomer with the gelatin-hardener mixture; coating the mixture of gelatin, hardener, and water soluble synthetic polymer on the support whereby the setting time of said coating is substantially longer than that which would be obtained if said gelatin, hardener and polymer were simultaneously mixed; and drying the coating.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,236 Dated November 9, 1971

Inventor(s) Glen M. Dappen and Grace E. Kane

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 42, the formula should be as follows: $R_4-N=C=N-R_5$

Column 5, line 27, "60:20" should read --60:20:20--.

Column 5, lines 45 and 46 "and coating" should read --the coating--.

Column 6, in line 11, the formula $R_4-N=C=N-R_5$ should be inserted.

Column 6, line 16 "30" should read --30 seconds--.

Signed and sealed this 11th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents