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[54] METHOD OF COATING DILUTE AQUEOUS EMULSIONS

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[58] **Field of Search** 96/114, 85, 86, 87

[56] **References Cited**

UNITED STATES PATENTS

2,772,163	11/1956	Tong	96/114
3,062,674	11/1962	Houck et al.	117/34
1,981,102	11/1934	Hagedorn et al.	96/35.1
3,220,844	11/1965	Houck et al.	96/85
3,493,379	2/1970	Donoghue	96/114
3,287,289	11/1966	Ream et al.	96/114
2,761,791	9/1956	Russell	117/34
2,603,565	7/1952	Land	96/61
3,297,446	1/1967	Dunn	96/107

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[57] **ABSTRACT**

An aqueous composition of a hydrophilic colloid, wherein said colloid comprises from about .1 to about 6 per cent by weight of said solution, is given increased viscosity by the low-level addition of a copolymer comprising: (1) at least 50 mole per cent of units of an acrylic acid and (2) up to 50 mole per cent of units of an alkyl acrylate. The copolymer is added at a concentration in the range of about 0.01 to about 1 per cent by weight of the aqueous composition. Aqueous compositions of hydrophilic colloids such as, for example, silver halide photographic emulsions, are thickened as described and can be coated on a wide variety of supports in single- or multi-layer photographic elements.

5 Claims, No Drawings

METHOD OF COATING DILUTE AQUEOUS EMULSIONS

Silver halide photographic emulsions improved as described can be incorporated as integral layers in photographic elements. They can be chemically sensitized, e.g., with noble metal sensitizers alone or in combination with sulfur or selenium sensitizers. They can also contain spectral sensitizers, incorporated color-forming couplers, incorporated developing agents, antifoggants, plasticizers, coating aids and other suitable photographic addenda, such as described in U.S. Pat. No. 3,297,446 (columns 4–9).

This invention relates to the use of viscosity-increasing materials or thickening agents in dilute aqueous compositions of hydrophilic colloids. In one specific aspect, this invention relates to the incorporation of acrylic acid-alkyl acrylate copolymers as thickening agents in dilute gelatin photographic emulsions to improve the coatability thereof.

It is well-known that photographic emulsions contain gelatin. It is also known that low gelatin concentrations permit coating of thin layers. Various thickening agents which facilitate the coating of dilute photographic emulsions include: carboxy-methylated carbohydrates, cellulose derivatives, carrageenans and alginic acid. Many of these materials exhibit problems producing haze, coagulation, brittleness, etc. Various acrylic acid polymers have also been used as a gelatin replacement.

However, improved silver halide emulsions having low gelatin content and increased viscosity are desired in order to coat improved thin layers in photographic elements without substantially affecting the other physical and photographic properties of the element.

I have now found a new method for coating thin layers which generally comprises utilizing very low concentrations of an acrylic acid-alkyl acrylate copolymer in an aqueous composition of low gelatin content.

In accordance with this invention, it has been found that the addition to a dilute aqueous composition of a hydrophilic colloid of low concentrations of an acrylic acid-alkyl acrylate copolymer in which the acid units comprise at least 50 mole per cent significantly increases the viscosity of said composition. In one embodiment, improved coatability of a dilute silver halide emulsion is achieved by the addition to said emulsion of an acrylic acid-methyl acrylate copolymer consisting of 90 mole per cent acid units and 10 mole per cent acrylate units.

Another embodiment of this invention comprises a dilute aqueous composition of a hydrophilic colloid thickened by the addition at low concentrations of an acrylic acid-alkyl acrylate copolymer comprising at least 50 mole per cent acid units and up to 50 mole per cent acrylate units. It is understood for purposes of this invention that acrylic acid units include substituted acrylic acid units such as methacrylic acid and that the alkyl acrylate units include substituted alkyl acrylates such as alkyl methacrylates and the like.

Another embodiment is a silver halide photographic emulsion containing less than 6 per cent gelatin by weight, thickened by the addition of a copolymer comprising 90 mole per cent acrylic acid units and 10 mole per cent methyl acrylate units.

Still another embodiment is an improved method for bead coating thin layers in a photographic element.

The practice of the invention as herein disclosed is a useful method of improving coating quality and versatility. The use of the acrylic acid-alkyl acrylate copolymers of the invention permits bead coating of more concentrated integral layers in photographic elements by the elimination of some of the gelatin vehicle without decreasing viscosity. The practice of the invention results in photographic elements of increased sharpness and faster processing characteristics without loss of coating uniformity. The compositions of the invention permit the combination of more layers into single multiple-hopper packs. They also facilitate the replacement of gelatin by other hydrophilic colloids, such as, for example, synthetic polymers where desired for faster drying, flexibility, improved covering power and dimensional stability, said polymers normally contributing too low a viscosity when used alone to allow good coating quality. They do not require the use of special hardeners to improve emulsion characteristics since conventional hydrophilic colloid hardeners such as gelatin hardeners can be used to harden the emulsions.

The colloidal materials whose properties are improved by mixing with an acrylic acid-alkyl acrylate copolymer are those whose aqueous dispersions are recognized as useful as vehicles in integral layer photographic elements. Included are gelatins, glues, pigmented gelatins, gelatin derivatives and other colloidal materials such as, for example, poly(acrylamide), poly(vinyl alcohol), poly(vinyl pyrrolidone), and the like. In one embodiment, the preferred hydrophilic colloid is gelatin.

The alkyl acrylate-acrylic acid copolymers generally useful in this invention comprise at least 50 mole per cent of units of an acrylic acid and up to about 50 mole per cent of units of an alkyl acrylate. In one preferred embodiment, the copolymer consists essentially of units of the monomers above in the specified ratios. In another preferred embodiment, the copolymer comprises from about 80 to about 95 mole per cent of units of an acrylic acid. The use of at least some units of the alkyl acrylate in the polymer used to increase viscosity is preferred in order to obtain flexibility and resiliency in the resultant emulsion and to avoid the brittleness and other undesirable properties often associated with polyacrylic acids when used in photographic emulsions.

Suitable alkyl acrylate units include any of those in which the alkyl radical contains from about one to about 10 carbon atoms, e.g., methyl, ethyl, propyl, hexyl, decyl, etc. Examples of suitable alkyl acrylate units include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, and the like, though methyl acrylate is preferred.

In general, copolymer additions in the range of about 0.01 to about 1, preferably about 0.1 to about 0.5, per cent by weight of said aqueous coating composition are sufficient. Preferably the coating compositions contain from 1 to 5 per cent of said copolymer based on the weight of the hydrophilic colloid.

The practice of this invention is most effective in aqueous compositions wherein the concentrations of the hydrophilic colloids are in the range of about 0.1 to about 6, preferably about 0.1 to about 4, per cent by weight.

Dilute aqueous compositions thickened as described can be coated on a wide variety of supports in single- or multi-layer photographic elements, for example, as disclosed in Russell, U.S. Pat. No. 2,761,791, issued Sept. 4, 1966. The compositions of this invention can also be coated by dip-coating methods or methods where high viscosity is quite advantageous such as in extrusion coating, curtain coating and doctor knife coating. Examples of suitable supports include cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthalate) film and related films or resinous materials as well as glass, paper, metal 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, e.g., polyethylene, polypropylene and ethylene butene copolymers, can also be employed.

Photographic elements can be produced comprising a support and integral layers in which at least one layer comprises a silver halide emulsion, for example, the improved viscosity compositions can be used to coat interlayers, silver halide emulsion layers, dye mordant layers, receiving layers and the like. The compositions of the invention improved as described can be coated in thin, uniform layers thereby permitting a combination of more of said layers into a thin photographic element.

Silver halide photographic emulsions and elements of the invention can be used in various kinds of photographic systems, e.g., monochromatic, orthochromatic, panchromatic, infrared, X-ray and other non-optically sensitized systems. Silver halide photographic emulsions and elements improved as described can be used in color photography, e.g., emulsions

containing color-forming couplers or emulsions to be developed by solutions incorporating couplers or other color-generating materials.

The integral layers of a photographic element can be chemically sensitized, e.g., with noble metal sensitizers alone or in combination with sulfur or selenium sensitizers. They can contain spectral sensitizers such as, for example, the cyanines, merocyanines, complex (trinuclear) cyanines, complex merocyanines, styryls and hemicyanines. Sensitizing dyes useful in such integral layers are described, for example, in U.S. Pat. Nos. 2,526,632 and 2,503,776.

The integral layers of a photographic element can also contain development modifiers such as polymeric thioethers, onium salts, polyalkylene glycols, etc. They can contain antifoggants and stabilizers, examples of which include seleninic acids, tetraazaindenes, oxypentamidines, etc.

This invention is further illustrated by the following examples:

EXAMPLE 1

A commonly obtained copolymer comprising 90 mole per cent acrylic acid units and 10 mole per cent methyl acrylate units, herein abbreviated as copolymer (90:10), contains about 10 per cent solids at pH 3.0. This very viscous solution (50,000-1,000,000 cps) is impractical for handling and coating. A working solution is prepared by diluting the copolymer to a 2 per cent solids solution without adjusting the pH. The effect of adding the acrylic acid-methylacrylate copolymer (90:10) to gelatin solutions gives the viscosity data set out in Table 1 below. Columns headed "Percent Copolymer Solids" and "Percent Gelatin Solids" give percent solids based on the total weight of the aqueous composition. The pH is adjusted on each sample to normal emulsion levels (6.0–7.0) and viscosity readings are taken at 105° F.

TABLE 1

% Copolymer Solids	% Gelatin Solids	Centipoise Control	Centipoise Copolymer Added
0.05	1	1.3	17.2
0.10	2	2.0	33.1
0.15	3	2.9	72.0
0.25	5	5.1	100+
0.50	10	25.9	—

EXAMPLE 2

The use of acrylic acid-methyl acrylate copolymer (90:10) in all layers of a multilayer-multicolor color reversal film containing incorporated couplers has allowed the bead coating of more concentrated, i.e., thinner, layers in the photographic element. The thinner photographic coatings produced in the manner disclosed above result in improved image sharpness and increased rate of processing.

The results are encouraging since in color photographic elements of this type, the high coupler, high silver and low gelatin content as well as the use of dye mordants in the upper layers of the element make concentration of these integral layers especially difficult. The mordant layers tend to be more susceptible to coagulation when concentrated than any of the other layers. The magenta and cyan layers would require about double the gelatin content to achieve the same viscosity as produced by the addition of acrylic acid-methyl acrylate copolymer (90:10) at a rate of 0.1 to about 0.5 per cent by weight of the composition.

EXAMPLE 3

The copolymers of this invention are particularly useful in dye-developer color transfer elements of the type described, for example, in Weyerts et al U.S. Pat. No. 3,146,102. The addition of small amounts of acrylic acid-methyl acrylate (90:10) in the cyan and magenta layers of a photographic element, as above, increases the viscosity and decreases silver halide grain sedimentation. Gelatin increases in these layers to accomplish the same purpose are unacceptable since they greatly decrease the maximum density of the final color transfer print. Acrylic acid-methyl acrylate copolymer (90:10) has no adverse effect on the sensitometric properties of the emulsion layers of either fresh or incubated (120° F. for one week) coatings.

Similar results are obtained when the copolymers acrylic acid-methyl acrylate (75:25), acrylic acid-methyl acrylate (50:50), methacrylic acid-propyl acrylate (90:10) and methacrylic acid-methyl methacrylate (90:10) are used in place of the acrylic acid-methyl acrylate (90:10) copolymer.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A composition of matter comprising an aqueous composition of (A) a silver halide photographic emulsion comprising hydrophilic colloid wherein said colloid comprises from about 0.1 to about 6 percent by weight of said composition and (B) a copolymer comprising: (1) from at least 50 to 95 mole percent of units of an acrylic acid and (2) from 5 up to about 50 mole percent of alkyl acrylate, wherein said copolymer comprises from about 0.1 to about 5 percent by weight of said colloid.

2. A photographic element comprising a support and integral layers, at least one layer comprising a silver halide emulsion, wherein said integral layers contain the composition of matter comprising an aqueous composition of (A) a hydrophilic colloid wherein said colloid comprises from about 0.1 to about 6 percent by weight of said solution and (B) a copolymer comprising: (1) from at least about 50 to 95 mole percent of units of an acrylic acid and (2) from 5 up to about 50 mole percent of units of an alkyl acrylate, wherein said copolymer comprises from about 0.1 to about 5 percent by weight of said colloid.

3. A method for increasing the viscosity of an aqueous composition of a silver halide photographic emulsion containing a hydrophilic colloid in an amount from about 0.1 to about 6.0 percent by weight of said composition, the improvement which comprises incorporating therein a copolymer comprising (1) from at least 50 to 95 mole percent of units of an acrylic acid and (2) from 5 up to about 50 mole percent of units of alkyl acrylate, wherein said copolymer comprises from about 0.1 to about 5 percent by weight of said colloid.

4. The method of claim 3 wherein the hydrophilic colloid is gelatin.

5. The method of claim 3 wherein the copolymer comprises from about 80 to about 95 mole percent acrylic acid units.

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