

[54] PHOTOGRAPHIC HYDROPHILIC
COLLOIDS AND METHOD OF COATING

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[51] Int. Cl. G03c 1/02

[58] Field of Search 96/94, 114.3

[56] References Cited

UNITED STATES PATENTS

3,392,019 7/1968 Barnes et al. 96/61

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Attorney—Robert W. Hampton et al.

[57] ABSTRACT

A composition is disclosed which comprises a solution of a hydrophilic colloid and a viscosity increasing concentration of a polysaccharide comprising a linear polymer in which either (1) at least one-third of the monosaccharide units are linked 1-2 and the remaining monosaccharide units are linked 1-4, or (2) substantially all monosaccharide units are linked 1-4 and at least 50 percent of the hydroxyl groups are acetylated or alkali metal sulfated.

4 Claims, No Drawings

PHOTOGRAPHIC HYDROPHILIC COLLOIDS AND METHOD OF COATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the use of viscosity-increasing materials or thickening agents in dilute compositions of hydrophilic colloids. In one specific aspect, this invention relates to the incorporation of linear polysaccharide polymers as thickening agents in dilute gelatin photographic emulsions to improve the coat-ability thereof.

2. Description of the Prior Art

It is well-known that most photographic emulsions contain gelatin. It is also known that low gelatin concentrations permit coating of thin layers. Various thickening agents which have been used to facilitate the coating of dilute photographic emulsions include: carboxy-methylated carbohydrates, cellulose derivatives, carrageenans, alginic acid, various acrylic acid polymers, water-soluble sulfonate polymers, pectic polysaccharides (Belgian Pat. No. 611,623), dextran (U.S. Pat. No. 3,063,838) and certain other polysaccharides (U.S. Pat. Nos. 2,942,974; 3,085,009 and 3,338,716 and Belgian Pat. No. 665,862). None of these materials has been entirely satisfactory and they exhibit problems producing haze, coagulation, brittleness, etc.

Materials used previously as viscosity increasers for hydrophilic colloids have exhibited still other problems such as salt-sensitivity, wherein reduced viscosity improvements are obtained in the presence of water-soluble salts. Increases in viscosity have also been restrained by particular pH environments and the presence of polyvalent cations like cadmium. The deleterious effect of polyvalent cations is most characteristic with thickening agents having carboxyl groups.

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.

Accordingly, an object of this invention is to increase the viscosity of hydrophilic colloid solutions, including gelatin solutions.

Other objects of this invention are to coat dilute aqueous hydrophilic colloid solutions of increased viscosity and to produce photographic elements using such colloid solutions.

Still other objects and advantages of the present invention will become apparent from a reading of the specification and claims.

SUMMARY OF THE INVENTION

Hydrophilic colloid solutions, e. g. gelatin solutions, exhibit an increase in viscosity in the presence of an effective amount, i.e., a viscosity increasing concentration, of a polysaccharide that is a linear polymer in which either (1) at least one-third of the monosaccharide units are linked 1-2 and the remaining monosaccharide units are linked 1-4 or (2) substantially all monosaccharide units are linked 1-4 and at least about 50 percent of the hydroxyl substituent groups on the monosaccharide units are acetylated or alkali metal sulfated. Exemplary polysaccharides of this type include bacterial heteropolysaccharides, including B-1459 and B-1973 polysaccharides. Viscosity increasing concentrations are widely variable, but ranges

of about 0.001 to about 0.5 percent by weight, based on the colloid, are typical. Polysaccharides of the present types are especially useful in aqueous colloid solutions wherein the colloid is present in an amount of from about 0.1 to about 6 weight percent, based on the total solution weight. Colloid solutions are useful as photographic solutions and can comprise photographic silver halide emulsions. Such solutions and emulsions can be used to advantage when coated to form photographic layers, for example, as an integral photographic layer in a photographic element.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one embodiment, the present invention relates to solutions including a hydrophilic colloid and a viscosity increasing concentration of a polysaccharide including linear polymers in which either (1) at least one-third of the monosaccharide units are linked 1-2 and the remaining monosaccharide units are linked 1-4, or (2) substantially all monosaccharide units are linked 1-4 and, as regards these polysaccharides with all monosaccharide units linked 1-4, at least about 50 percent of the hydroxyl groups are acetylated or alkali metal sulfated. Polysaccharides of this type are especially useful for increasing the viscosity of aqueous colloid solutions wherein the colloid ranges from about 0.1 to about 6 percent by weight, based on total solution weight. Most generally, viscosity increasing concentrations range from about 0.001 to about 0.5 weight percent, preferably from 0.001 to about 0.2 weight percent, based on the colloid, but more extensive variations are possible where desired. A wide range of hydrophilic colloid solutions can be increased in viscosity with polysaccharides of the present types, and they are especially useful for thickening photographic hydrophilic colloid solutions, gelatin for example.

In a preferred aspect, the present invention includes compositions comprising a solution of a hydrophilic colloid, e.g. gelatin, preferably in the range of from about 0.1 to about 6 percent by weight of the composition and a viscosity increasing concentration of a bacterial polysaccharide that is either a B-1459 or a B-1973 polysaccharide. Viscosity increasing concentrations are widely variable, but concentrations (as described elsewhere herein) are used for conventional situations.

Polysaccharides such as the B-1459 and B-1973 polymers described herein are specific polymers that are biosynthesized by particular bacterial strains. Polysaccharides of this type are named as a function of the bacteria that effects the biosynthesis. This is a method well recognized in the literature and provides a complete description for stereospecific bacterial polysaccharides.

References identifying polysaccharides B-1459 and/or B-1973 include the following:

Orentas, D. G., et al., *Canadian J. Microbiology*, 9, 427 (1963).

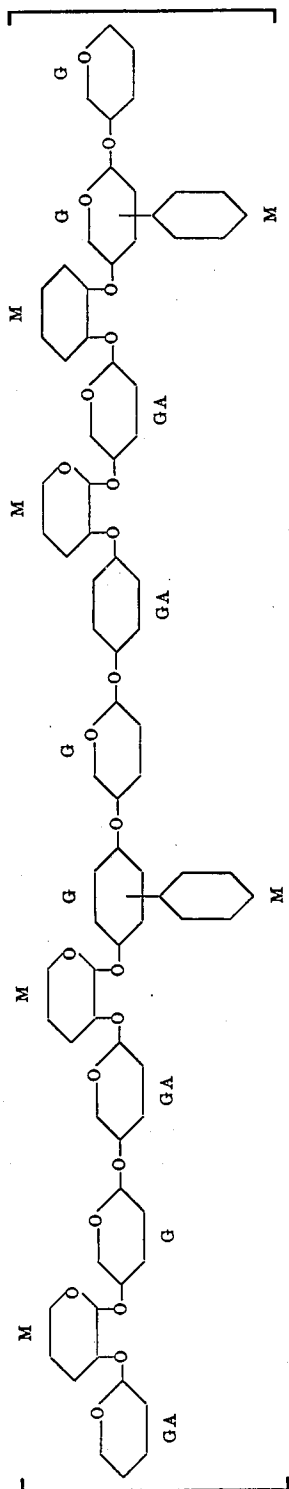
Sloneker, J. H., et al., *Canadian J. Chemistry*, 46, 3,353 (1968).

Wallen, L. L., et al., *Appl. Microbiology*, 13, 272 (1965).

Slodki, M. E., *Biochim. Biophys. Acta* 69, as well as U.S. Pat. Nos. 3,383,307; 3,516,983; 3,391,061 and 3,000,790.

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Further, the theoretical structure of polysaccharides B-1459 and B-1973 has been characterized by the following structural formulas



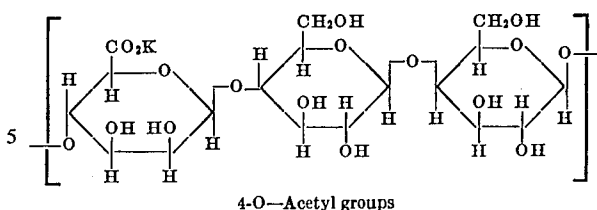
B-1459

M = B-D-mannose

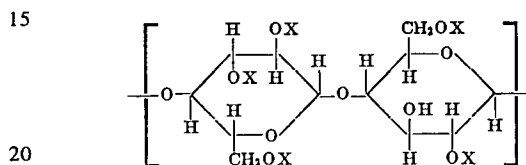
G = B-D-glucose

GA = B-D-glucuronic acid

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In addition to the above, another polysaccharide that is commercially available from the Kelco Company of Clark, New Jersey, designated KELCO SCS, has been employed successfully in the practice of this invention. Its structure is understood to be:



where X is $-\text{SO}_3\text{M}$ and M is an alkali metal.

Using polysaccharides of the types described herein, another embodiment of the present invention relates to dilute silver halide photographic emulsions of improved coatability, particularly to gelatino silver halide emulsions containing less than about 6 weight percent gelatin, that are thickened by the addition of a viscosity increasing concentration of a polysaccharide as described herein. Still another embodiment of this invention is a coating process for preparing layers from improved hydrophilic colloid compositions particularly aqueous gelatin compositions including silver halide emulsions and especially those having less than 6 weight percent gelatin.

Using the dilute hydrophilic colloid compositions and processes of this invention permits the coating of thinner layers in photographic elements by eliminating a portion of the colloid vehicle without decreasing viscosity. This results in photographic elements of increased image sharpness and more rapid processing characteristics without loss of coating uniformity. Also, a greater numbers of layers can be incorporated into multilayer packs. Special hardeners are not required since conventional hydrophilic colloid hardeners such as gelatin hardeners can be used to harden the emulsions or other compositions.

The colloidal materials whose properties are improved by mixing with a polysaccharide of the present types are those whose dispersions or solutions are recognized as desirable vehicles in photographic emulsions and elements, especially those photographic elements having multiple layers. Included are gelatins, glues, pigmented gelatins, gelatin derivatives and other colloidal materials like poly (acrylamide), poly(vinyl alcohol), poly(vinyl pyrrolidone), polysaccharides such as dextran, gum arabic and the like, either alone or in combination with gelatin being preferred.

The described colloid solutions or photographic emulsions can also contain dispersed vinyl polymers, particularly those which increase the dimensional stability of photographic materials. Suitable synthetic polymers include those described, for example, in U. S. Pat. Nos. 3,142,568; 3,193,386; 3,062,674; 3,220,844; 3,287,289 and 3,411,911; and include, for example, the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkylacrylates or methacrylates and the like.

Polysaccharides of the present types can be added to a photographic emulsion or solution at any appropriate point in the process. It can be added during the preparation of a silver halide emulsion. It can be added during one or more of the digestion stages of a silver halide emulsion preparation. And it can be added to a silver halide emulsion just prior to its being coated as a layer onto the film or paper support.

As mentioned elsewhere, the polysaccharide need not necessarily be added to a silver halide emulsion or layer, but can be added to photographic solutions or emulsions used as subcoats or overcoats for the photographic element.

Dilute aqueous compositions thickened as described can be coated on a wide variety of supports in single- or multilayer 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, oxypentamides, etc.

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

EXAMPLE 1

A 1 percent aqueous solution of a commercially available *Xanthomonas* polysaccharide marketed under the trade name Kelzan by the Kelco Company and produced by the aerobic fermentation of glucose by the bacterium *Xanthomonas Campestris* NRRL B-1459 was filtered through paper in a pressure filter and the concentration determined gravimetrically by evaporation.

Nine solutions (Nos. 1-9) of gelatin from 1 to 7 percent bone gelatin were made, each containing 0.1 percent polysaccharide. The Brookfield viscosities of these solutions, as well as the corresponding gelatin solutions, were determined in centipoises (cps.) at 40° C. The results in Table I demonstrate the large viscosity increase produced by a small amount of the *Xanthomonas Campestris* polysaccharide (B-1459) in aqueous gelatin.

TABLE I

Viscosity of Gelatin-B-1459 Polysaccharide Solutions

Solution No.	Gelatin %	Kelzan %	Brookfield Viscosity of 40° (cps)
1	2	—	4
2	4	—	6
3	7	—	11
4	1	0.1	40
5	2	0.1	49
6	3	0.1	59
7	4	0.1	69
8	5	0.1	79
9	7	0.1	103

EXAMPLE 2

A solution of 0.1 percent B-1459 polysaccharide and 5 percent bone gelatin was prepared at 40° C. The Brookfield viscosity was determined as the pH was raised by the addition of dilute sodium hydroxide. The results are summarized in Table II and they indicate that over the pH range considered the viscosity was not very sensitive to pH change.

TABLE II

Effect of pH Change on Viscosity of Gelatin-B-1459 Polysaccharide Solution

pH	Brookfield Viscosity 40° (cps)
5.25	71
5.75	69
6.10	70
6.53	72
6.93	72
8.10	68
8.70	66

EXAMPLE 3

A solution of 0.1 percent by weight based on the gelatin of B-1459 polysaccharide and 5 percent by weight bone gelatin was prepared at 40° C and the pH adjusted to 6.1. Addition of sodium chloride in increments up to 0.2 molar had little effect on the Brookfield viscosity.

TABLE III

Effect of Concentration of Sodium Chloride on the Viscosity of Gelatin-B-1459 Polysaccharide Solution

NaCl Molarity	Brookfield Viscosity 40° (cps)
0	73
0.02	71
0.045	69
0.10	69
0.20	67

7 EXAMPLE 4

Coatings of a bone gelatin solution containing increasing amounts of B-1459 polysaccharide were made on poly(ethylene terephthalate) support. The results summarized in Table IV indicate that the polysaccharide at useful levels has little or no effect on the light transmittance of the gelatin coatings.

TABLE IV

Gelatin Wt. %	B-1459 at 520nm Wt. %	Spread		Light Transmission	
		Gelatin mg/ft ²	B-1459 mg/ft ²	Specular	Total
0	0	—	—	90.0	91.2
5	0	1000	0	90.5	91.0
5	0.017	1000	3.3	90.5	91.0
5	0.025	1000	5.0	90.5	91.0
5	0.05	1000	10	90.5	91.0
5	0.10	1000	20	90.0	91.0
5	0.20	1000	40	89.8	91.0

EXAMPLE 5

One mole of a silver bromoiodide emulsion containing 47 g. of gelatin was adjusted to a total weight of 835 g. with distilled water. Increasing levels of B-1459 polysaccharide, varying from 0.01 percent to 0.10 percent by weight, based on the gelatin, were added to three separate aliquot portions of the gelatino emulsion. A fourth portion with no polysaccharide served as the control. The Brookfield viscosity was measured at 40° C at a pH of 6.5. The results summarized below in Table V, demonstrate the efficacy of small amounts of B-1459 polysaccharide for increasing the viscosity of a gelatino-silver halide emulsion.

TABLE V

B-1459 Wt. %	Brookfield Viscosity 40° (cps.)
0	18
0.021	37
0.042	67
0.084	150

EXAMPLE 6

Two identical melts (A and B) containing a silver bromoiodide emulsion and B-1459 polysaccharide were prepared. Each melt was then divided into three portions. The portions of melt B were hopper coated immediately after preparation, while the portions of melt A were held 4 hours at 40° C before being hopper coated. Each melt portion was coated on a polyethylene terephthalate support. The photographic elements so prepared were then exposed for 1/25 second on an EGG Mark VI Sensitometer, processed for 5 minutes in an Elon-hydroquinone developer, fixed, washed and dried. The following results, summarized in Table VI, indicate that the B-1459 polysaccharide does not interfere with the sensitometry of photographic emulsions.

TABLE VI

Sensitometric effect of B-1459 polysaccharide on a gelatino-silver halide emulsion

Melt	Hold time at 40° C. (hr.)	B-1459 g./mole Ag	Fresh			1 wk. inc. 120°, 50% R.H.		
			Rel. speed	γ	Gross fog	Rel. speed	γ	Gross fog
A1-----	4	0	100	1.27	.08	67	0.92	.08
B1-----	0	0	120	1.39	.07	80	1.00	.06
A2-----	4	2	115	1.34	.08	80	.98	.08
B2-----	0	2	126	1.35	.08	87	1.05	.06
A3-----	4	4	126	1.41	.08	87	1.05	.08
B3-----	0	4	120	1.36	.08	87	1.05	.08

EXAMPLE 7

The viscosities of various aqueous solutions were measured on an "Epprecht Rheomat 15" at a tempera-

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ture of 40° C. These data, which appear in the following table, were computer analyzed resulting in the viscosity as a function of shear rate.

The polysaccharide-gelatin solutions decrease exponentially in viscosity as the shear rate is increased. The gelatin solutions do not vary significantly in viscosity with increasing shear rates and is considered to be Newtonian behavior.

Kelzan D is a form of polysaccharide B-1459 which has been modified for use in systems with other gum or cellulose materials (Kelco Co., Technical Bulletin 15).

TABLE VII

Solution	Viscosity (centipoise)	Shear Rate (sec ⁻¹)	pH
5% Bone gelatin	7.6	10	6.5
	7.1	100	6.5
3% Bone gelatin	4.0	10	6.5
	3.6	100	6.5
0.2% Kelzan D, 5% Bone gelatin	217.0	10	5.6
	65.4	100	5.6
0.1% Kelzan D, 3% Bone gelatin	51.4	10	5.6
	21.2	100	5.6
0.1% Kelzan D, 0.01M KBr, 5% Bone gelatin	42.8	10	7.1
	19.5	100	7.1
0.2% B-1973, 5% Bone gelatin	109.8	10	5.6
	34.8	100	5.6

EXAMPLE 8

Kelco SCS is a water soluble sodium cellulose sulfate gum having a high degree of substitution (approximately 2.5 sulfate groups per anhydroglucose unit).

Kelco SCS was added as an aqueous solution (0.1 percent by weight) to an aqueous solution of gelatin (5 percent by weight) and the viscosities (poise) was measured at various pH's and at two shear rates (27 sec⁻¹ and 48 sec⁻¹) at 40° C.

pH	Shear Rate	
	27 sec ⁻¹	48 sec ⁻¹
4.93	0.873 poise	0.779 poise
5.85	0.786 poise	0.676 poise
7.33	0.385 poise	0.349 poise
9.16	0.281 poise	0.256 poise
control (no Kelco SCS)	—	0.053 poise

The salt sensitivity of Kelco SCS is determined by adding increasing amounts of an aqueous solution of potassium nitrate to a gelatin solution (5 percent by weight) and measuring the viscosity (poise) at a constant shear rate (sec⁻¹).

TABLE VIII

	27 sec ⁻¹		48 sec ⁻¹	
1. 5% gelatin	—	—	0.052 poise	—
2. 1 + 1% Kelco SCS	0.685 poise	—	0.605 poise	—
3. 2 + 0.025M KNO ₃	0.293 poise	—	0.270 poise	—
4. 2 + 0.05 KNO ₃	0.180 poise	—	0.166 poise	—
5. 2 + 0.10M KNO ₃	0.010 poise	—	0.096 poise	—

The above data show that Kelco SCS exhibits salt sensitivity at high concentrations of potassium nitrate but shows only moderate pH sensitivity.

This 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.

What is claimed is:

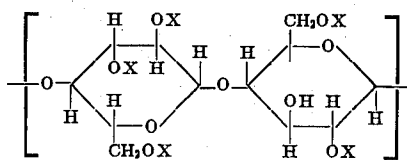
1. In a method for increasing the viscosity of an aqueous composition of a photographic silver halide emulsion containing a hydrophilic colloid, the improvement which comprises incorporating therein a viscosity increasing concentration of a polysaccharide comprising a linear polymer in which either (1) at least one-third

of the monosaccharide units are linked 1-4, or (2) substantially all monosaccharide units are linked 1-4 and at least 50 percent of the hydroxyl groups are acetylated or alkali metal sulfated.

2. A photographic element comprising a support and integral layers, at least one layer comprising a photographic silver halide emulsion, wherein said integral layers contain a composition of matter comprising a solution of a hydrophilic colloid and a viscosity increasing concentration of a polysaccharide comprising a linear polymer in which either (1) at least one-third of the monosaccharide units are linked 1-2 and the remaining monosaccharide units are linked 1-4, or (2) substantially all monosaccharide units are linked 1-4, and at least 50 percent of the hydroxyl groups are acetylated or alkali metal sulfated.

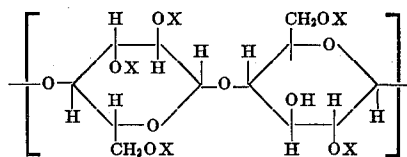
3. A photographic element comprising a support having thereon at least one layer comprising a silver halide emulsion and at least one layer, which can be the same as or different from said emulsion layer, comprising a hydrophilic colloid having therein, in a concentration of from about 0.001 to about 0.2 weight percent based on the colloid, of a bacterial polysaccharide that is either a B-1459 polysaccharide, a B-1973 polysaccharide or a polysaccharide of the structure

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where X is -SO₃M and M is an alkali metal.

4. A silver halide emulsion comprising a photographic hydrophilic colloid solution comprising about 0.1 to about 6 weight percent colloid and a bacterial polysaccharide that is either a B-1459 polysaccharide, a B-1973 polysaccharide or a polysaccharide of the structure



wherein X is -SO₃M and M is an alkali metal, said polysaccharide being in a concentration of from about 0.001 to about 0.2 percent by weight based on the colloid.

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Disclaimer

3,767,410.—*David Philip Brust* and *Grace Eileen Kane*, Rochester, N.Y. PHOTOGRAPHIC HYDROPHILIC COLLOIDS AND METHOD OF COATING. Patent dated Oct. 23, 1973. Disclaimer filed July 11, 1974, by the assignee, *Eastman Kodak Company*.

Hereby enters this disclaimer to claims 1, 2, 3 and 4 of said patent.

[*Official Gazette June 10, 1975.*]