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GELATIN COATING COMPOSITIONS

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5 Claims. (Cl. 96—94)

This invention relates to gelatin compositions containing as coating aids therein alkyl-aryl polyether compounds.

In the application of gelatin coatings to surfaces, particularly in the photographic industry, it is desirable to apply layers of gelatin compositions to surfaces, uniformly and at good production speeds. In many cases it is desirable to apply gelatin coatings over previous layers, either of gelatin or of some other material, the previous layers being either wet or dry.

In the coating of film or paper with a gelatin layer, such as of a photographic emulsion or some other gelatin composition, evenness of coating is desirable. When no coating aid is used, coating defects are evident, for example, the final product may show numerous crescent-shaped uncoated areas, i.e. repellency spots, about the size of a pin head with streaks running from the points of the crescent in a direction opposite to that of the coating. Often lightly coated areas of 5–10 mm. in diameter will appear.

When saponin, the conventional coating aid, is used in gelatin coating compositions, the layer obtained when dried is ordinarily a uniformly even coating, which can be rewet readily. Saponin, however, may vary markedly from batch to batch both in quality and composition. This may adversely affect a photographic emulsion containing it or it may result in little or no improvement in coating properties in the composition to which it is added.

A number of synthetic materials have been suggested as coating aids in gelatin compositions, but often these synthetic materials are deficient in one respect or another. For instance, a synthetic coating aid which may overcome repellency satisfactorily and produce uniform coatings of photographic paper emulsions by a hopper technique, may result in surfaces that cannot be rewet readily, so that the product tends to form "air bells" on the emulsion surface during processing in commercial processing machines. These difficult-to-rewet areas where the "air bells" form will manifest themselves as small undeveloped areas in the processed product. To overcome this disadvantage, saponin has been employed as an additive to the emulsion, but due to the desirability of finding substitutes for saponin, other materials are believed to be more useful in this connection.

In the manufacture of photographic film and paper, extreme surface smoothness of the gelatinous coating in the finished product is frequently disadvantageous while surface roughness is often a very desirable property. For instance, in the manufacture of sensitized paper when certain synthetic surfactants are used as coating aids the extreme smoothness of the surface of the product introduces a very serious handling problem due to the slippage of the sheets one over the other when they are stacked for cutting or any other purpose. In the case of photographic film, extreme smoothness of the surface of the final product may result from the type of drying conditions as well as from the surfactants used as coating aids. In many types of products this extreme smoothness has come to be associated with static and ferrotyping difficulties in certain products.

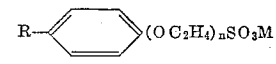
This invention has for an object to provide an improved coating aid for applying aqueous gelatin coatings to either wet or dry surfaces. Another object of our invention is to provide a coating aid for use in photosensitive gelatin

emulsions to facilitate the obtaining of coatings which are uniformly even and repellency-free without adversely affecting the emulsion. A further object of our invention is to supply coating aids which will result in gelatin layers which can be rewet readily. A still further object of our invention is to provide compositions of gelatin and certain synthetic chemical compounds having valuable characteristics as photographic layers. A still further object is to supply coating aids which have a tendency to maintain the surface friction of the coating while improving the rewettability characteristics. Other objects of our invention will appear herein.

We have found that certain polyether compounds are of value in gelatin compositions as coating aids and that these compounds will endow the dried surface of the gelatin coatings with susceptibility to rewetting when used as the coating aid either alone or with sodium maleopimarate. These coating aids have been found to impart valuable characteristics to gelatin compositions when incorporated therein in very small quantities such as in amounts of 0.01% based on the weight of the gelatin. Larger quantities of these compounds, however, can be used in gelatin compositions to impart good properties such as in proportions of from 0.01% to 0.1% or even up to 2% based on the weight of the gelatin.

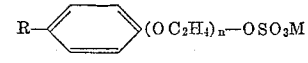
The compounds which we have found to be useful as coating aids are alkyl-aryl polyether compounds such as the following:

(1) The salts of alkyl aryl polyether sulfonates having the formula



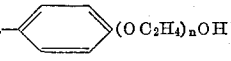
wherein R is an alkyl group containing 8–12 carbon atoms, M is alkali metal or ammonium and n is an integer within the range of 1–10.

(2) The salts of alkyl aryl polyether sulfates having the formula



where R is an alkyl group containing 8–12 carbon atoms, and M is alkali metal or ammonium, and n is an integer within the range of 1–10.

(3) Alkyl aryl polyether alcohols having the formula



where R is an alkyl group containing 8–12 carbon atoms and n is an integer within the range of 5–13.

The methods for making the alkylaryl polyether compounds in general are described in "Surface Active Agents," by A. M. Schwartz and J. W. Perry, 1, 79 and 108 (1949). The preparation of the polyethoxyethanols are described on page 202 of this book.

In the above formulas, the groups represented by R may be either branched or straight chain alkyls. Instead of alkali metals or ammonium in the formulas given, M may be some other cation such as a substituted ammonium radical in which one or more substituents is a short chain alkyl such as CH_3 or C_2H_5 or hydroxyethyl.

Our invention relates to coating a support with a gelatin coating composition, either as an aqueous solution of gelatin or as a photographic emulsion which ordinarily is composed of an aqueous solution of gelatin containing as the light sensitive material therein, a silver halide such as silver bromide, silver chloride, silver iodide, or their mixture. The emulsion may contain other added materials such as sensitizing dyes, hardeners, or the like. Descriptions of photographic emulsions are found in various places in the prior art such as in "Fundamentals of Photographic Theory" by James and Higgins; John Wiley and Sons, 1948, chapter 2.

The following examples illustrate the use of these coating aids either alone or with sodium maleopimarate in applying gelatin layers to supports therefor. The spread values given were obtained by measuring the areas covered by 1 ml. of Kodak Developer D–72 on a flat dried surface. Good rewettability is indicated if the spread value is at least 4. The coefficient of friction indicates smoothness, the higher the coefficient of friction, the less smooth the surface. Repellency refers to the number of uncoated spots in 5 square feet.

Example 1

There was added to a gelatin silver halide photographic emulsion the sodium salt of p-tertiary octylphenoxyethoxyethyl sulfonate as prepared by the reaction of p-tertiary octylphenol with β,β′-dichloroethylether followed by mixture with sodium sulfite, the latter referred to herein as Triton X–200. This composition was coated on a paper support and was compared with a coating in which no coating aid was used. The results obtained when using Triton X–200 alone and mixed with sodium maleopimarate (SMP) were as follows:

Surfactant	Surfactant conc., gm./lb. Emulsion		Repellencies in 5 sq. ft.	Spread Value	Coefficient Of Friction
Control			10+	3.1	.430
Triton X-200		0.5	0	7.1	.387
SMP+Triton X200	4:1	0.5	1	6.6	.398
SMP+Triton X200	9:1	0.5	0	4.2	.387
SMP+Triton X200	19:1	0.5	0	3.8	.463

Example 2

The coating aid employed in a gelatin silver halide emulsion composition and coated onto a paper support, as in Example 1, was the sodium salt of a p-tert.-octylphenoxypolyether sulfate, known commercially as Triton X–301. These coatings were compared with a coating of a control containing no coating aid (in which no coating aid has been incorporated). Also used as coating aids were mixtures of Triton X-301 and sodium maleopimarate.

Surfactant	Surfactant conc., gm./lb. Emulsion		Repellencies in 5 sq. ft.	Spread Value	Coefficient Of Friction
Control			10+	3.1	0.430
Triton X-301		0.5	0	6.6	0.343
SMP+Triton X301	4:1	0.5	0	4.2	0.343
SMP+Triton X301	9:1	0.5	0	3.8	0.387
SMP+Triton X301	19:1	0.5	0	3.8	0.419

Example 3

Coatings were applied in the same manner as described in Example 1 except that as the coating aid, tertiary octylphenoxypolyether alcohol, designated OPE5, was used in conjunction with sodium maleopimarate as the coating aid.

Surfactant	Surfactant conc., gm./lb. of Emulsion		Repellencies in 5 sq. ft.	Spread Value	Coefficient Of Friction
Control			0	3.1	0.354
SMP+OPE5	4:1	0.5	4	5.3	0.276
SMP+OPE5	9:1	0.5	1	4.5	0.320
SMP+OPE5	19:1	0.5	1	4.2	0.309

The increased repellency noted with the use of the combination of SMP and a coating aid as shown in Example 3 above may be caused by the interaction of emulsion addenda in certain photographic emulsions with the coating aid, resulting in not only decreasing the effective concentration of the coating aid, but also forming products which cause repellency. This repellency may even be a function of the concentration of the coating aid. However, it will be seen from the above-mentioned examples that the rewettability of the coatings is improved by these coating aid mixtures without seriously affecting the smoothness or slipperiness of the coating surface, especially where such a surface, in certain instances as mentioned previously, is advantageous.

The coating aids described herein either alone or in admixture with other coating aids, particularly sodium maleopimarate, are useful in various coating operations. When used in admixture with other coating aids even a very minor proportion of coating aid in accordance with our invention will exert a favorable effect. However, for best results, it is desirable that the coating aid in accordance with our invention constitute at least 10% of the total coating aid employed.

The coating procedure outlined may comprise any of the standard procedures employed in the industry. As an instance of such procedure paper base to be coated is passed through a trough or other reservoir whereby a coating is applied to the paper base. The coating is applied in greater thickness than desired and the surface is then subjected to the action of some leveling means such as a doctor blade or an air brush which causes run back of the coating composition and results in an even surface. In some cases it may be desirable to apply several coatings simultaneously in the manner described in U.S. Patent No. 2,761,791 of T. A. Russell or in the coating operations described in U.S. Patents 2,761,417, 2,761,418 and 2,761,419. In some cases the coating method may involve a hopper technique in which the thickness of the layer is regulated by the rate at which the coating composition is deposited upon the base which is moved along adjacent thereto.

In the use of the gelatin coating compositions in accordance with our invention if a film base is to be coated, it may be composed of any of the usual conventional film base materials. This may be a sheet of cellulose nitrate or of an organic acid ester of cellulose. It is often desirable first to apply a subbing layer to the cellulose ester base to facilitate adhesion of the photographic emulsion thereto, this practice of subbing being well known in the art. As for photographic paper a description thereof is found in Kodak Data Book 5th edition, "Kodak Papers," pages 3 and 4. A base material of the type described there would preferably be employed for preparing photographic paper in accordance with the present invention.

Not only are the coating aids of our invention and their mixtures with other coating aids useful in gelatin overcoating compositions, but they are also useful in various other types of coating compositions in which gelatin is an important constituent. For instance, these coating aids are useful in gelatin photographic emulsions, not only those which are nonoptically sensitized, but also in orthochromatic, panchromatic and X-ray emulsions, either before or after the addition of any sensitizing dyes or sensitizer or other addenda. This also includes gelatin emulsions intended for color photography such as those containing color forming couplers. Coating aids in accordance with our invention are also useful in gelatin coating compositions to be applied, for example, as antihalation layers, antistatic layers, filter layers, or in any type of gelatin layer which is coated from a composition consisting essentially of an aqueous solution of gelatin.

The emulsions can 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; Sheppard and Punnett U.S. Patent 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. 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 an 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, Collins, 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 optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301; 1,846,302; and 1,942,-854; White U.S. Patent 1,990,507; Brooker and White U.S. Patents 2,112,140; 2,165,338; 2,493,747; and 2,739,-964; Brooker and Keyes U.S. Patent 2,493,748; Sprague U.S. Patents 2,503,776 and 2,519,001; Heseltine and Brooker U.S. Patent 2,666,761; Heseltine U.S. Patent 2,734,900; Van Lare U.S. Patent 2,739,149; and Kodak Limited British Patent 450,958.

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 triazoles of Heimbach and Kelly U.S. Patent 2,444,608; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,-605 and 2,444,606; Heimbach U.S. Patents 2,444,607 and 2,450,397; Heimbach and Clark U.S. Patent 2,444,609; Allen and Reynolds U.S. Patents 2,713,541 and 2,743,181; Carroll and Beach U.S. Patent 2,716,062; Allen and Beilfuss U.S. Patent 2,735,769; Reynolds and Sagal U.S. Patent 2,756,147; Allen and Sagura U.S. Patent 2,772,164, and those disclosed by Birr in the Z. Wiss. Phot., 47, 2 (1952); the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038; and the zinc and cadmium salts of Jones U.S. patent application Serial No. 493,047.

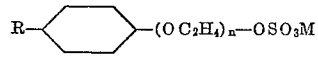
The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623; Carroll and Allen U.S. Patent 2,288,-226; and Carroll and Spence U.S. Patent 2,334,864; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in U.S. application Serial No. 588,951, of Milton and Murray; an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in U.S. application Serial No. 662,564 of Milton; bis-(ethoxy diethylene glycol) succinate as described in U.S. application Serial No. 604,333 of Gray or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in U.S. application Serial No. 311,319 of Tong. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in U.S. Patent 2,080,019 of White; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2) - 7 - octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene - 1,5 - disulfonyl chloride as described in U.S. Patents 2,725,294 and 2,725,295 of Allen and Carroll; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in U.S. Patent 2,725,305 of Allen and Byers; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonoxy)-ethane as described in U.S. Patent 2,726,162 of Allen and Laakso; 1,3-dihydroxymethylbenzimidazole-2-one as described in U.S. Patent 2,732,316 of July, Knott and Pollak; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in U.S. application Serial No. 599,891 of Allen and Webster; or 2,3-dihydroxy dioxane as described in U.S. application Serial No. 624,968 of Jeffreys.

We claim:

1. A composition of matter comprising gelatin containing 0.01–2% by weight, based on the gelatin, of salt of the formula



wherein R is alkyl of 8–12 carbon atoms, M is selected from the group consisting of alkali metal and ammonium and *n* is an integer within the range of 1–10.

2. A gelatin composition containing therein as a coating aid the sodium salt of a p-tertiary octylphenoxyethoxyethyl sulfate.

3. A gelatin-silver halide photographic emulsion containing therein as a coating aid the sodium salt of p-tertiary octylphenoxyethoxyethyl sulfate.

4. A composition comprising gelatin containing therein as a coating aid a mixture of the sodium salt of p-tertiary octylphenoxyethoxyethyl sulfonate and sodium maleopimarate.

5. A composition comprising gelatin containing therein as a coating aid a mixture of the sodium salt of p-tertiary octylphenoxyethoxyethyl sulfate and sodium maleopimarate.

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2,752,246	Weaver	June 26, 1956
2,823,123	Knox et al.	Feb. 11, 1958

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Schwartz and Perry: Surface Acting Agent, vol. II (1958), pp. 732–3, Interscience Co. Publishers, New York.