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GELATIN COATING COMPOSITIONS

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This invention relates to gelatin compositions for coating purposes having improved properties which compositions contain therein diols of 4–7 carbon atoms, the hydroxyls therein being separated by at least three carbon atoms.

Gelatin coatings are ordinarily characterized by inadequate flexibility under conditions of low humidity; also those coatings often exhibit a photographic sensitivity to mechanical strain which is undesirable. Various materials have been mentioned as useful as improvement additives to gelatin compositions such as glycerin, ethylene glycol and certain other polyols. However, the effect from these materials has been due primarily to their hygroscopicity. The use of sufficient of such polyols to improve gelatin compositions such as photographic emulsions at low humidities, however, is often prevented because of the formation of undesirable physical and sensitometric properties in the coatings containing them when at high humidities and high temperatures.

One object of our invention is to prepare gelatin coating compositions having improved properties. Another object of our invention is to provide gelatin compositions from which coatings may be prepared having greatly improved flexibilities over coatings which have been prepared heretofore from gelatin. A further object of our invention is to provide gelatin coatings which give films which are relatively insensitive to photographic effects of mechanical strain. A still further object of our invention is to provide gelatin compositions containing therein diols which are free of volatility or hygroscopicity, but which do not decrease in plasticizing efficiency in the gelatin under low humidity conditions. Other objects of our invention will appear herein.

We found that aqueous gelatin compositions provide coatings of greatly improved properties if there are present in those compositions a small amount of a diol of 4–7 carbon atoms, the hydroxyls of which are separated by at least three carbon atoms. Compounds which we have found to be especially useful in this connection are 2-methyl-2,4-pentanediol; 1,5-pentanediol; 1,4-butanediol and 1,6-hexanediol. These compounds are found to improve gelatin when present therein in the proportion within the range of 5–25% based on the weight of the gelatin. In proportions of 5–20% these compounds are found to be effective for reducing the photographic sensitivity of a photographic emulsion to mechanical strain which might be encountered when in the form of sheets or when coated out as a layer. For substantially enhanced plasticization, it is usually desirable that at least 10% of these materials be present in the gelatin and effective plasticization is obtained in proportions up to at least 25%.

The gelatin coating compositions may be in the form of aqueous gelatin solutions or they may be in the form of silver halide-gelatin photographic emulsions. These compositions may be coated out onto a surface from which they may be stripped to form a stripping layer

or they may be coated onto a photographic film base or onto a photographic paper base to form photographic products. The resulting layers are found to have improved properties as regards either plasticity, i.e., flexibility or tolerance of mechanical strain or both. In some cases it may be desirable to dry the gelatin coating at a slow rate to obtain the highest flexibility, while in other cases fast drying rates have been found to give coatings of superior flexibilities. We have found that the gelatin coating obtained from compositions in accordance with our invention exhibit good flexibility both at low and at high humidity as distinguished from gelatin coatings without added improving agents, or gelatin coatings which contain therein materials which are hygroscopic such as glycerin or the like.

CASE I

Gelatin sheets containing	Percent of additive	Flexibilities in MIT folds	
		10% R.H.	15% R.H.
No additive		1	4
Glycerin	10	1	4
Do	20	1	10
1,5-pentane-diol	20	12	13
1,6-hexane-diol	20	12	15
1,4-butane-diol	20	6	7

CASE II

Gelatin sheets containing	Percent of additive	Flexibilities in MIT folds 15% R.H.
No additive		2
Glycerin	10	2
Do	20	6
1,5 pentane-diol	20	11
1,6 hexane-diol	20	13

CASE III

Gelatin sheets and photographic emulsion sheets containing	Percent of additive	Flexibilities in MIT folds at 20% R.H.	
		gelatin sheets	emulsion sheets
No additive		24	14
Glycerin	10	25	22
Do	15	39	32
Do	20	54	53
1,4 butane-diol	15	55	53
Do	20	63	74
1,5 pentane-diol	15	55	42
Do	20	66	56

Oftentimes flexibilities depend on the method of drying the gelatin coatings as shown by the following table:

CASE IV

Gelatin sheets containing—	Flexibilities in MIT folds at 20% R.H.	
	Skins dried for 2½ days at 70° F. and wet bulb T°. of 64° F.	Skins dried for 1 hr. at 120° F. and wet bulb T.° of 75° F.
A. No additive	25	21
B. 20% pentane-diol	63	19
C. 20% 2-methyl-2,4-pentane-diol	47	127
D. 20% glycerin	54	28

These compositions were also coated onto cellulose

acetate support and the flexibilities of samples thereof were determined the results being as follows:

Cellulose acetate films having gelatin coatings containing—	Flexibilities in MIT folds at 20% R.H.	
	Films dried at 70° F. and 60° F. wet bulb for 1 hour	Films dried at 120° F. and 75° F. wet bulb for 35 min.
A. No additive	6	8
B. 20% pentane-diol	15	6
C. 20% 2-methyl-2,4-pentane-diol	14	13
D. 20% glycerin	11	7

Photographic emulsion compositions were prepared having the proportions of additive specified (dry weight of gelatin). These emulsions were coated on to cellulose acetate film base and the flexibilities of the coated films were tested, the results being as follows:

Cellulose acetate films having photographic emulsion coatings containing—	Flexibilities in MIT folds at 15% R.H.	
	Films dried at 67° F. and wet bulb T.° of 60° F. for 1 hour	Films dried at 110° F. and wet bulb T.° of 70° F. for 1¾ min.
A. No additive	5	0
B. 20% pentane-diol	15	1
C. 20% 2-methyl-2,4-pentane-diol	14	19
D. 20% glycerin	14	0

The following examples illustrate the invention:

Example 1

Gelatin sheets were prepared from solution containing 8% of photographic gelatin and the indicated amounts of improvement agent. These solutions were coated out onto plates from which they could be readily stripped in such volume that the coatings had a dried thickness of 4 mils. The sheets were cured at 70° F. and 70% relative humidity until dry. They were then stripped from the plates, slit to widths of 15 mm. and conditioned at 70° F. and 20% relative humidity. Their folding endurance was tested by an MIT fold tester using a tension of 1 kilogram and jaws of 0.0155-inch radius of curvature with a separation of 0.01 inch. The following results were obtained:

Percent	Additive	MIT folds at 20% R.H.
0	None	24
20	1,4-butane-diol	71
20	1,5-pentane-diol	74
20	1,6-hexane-diol	69
20	1,3-butane-diol	62
20	2,5-hexane-diol	59

Example 2

A series of sheets were prepared as described in the preceding example using the amounts of improvement agent indicated below. The sheets obtained were tested and the results obtained were as follows:

Percent	Additive	MIT folds at 20% R.H.
0	None	24
15	1,4-butane-diol	56
15	1,5-pentane-diol	55

The presence of the diols of our invention causes a marked reduction in the adverse photographic effect resulting from physical stresses applied to the silver halide gelatin emulsion layer containing them. The benefit is illustrated in the following two examples:

Example 3a

To separate portions of a panchromatically sensitized gelatin-silver-bromoiodide emulsion were added respectively:

(*a*) 13 g. glycerin per mole of silver
(*b*) 10 g. 2,2-dimethyl-1,3-propanediol per mole of silver
(*c*) 10 g. 2-methyl-2,4-pentanediol per mole of silver

Each sample was coated on a cellulose acetate support. Two strips from each of these coatings were equilibrated at 70° F. and 50% relative humidity for 3 hours. To one of these strips from each coating tension was applied at a constant rate of elongation until 8% elongation was obtained, at which point the tension was released. All strips were then given identical step wedge exposures to light and developed in Kodak Developer DK–50 for 5 minutes at 68° F.

The effect on developed density resulting from the elongation stress was measured at an exposure which yielded a density of 0.8 in the unstretched control strip in each case.

In the strip containing glycerin, the elongation stress resulted in a 0.14 (approximately 18%) reduction in density. There was no density loss resulting from stress with the strip containing 2,2-dimethyl-1,3-propanediol and only 0.04 (5%) density loss with that containing 2-methyl-2,4-pentanediol. The results are tabulated as follows:

Additive	g./mole Ag	Percent Elongation	Relative Speed	Density [1]
Glycerin	13	0	100	0.80
		8	75	0.66
2,2-Dimethyl-1,3-propanediol	10	0	100	0.80
		8	92	0.80
2-Methyl-2,4-pentanediol	10	0	100	0.80
		8	86	0.76

[1] At exposure which gave a density of 0.8 in the unstressed control strips.

Example 3b

Similarly, glycerin and 1,5-pentanediol were added to separate portions of a fast negative emulsion. The emulsions were coated and handled in the same manner as in Example 3*a*. Elongation stress resulted in very much less density and speed loss with the coating containing 1,5-pentanediol as is shown in the following table:

Additive	Percent Elongation	Relative Speed	Density [1]
Glycerin	0	100	1.00
	8	50	0.83
1,5-Pentanediol	0	100	1.00
	8	85	0.99

[1] At exposure which gave a density of 1.0 in the unstressed control strips.

The photographic emulsions used in practicing our invention are generally of the developing-out type; also, it is to be understood that photographic emulsions of varying halide content can advantageously be used.

The emulsions can also be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944 and U.S. 1,623,499, and Sheppard and Brigham U.S. Patent 2,410,689.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, all of which belong to group VIII of the periodic table of elements and have an atomic weight greater than 100. Representative compounds are

ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions can also be chemically sensitized with gold salts as described in Waller and Dodd U.S. Patent 2,399,083 or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856 and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850), polyamines such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925), or bis-(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926).

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, Carroll and Murray U.S. Patent 2,728,664, and Leubner and Murray U.S. Patent 2,728,665, the tetrazaindenes of Carroll U.S. Patent 2,716,062, and the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, Carroll and Allen U.S. Patent 2,288,-226, and Carroll and Spence U.S. Patent 2,334,864, and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162.

The plasticizing agents and other addenda which we have described may be used in various kinds of photographic emulsions. In addition to being useful in non-optically sensitized emulsions they may also be used in orthochromatic, panchromatic and X-ray emulsions. They may be added to the emulsion before or after any sensitizing dyes which 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 agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers.

The dispersing agent for the silver halide may be gelatin or other colloidal material such as collodion, albumin, cellulose derivatives or synthetic resins.

We claim:

1. An improved gelatin composition predominantly consisting of an aqueous solution of gelatin containing therein 5–25%, based on the weight of the gelatin, of a dihydroxy alkane which contains, except for the hydroxyl groups therein, only hydrogen and 4–7 carbon atoms, the hydroxyls of the dihydroxy alkane being separated by at least 3 of the carbon atoms.

2. An improved gelatin composition predominantly consisting of an aqueous solution of gelatin containing

therein 10–25%, based on the weight of the gelatin, of a dihydroxy alkane which contains, except for the hydroxyl groups therein, only hydrogen and 4–7 carbon atoms, the hydroxyls of the dihydroxy alkane being separated by at least 3 of the carbon atoms.

3. An improved gelatin composition predominantly consisting of an aqueous solution of gelatin which contains 5–25%, based on the weight of the gelatin, of 1,5-pentanediol.

4. An improved gelatin composition predominantly consisting of an aqueous solution of gelatin which contains 5–25%, based on the weight of the gelatin, of 1,4-butanediol.

5. An improved gelatin composition predominantly consisting of an aqueous solution of gelatin which contains 5–25%, based on the weight of the gelatin, of 1,6-hexanediol.

6. An improved gelatin composition predominantly consisting of an aqueous solution of gelatin which contains 5–25%, based on the weight of the gelatin, of 2-methyl-2,4-pentanediol.

7. A gelatin-silver halide photographic emulsion predominantly consisting of silver halide in an aqueous solution of gelatin containing 5–25%, based on the weight of the gelatin, of a dihydroxy alkane which contains, except for hydroxyl groups, only hydrogen and 4–7 carbon atoms, the hydroxyls of the dihydroxy alkane being separated by at least 3 of the carbon atoms.

8. A gelatin-sliver halide photographic emulsion predominanly consisting of a silver halide and an aqueous solution of gelatin containing 5–25%, based on the weight of the gelatin, of 1,5-pentanediol.

9. A gelatin-silver halide photographic emulsion predominantly consisting of a silver halide and an aqueous solution of gelatin containing 5–25%, based on the weight of the gelatin, of 1,4-butanediol.

10. A gelatin-silver halide photographic emulsion predominantly consisting of a silver halide and an aqueous solution of gelatin containing 5–25%, based on the weight of the gelatin, of 1,6-hexanediol.

11. A gelatin-silver halide photographic emulsion predominantly consisting of a silver halide and an aqueous solution of gelatin containing 5–25%, based of the weight of the gelatin, of 2-methyl-2,4-pentanediol.

References Cited in the file of this patent

UNITED STATES PATENTS

1,757,482	Seel	May 30, 1930
2,009,029	Sly	July 23, 1935
2,364,017	Baldsiefen	Nov. 28, 1944
2,441,389	Blake	May 8, 1948
2,477,742	Hall	Aug. 2, 1949
2,606,124	Schmutzler	Aug. 5, 1952
2,616,812	Kramskey et al.	Nov. 4, 1952
2,629,659	Mueller	Feb. 24, 1953
2,704,269	Tice	Mar. 15, 1955
2,870,062	Stanley et al.	Jan. 20, 1959

OTHER REFERENCES

Doolittle: The Technology of Solvents and Plasticizers, page 673, John Wiley & Sons, Publ. N.Y. (1954).