

1

3,201,252

GELATIN COMPOSITIONS CONTAINING SALTS OF HALF ESTERS OF SULFOSUCCINIC ACID AS COATING AIDS THEREFOR

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8 Claims. (Cl. 96—94)

This invention relates to gelatin compositions containing certain salts of half esters of sulfosuccinic acid as coating aids therein.

In the application of gelatin coatings in the preparation of photographic elements such as to film base or paper, either in the form of a single layer or as multi-layers coated simultaneously, the addition of a suitable coating aid permits the obtaining of dried coatings free of such coating defects as repellencies, pencil line streaks and the like. However, dried coatings involving the usual synthetic surfactants are characterized by surface slipperiness resulting in handling difficulties and/or inadequate rewettability. The latter introduces difficulties in the processing of photographic products. Surfactants or coating aids which cause coatings having good rewettability often give a gelatin layer with a slippery surface.

In order to take advantage of the superior coating properties of synthetic coating aids, especially in simultaneous multi-layer applications, it has been desirable to use these agents in combination with saponin to achieve both adequate surface roughness and satisfactory rewettability. However, saponin, being a naturally occurring substance of considerable variation from batch to batch, its use may cause an increase in fog, a change in photographic sensitivity or sometimes may not even improve the rewettability of the gelatin layer obtained. Because of these variations in the quality of saponin, it is desirable that the combination of characteristics desired be obtained by the use of a single synthetic coating aid rather than by a combination in which saponin is employed.

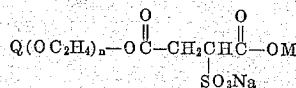
One object of our invention is to provide coating aids which when employed in gelatin coating compositions will give layers having adequate rewettability without any appreciable decrease of surface roughness. Another object of our invention is to provide gelatin coating compositions containing as coating aids therein alkali metal salts of half esters of sulfosuccinic acid in which the alcohol groups which esterify one carboxyl of the sulfosuccinic acid include highly branched chain alkyls. Other objects of our invention will appear herein.

We have found that gelatin compositions containing alkali metal salts of certain half esters of sulfosuccinic acid in which branched chain alkyl alcohol radicals satisfy one of the carboxyl groups of the sulfosuccinic acid give gelatin coatings having adequate rewettability without any appreciable drop in frictional characteristics. It is desirable that the coating aid be present in the gelatin composition in an amount of 0.5–10%, based on the weight of the gelatin. The gelatin compositions in accordance with our invention may be those which are used merely to coat multiple gelatin layers which contain no sensitized addenda or they may be gelatin-silver halide photographic emulsions. The gelatin compositions in accordance with our invention are particularly useful in the preparation of photographic elements, such as in coating

2

of film base or paper. It is particularly desirable in the forming of photographic paper products that the surfaces of the products have little or no slipperiness to facilitate handling thereof. It is desirable in general that the gelatin coatings have a coefficient of friction greater than 0.30 and a developer spread greater than 4.00 cm.² to give products which are satisfactory for actual use.

The coating aids in accordance with our invention are the sulfosuccinic acid ester salts having the formula:



in which n is 0 to 10, M is an alkali metal substituent and Q is either a branched-chain alkyl radical of 10–16 carbon atoms having at least 3 points of branching or



in which R' is a branched-chain alkyl radical of 8–14 carbon atoms having at least 2 points of branching. Examples of materials of this nature are the sodium salts of half esters of sulfosuccinic acid, having on one of the carboxyls a radical derived from p-tertoctylphenoxyethanol or its ethylene oxide derivatives and sodium salts of half esters of sulfosuccinic acid in which one of the carboxyls is esterified by tridecyl alcohol or its ethylene oxide derivatives. Tridecyl alcohol is a commercial material prepared from tetrapropylene by means of the oxo reaction and is a mixture of primary branched-chain C_{13} alcohols. Compounds of this nature may be prepared as follows:

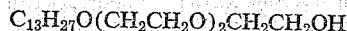
TRIDECOXYETHYLSULFOSUCCINATE (SODIUM SALT)

A mixture of 38.9 parts of maleic anhydride and 100 parts of tridecoxyethanol was heated on a steam bath with occasional stirring until a homogeneous product resulted. Heating was continued for an additional 5 hours, whereupon the adduct was poured into a well-stirred solution of 50 parts of sodium sulfite in 500 parts of water. A gelatinous mixture resulted. Complete solution was effected by heating his mixture on the steam bath for an hour with stirring. A solution of a compound having the formula



was obtained. The resulting solution can be diluted with water to any desired strength.

Derivatives from tridecoxydiethoxyethanol,



and from tridecoxypentaethoxyethanol,



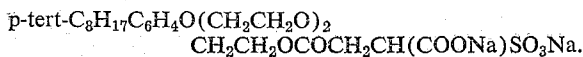
were prepared by similar procedures. Also tridecylalcohol itself gave solutions free from cloudiness when the anhydride and alcohol were heated together for but an hour before pouring into the sodium sulfite solution.

P-TERT-OCTYLPHENOXYDIETHOXYETHYL-SULFOSUCCINATE (SODIUM SALT)

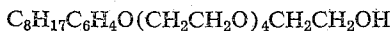
In preparing this product 134.2 parts of p-tert-octylphenoxydiethoxyethanol, 38.9 parts of maleic anhydride and 50 parts of sodium sulfite were used in accordance

3

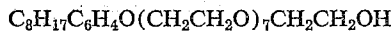
with the procedure described above. There was thus obtained a compound having the formula



p-Tert-octylphenoxytetraethoxyethanol, p-tert-



and p-tert-octylphenoxyheptaethoxyethanol, p-tert-



gave similar products by the same procedure. p-Tert-octylphenoxyethanol failed to give a clear solution, but precipitation of the product by pouring into acetone and washing by decantation with acetone gave a solid which redissolved to give a clear solution.

The various compounds prepared as described above and with varying proportions of ethylene oxide units (such as 1, 3, 5, 6, 7.5 and the like) were incorporated in gelatin compositions in various proportions. Coatings prepared from those compositions exhibited good developer spreads and coefficients of friction greater than 0.300. Developer spread is determined by measuring the area covered by 1 ml. of developer delivered in a standard manner to a flat, dried coating surface. A developer spread greater than 4 cm.² is considered adequate for developer wettability in photographic uses.

The following examples illustrate coating operations in accordance with our invention:

Example 1

There was simultaneously applied to paper a gelatin-silver halide photographic emulsion and a clear gelatin overcoat by means of the hopper technique as described in U. S. Patents No. 2,761,417, 2,761,418 and 2,761,791 of T. A. Russell. The surfactant used was disodium p-tert-octylphenoxyethylsulfosuccinate except in the control in which case no coating aid was employed. The various coated papers obtained were tested for developer spread and coefficient of friction and the following results were obtained:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
A.....	0.13	0.5	4.15	0.540
B.....	0.25	0.5	4.15	0.507
C.....	0.5	0.5	4.15	0.497
Control.....	None	None	3.14	0.540

Example 2

A coating method was carried out similar to that in the preceding example except that disodium p-tert-octylphenoxydiethoxyethylsulfosuccinate was used as the coating aid, except in the case of the control wherein no surfactant was employed. The proportions of coating aid used and the developer spreads and coefficients of friction obtained with the various papers were as follows:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
G.....	0.13	0.5	4.90	0.551
H.....	0.25	0.5	5.72	0.551
I.....	0.5	0.5	6.16	0.517
Control.....	None	None	3.80	0.660

Example 3

A coating procedure was carried out similar to that described in Example 1, except that the coating aid

4

used was sodium p-tert-octylphenoxytetraethoxyethylsulfosuccinate except in the case of the control wherein no coating aid was used. The proportions of surfactant employed in the emulsion layer and the overcoating layer and the developer spreads and coefficients of friction of the various papers were as follows:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
J.....	0.13	0.5	6.60	0.485
K.....	0.25	0.5	6.16	0.430
L.....	0.5	0.5	5.72	0.457
Control.....	None	None	3.14	0.574

Example 4

Paper was coated by a multi-layer coating technique as described in Example 1, except that the coating aid used in each case, except the control, was disodium p-tert-octylphenoxyethylsulfosuccinate. The proportions of coating aid employed in the various coatings and the developer spreads and coefficients of friction obtained in each were as follows:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
D.....	0.13	0.5	10.70	0.375
E.....	0.25	0.5	9.08	0.398
F.....	0.5	0.5	11.90	0.320
Control.....	None	None	3.45	0.606

Example 5

In a coating operation as described in Example 1 sodium tridecylsulfosuccinate was used as the coating aid in every case except in the control. The proportions of coating aid used and the developer spreads and coefficients of friction of the papers obtained were as follows:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
M.....	0.13	0.5	4.52	0.517
N.....	0.25	0.5	4.52	0.474
O.....	0.5	0.5	4.90	0.457
Control.....	None	None	3.14	0.540

Example 6

A coating procedure was carried out as described in Example 1 except that disodium tridecoxyethylsulfosuccinate was employed as the coating aid in every case except in the control. The proportions of coating aid employed and the developer spreads and coefficients of friction of the various photographic papers obtained were as follows:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
M'.....	0.13	0.5	4.52	0.517
N'.....	0.25	0.5	4.52	0.463
O'.....	0.5	0.5	4.90	0.419
Control.....	None	None	3.14	0.540

Example 7

The procedure of Example 1 was repeated except that disodium tridecyldiethoxyethyl sulfosuccinate was used as the coating aid. The proportions used and the developer spreads and coefficients of friction of the resulting papers were as follows:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
J'-----	0.13	0.5	4.90	0.419
K'-----	0.25	0.5	6.16	0.375
L'-----	0.5	0.5	7.55	0.343
Control-----	None	None	3.80	0.660

Example 8

The operation as described in Example 1 was repeated except that disodium tridecypentaethoxyethylsulfosuccinate was employed as the coating aid. The proportions of coating aid used and the developer spreads and coefficients of friction of the various papers resulting were as follows:

	Surfactant concentration		Developer spread (cm. ²)	Coefficient of friction
	Emulsion coat composition (g./lb.)	Overcoat composition (g./lb.)		
P-----	0.13	0.5	6.60	0.298
Q-----	0.25	0.5	7.70	0.276
R-----	0.5	0.5	8.04	0.276
Control-----	None	None	3.14	0.540

Example 9

A single-layer hopper coating was applied to film base by a conventional hopper technique using coating aid at the concentration of 0.22 g./lb. of wet coating melt. The coating aid used was sodium p-tert-octylphenoxyethylsulfosuccinate (I). The characteristics of the material obtained as compared with the control in which no coating aid was used were as follows:

Surfactant	Repellencies (25 ft. ²)	Mottle	Longitudinal Streaks
Control-----	4	Slight-----	Slight+.
I-----	3	Slight-----	Slight.

Example 10

A single-layer hopper coating was applied to film base by conventional hopper technique using coating aid at the concentration of 0.22 g./lb. of wet coating melt. The coating aid used was disodium p-tert-octylphenoxytetraethoxyethylsulfosuccinate (II). The characteristics of the material obtained as compared with the control in which no coating aid was used were as follows:

Surfactant	Repellencies (25 ft. ²)	Mottle	Longitudinal Streaks
Control-----	21	Slight-----	Very slight.
II-----	0	Very slight-----	Very slight.

Example 11

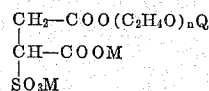
A single-layer hopper coating was applied to film base by conventional hopper technique using coating aid at the concentration of 0.22 g./lb. of wet coating melt. The coating aid used was sodium tridecoxyethylsulfosuccinate (III). The characteristics of the material obtained

as compared with the control in which coating aid was used were as follows:

Surfactant	Repellencies (25 ft. ²)	Mottle	Longitudinal Streaks
Control-----	4	Slight-----	Slight+.
III-----	0	Very slight-----	Slight+.

We claim:

1. A composition of matter comprising gelatin containing as a coating aid therein a compound having the formula

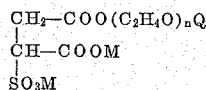


in which $n=0-10$, M is an alkali metal substituent and Q is a substituent selected from the group consisting of the branched-chain alkyl radicals of 10-16 carbon atoms with at least three points of branching and the alkaryl radicals,



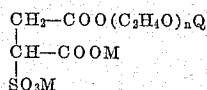
R' being a branched-chain alkyl radical of 8-14 carbon atoms with at least two points of branching.

2. A composition of matter comprising gelatin containing as a coating aid therein a compound having the formula



in which $n=0-10$, M is an alkali metal substituent and Q is a branched-chain alkyl radical of 10-16 carbon atoms with at least three points of branching.

3. A composition of matter comprising gelatin containing as a coating aid therein a compound having the formula



in which $n=0-10$, M is an alkali metal substituent and Q is an alkaryl,



R' being a branched-chain alkyl radical of 8-14 carbon atoms with at least two points of branching.

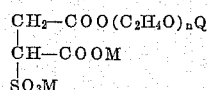
4. A composition of matter comprising gelatin containing as a coating aid therein alkali metal salt of tridecoxyethylsulfosuccinate.

5. A composition of matter comprising gelatin containing as a coating aid therein alkali metal salt of p-tert-octylphenoxydiethoxyethylsulfosuccinate.

6. A composition of matter comprising gelatin containing as a coating aid therein alkali metal salt of p-tert-octylphenoxytetraethoxyethylsulfosuccinate.

7. A composition of matter comprising gelatin containing as a coating aid therein an alkali metal salt of tridecypentaethoxyethylsulfosuccinate.

8. A gelatin-silver halide photographic emulsion containing as a coating aid therein a compound having the formula



in which $n=0-10$, M is an alkali metal substituent and Q is a substituent selected from the group consisting of the branched-chain alkyl radicals of 10-16 carbon atoms with at least three points of branching and the alkaryl radicals,



R' being a branched-chain alkyl radical of 8-14 carbon atoms with at least two points of branching.

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