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(54) **Glycoside surfactants as coating aids for photographic layers.**

(57) Photographic material having one or more layers with improved thickness uniformity conferred by the addition of a long chain alkyl glycoside surfactant, and one or more auxiliary anionic or nonionic surfactants.

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This invention relates to surfactants as coating aids for gelatin coating solutions, particularly to such solutions used for photographic purposes. This invention also relates to the use of long chain alkyl glycosides as coating aid surfactants for such solutions.

In the preparation of a photographic material, it is usual to coat a support with one or more layers comprising an aqueous solution of a hydrophilic colloid binder, e.g. gelatin. Such layers include, for example, silver halide emulsion layers, intermediate layers, antihalation layers, filter layers, antistatic layers and protective layers. For multilayer materials, the layers may be coated simultaneously on conventional photographic supports as described in U.S. Pat. Nos. 2,761,791 and 3,508,947.

There are two primary methods for coating photographic materials. One is the bead coating process; see U.S. 2,681,294, 2,761,417, and 4,525,392. These references illustrate applying multiple layers of photographic materials using the bead coating method, and also illustrate apparatus for carrying out the method. The second primary method is the curtain coating process. U.S. 3,632,372 and 4,569,863 illustrate coating and apparatus for conducting the Process.

In producing the thin hydrophilic colloid layers of such photographic materials, it is required that coating solutions be coated uniformly without the formation of repellency spots or craters, also referred to as repellencies. A repellency is a round, oval-shaped or comet-shaped indentation or crater, or a vestige of such a disturbance which has partially healed after formation. Imperfections of this type are present in the layer being coated, if one layer is coated, or in one or more layers, if more of than one layer is coated simultaneously. Repellencies are formed during the coating process, or shortly thereafter, that is, when the solution of gelatin (or other hydrophilic colloid) in the coating is still fluid or mobile. Repellencies are usually produced by the presence of small particles or droplets of insoluble materials in the form of addenda, impurities or contaminants which are (i) in contact with the uppermost liquid-air interface of the coated layer(s) and (ii) have surface activity, that is, they are capable of reducing the surface tension of the liquid-air interface in isolated areas during the coating process.

Solutions coated in the preparation of photographic materials often contain dispersed, insoluble photographic addenda, which might include organic solvents, or addenda to alter certain physical properties, which might include lubricants and impurities in the lubricants, each of which may be capable of imparting repellencies to the coated layer(s). Even photographic gelatin may contain insoluble residues of naturally-occurring animal fats and fatty acids which are capable of imparting repellencies to the coated layer(s). Also, surface active contaminants may originate from external sources during the preparation of the coating composition or during coating. For example, the layer(s) being coated, or immediately after coating, may be unintentionally showered by droplets of lubricating oils used in the apparatus.

In the application of gelatin coating compositions to a support such as film base or paper, it is desirable to have a coating aid surfactant present in the coating composition, in order to facilitate application of the coating to the surface being coated. In this context, the compound or compounds used as coating aid surfactants in this invention are compounds which are effective in reducing the surface tension of the hydrophilic colloid-containing coating composition, e.g. a gelatin-containing coating composition. The presence of a coating aid surfactant, in the coating or coatings, assists in obtaining layers which, when dry, are of uniform or substantially uniform thickness,and are free, or substantially free, of imperfections such as repellencies.

Over the years, many compositions have been suggested for use as coating aids. In this regard, reference is made to section XI of Research Disclosure, Issue **308**, (December 1989), pp.993-1015. However there are relatively few water soluble surfactants that have achieved wide spread use as coating aids, since any surfactants of this type are not very effective in controlling imperfections such as repellencies, or have undesirable photographic properties, and very few of these preferred surfactants have nonionic structures.

One category of nonionic saccharidic coating aid surfactants described in the prior art comprises long-chain alkyl ethers, esters, and urethane of sucrose, where sucrose is the hydrophilic group of the surfactant molecule. In U.S. 3,507,660, Nishio, et al. describe long-chain alkyl ethers and urethanes of sucrose as coating aid surfactants of photographic materials. In U.S. 3,516,833, Haage, et al. describe long-chain alkyl esters of sucrose as coating aid surfactants. In U.S. 3,220,847, Knox describes the half esters of sucrose and alkyl succinic acids as coating aid surfactants, and in U.S. 3,564,576, Knox describes long chain alkyl esters of sucrose in combination with sodium maleopimarate as mixtures of surfactants with good coating aid properties.

Surfactants of the type disclosed in this invention are among the materials taught as useful with compositions comprising couplers in a fine state of subdivision; U.S. 5,013,140.

The use of these prior art compositions as coating aids has been limited by their limited water solubility, by their limited solubility in gelatin containing solutions, or by their limited ability to minimize repellency formation.

Thus a need exists for a new nonionic surfactant having increased solubility properties in gelatin/water solutions over the prior art materials.

This invention provides a composition of matter comprising (i) gelatin (or other hydrophilic colloid) in water, and (ii) as a coating aid surfactant, a glycoside having the formula

$$C_nH_{2n+1}\text{-}O\text{-}(C_6H_{10}O_5)_x\text{-}H, \qquad (I)$$

wherein the group within the parentheses represents a unit of glucose, n represents mean values of 9, up to about 16, and x is a distribution with a mean value greater than 1 and less than 2, and (iii) an auxiliary anionic or nonionic surfactant in sufficient amount to completely dissolve or substantially completely dissolve the glycoside in the composition.

In a highly preferred embodiment, the above composition comprises a top layer of a simultaneously coated multilayer pack of a photographic material coated by bead coating methods. In another embodiment, the above composition comprises a top layer and/or a bottom layer of a simultaneously coated multilayer pack of a photographic material coated by curtain coating methods. For the purpose of this invention, a "top" layer of a simultaneously coated multilayer pack, that is, a pack of two or more layers coated together, is defined as the layer farthest from the web. Similarly, the "bottom" layer of a simultaneously coated multilayer pack is defined as the layer closest to the web. The term "web" refers to a continuous length of prepared film base or paper base and can include previously coated and dried layers, such as emulsion layers or antihalation layers. In another embodiment, the above composition comprises a single layer, coated alone, of a photographic material.

In the embodiments described in the paragraph immediately above, the layer having the coating aid surfactant of formula (I) may also contain a silver halide and/or other image forming material, or, alternatively, it may not contain image forming materials. The layer having the above composition can be a protective overcoat layer of one or more image forming layers coated on one or both sides of the web, for example, either a color or black-and-white film or paper product. Alternatively, the layer having the above composition can be a protective overcoat layer of a pelloid backing coating of a color or black-and-white film product. An overcoat layer may contain other ingredients commonly present in such layers, and known in the art. Alternatively, the layer having the above composition can be a layer other than the overcoat layer of a multilayer color photographic material, such as a nonimage forming layer located between image forming layers, resulting from the stepwise application of two or more separate multilayer packs in the process of manufacturing a photographic material with a large number of individual layers.

The glycoside surfactants employed in this invention are useful as coating aids in such gelatin-containing layers for photographic materials, because they confer improved thickness uniformity, i.e., fewer repellency spot imperfections in the layers.

This invention is a substantial improvement in the art. Glycoside surfactants of the type employed in this invention are readily available; hence this invention is readily adaptable by industry.

In this invention the glycoside surfactants are used as coating aid surfactants which are effective in reducing the surface tensions of gelatin-containing coating compositions. The reduction in the surface tension of gelatin solution by the addition of the glycoside surfactants can be demonstrated by laboratory measurements of surface tensions using the Wilhelmy plate technique. The surface tension of a solution of nondeionized, lime derived bone gelatin (70 grams per liter) in a glass beaker at a temperature of 110°F (43°C) is 40-42 dynes/cm, and after adding glycoside surfactant APG 325 at 1.0 gram per liter is 28 dynes/cm.

This invention provides a composition comprising from 2.5 weight percent to 20 weight percent of gelatin in water and from 0.01 to 0.50 of the coating aid surfactant having formula (I) as above described, and preferably from about 5 to about 12 weight percent gelatin in water, and from about 0.05 to about 0.3 weight percent of the coating aid surfactant. Thus, the compositions of this invention provide one or more layers of a photographic material.

In another preferred aspect, this invention provides a photographic material, e.g. a film or paper, having at least one layer comprising a dried layer formed from a coat or melt having the above composition.

This invention can be used with any gelatin that is employed in photographic products, including bovine bone gelatin derived by treatment with base, e.g. lime. However, the invention is not limited to such a gelatin. In this regard, the utility of the invention is demonstrated below in a composition based on acid derived porcine skin gelatin. This type of gelatin generally gives rise to a more frequent occurrence of repellencies than the above-mentioned bovine gelatin.

As indicated above, it is to be understood that this invention is not limited to compositions that contain gelatin. Thus this invention can be extended to use of the aforementioned coating aids with compositions containing other suitable hydrophilic colloids made from natural or synthetic substances. Naturally including substances include materials such as proteins, protein derivatives, cellulose derivatives e.g. cellulose esters, polysaccharides e.g. dextran, gum arabic, zein, casein and pectin, collagen derivatives, agar-agar, arrowroot and albumin. Examples of suitable synthetic hydrophilic colloids include polyvinyl alcohol, acrylamide polymers, maleic acid copolymers, acrylic acid copolymers, methacrylic acid copolymers and polyalkylene oxides.

The gelatin in the compositions of this invention can optionally be hardened by any hardener that is known

in the art. Hardeners and their use are described in Section X of Research Disclosure, *supra*. It is to be understood that the presence or absence of a hardener is not a critical feature of this invention.

The compositions of this invention comprise a hydrophilic colloid such as gelatin in water. Typically the gelatin concentration in a coating composition to be applied to paper or a film-base support is from about 2.5 to about 20 weight percent gelatin. Top layer coating compositions of this invention preferably have from about 5 to about 12 weight percent gelatin.

In addition to hardeners and/or the reaction product of the gelatin and the hardener, the compositions of this invention may contain other photographic chemicals of the usual types found in photographic layers. For example, the top layers within one of the preferred embodiments of this invention may contain antistatic agents, matting agents, plasticizers, lubricants, and other materials that are not involved in image formation. For examples of matting agents, see Section XVI of the Research Disclosure, *supra*, for antistatic materials, Section XIII, and pasticizers and lubricants, Section XII.

As described above, a glycoside surfactant of the type described above is used as a coating aid in the formation of a hydrophilic colloid layer. Preferably, the coating aid surfactant is used in an amount from 0.01 to 0.50, more preferably from 0.05 to 0.30, weight percent based on the weight of the hydrophilic colloid coating composition. The range of concentration within which the coating aid is used depends on the source of repellency. It also depends on whether other surface active agents in addition to the auxiliary surfactant are present.

Preferred glycosides for use in this invention, and within the above general formula, are manufactured by the Henkel Corporation and sold as APG Glycosides. Such glycosides are described in Henkel technical bulletins. Preferred APG Glycosides are APG 225, APG 300, and APG 325 Glycosides.

The glycoside coating aid surfactants is used with an auxiliary surfactant to increase the solubility of the glycoside surfactant in the composition. Thus for example, in compositions in which gelatin is the hydrophilic colloid the glycoside is admixed with an auxiliary nonionic or anionic surfactant. Example of such auxiliary surfactants are nonionic long-chain alkyl (6-18 carbons) aryl polyglycidol (5-20) ethers, and representative anionic surfactants are alkyl sulfates, alkyl sulfonates, alkyl aryl sulfonates, alkyl polyethoxy sulfates, alkyl aryl polyethoxy sulfates, and alkyl aryl polyethoxy sulfonates, containing 6-18 carbons in their alkyl groups.

In general, the amount of the auxiliary surfactant is about 25 to 200 percent by weight based on the weight of the glycoside coating aid surfactant.

Photographic elements according to the invention generally comprise at least one light-sensitive layer, such as a silver halide emulsion layer. This layer may be sensitized to a particular spectrum of radiation with, for example, a sensitizing dye, as is known in the art. Additional light-sensitive layers may be sensitized to other portions of the spectrum. The light-sensitive layers may contain or have associated therewith dye-forming compounds or couplers. For example, a red-sensitive emulsion would generally have a cyan coupler associated therewith, a green-sensitive emulsion would be associated with a magenta coupler, and a blue-sensitive emulsion would be associated with a yellow coupler. Other layers and addenda, such as antistatic compositions, subbing layers, surfactants, filter dyes, protective layers, barrier layers, development inhibiting releasing compounds, and the like can be present in photographic elements of the invention, as is well-known in the art. Detailed description of photographic elements and their various layers and addenda can be found in *Research Disclosure* 17643 Infra, and in James, *The Theory of the Phonographic Process*, 4th, 1977.

The gelatin-containing layer of this and other layers in the element may be coated by any of the known coating methods, such as curtain coating, roller coating, bead coating, doctor blade coating, dip and air knife coating, and the like. The layer is generally dried by simple evaporation, which may be accelerated by known techniques such as convection heating. Known coating and drying methods are described in more detail *Research Disclosure* 17643, December, 1978. To demonstrate the advantage of the coating aids of this invention over prior art surfactants, coatings of gelatin solutions were made on a narrow width coating machine and the coatings were visually examined for comparisons of uniformity of layer thicknesses. For the purposes of the following example, a variety of gelatin which has a high propensity for forming repellency spots was used in the top layer. Coatings made without any coating aid surfactant in the top layer had a large number of repellency spots, and repellency spots were also observed in coatings containing APG 300 or 325 alone or the comparison compound sucrose laurate atone in the top layer solution. But when the mixtures of APG 300 or 325 and nonionic auxiliary surfactant were added to the top layer, the resulting coatings had fewer repellency spots than the coatings made with sucrose laurate alone or combined with the nonionic auxiliary surfactant or with sodium maleopimerate. Experimental details are set forth below.

Example 1

A simultaneous 3-layer coating was made with a conventional, multi-slide, bead coating hopper onto subbed polyester film support at a coating speed of 90 meters per minute. A solution of acid-derived photographic

grade pigskin gelatin (100 grams per liter of solution) was prepared for the top layer. The middle layer consisted of a solution of time-derived bone gelatin to which dispersed carbon particles were also added to provide an optical density in the middle layer of about 1.0, to allow the observation of layer thickness uniformity by visual examination. The bottom layer consisted of a solution of lime-processed bone gelatin without any carbon added. Repellency spots forming in the top layer during the coating process also disturbed the middle layer (containing the carbon) and were observed by visual inspection and counted according to number and size per unit area. Spots were counted in two categories, large enough to see without magnification and small enough that 7x magnification was required. The results comparing various surfactants are shown in Table I. Without surfactant in the top layer solution, the coatings had a large number of repellency spots in both size categories. Coatings made with APG 300 (0.1 percent) or APG 325 (0.1 percent) alone or with the comparison compound sucrose laurate (0.1 percent) alone in the top layer solution also had large numbers of repellency spots. Although the numbers of repellency spots were much lower in coatings containing 0.1 or 0.2 percent of Surfactant 10G (used in other coatings as an auxiliary surfactant) alone, the coatings containing the fewest repellency spots of all the conditions shown were those containing mixtures of APG 300 (0.1 percent) and Surfactant 10G (0.08 or 0.16 percent) as an auxiliary surfactant or mixtures of APG 325 (0.1 percent) and Surfactant 10G (0.08 or 0.16 percent) as an auxiliary surfactant. The mixtures of the glycoside coating aid surfactants of this invention and a nonionic auxiliary surfactant were much more effective in preventing the formation of repellency spots in coating than the representative prior art surfactant alone or in mixtures with sodium maleopimarate or with Surfactant 10G.

Materials used in this example are described as follows:

(C) Sucrose monolaurate, representative comparison compound (prior art, U.S. 3,516.833); material used was GRILLOTEN LSE 65, R.I.T.A. Corporation, P.O. Box 585, Woodstock, IL, 60098.

(A1) APG 300 glycoside compound where n = mixture of 9, 10, and 11, and $\overline{x} \simeq 1.4$ in formula (I) (Henkel product literature).

(A2) APG 325 glycoside compound where n = mixture of 9, 10, and 11, and $\overline{x} \simeq 1.6$ in formula (I) (Henkel product literature).

(B1) Surfactant 10G from Olin Corporation is a mixture of nonyl phenoxy polyglycidol (5-14) ethers.

(B2) Sodium maleopimarate (used in mixture in the prior art, U.S. 3,564,576) is a compound prepared by reacting maleic anhydride with pimaric acid and neutralizing with sodium hydroxide.

TABLE I

Surfactant (first)[1]		Surfactant (second)[1]		Repellency spots, number observed	
compound	conc. wt. %	compound	conc. wt. %	w/o mag[2]	magnified 7x[3]
none	---	none	---	220	1800
A1	0.1, 0.2	none	---	VH[4]	VH
A2	0.1, 0.2	none	---	VH	VH
C	0.1, 0.2	none	---	VH	VH
B1	0.1	none	---	19	600
B1	0.2	none	---	10	700
A1	0.1	B1	0.08	8	3
A1	0.1	B1	0.16	0	6
A2	0.1	B1	0.08	0	11
A2	0.1	B1	0.16	1	21
C	0.1	B1	0.05	VH	VH
C	0.1	B1	0.12	7000	VH
C	0.1	B1	0.22	9000	VH
C	0.1	B2	0.1	1800	1900
C	0.1	B2	0.2	1100	760

key:

1 in top layer solution, wt. % based on solution wt.

2 in area 0.46 m^2 of coating

3 in area 310 cm^2 of coating

4 VH = very high number

Claims

1. A composition characterized in that it comprises (i) gelatin in water, (ii) a coating aid surfactant having the formula:

$$C_nH_{2n+1}\text{-}O\text{-}(C_6H_{10}O_5)_x\text{-}H$$

wherein $C_6H_{10}O_5$ represents a glucose unit, n represents mean values of 9 to about 16, and x is a distribution with mean values greater than 1 and less than two, and (iii) an auxiliary nonionic or anionic surfactant in an amount sufficient to dissolve completely said coating aid surfactant in said composition.

2. A composition of Claim 1, characterized in that it comprises from 2.5 to 20 weight percent gelatin, based on gelatin in water and from 0.01 to 0.5 weight percent of the coating aid surfactant, based on the solution weight.

3. A composition of Claim 1 characterized in that the amount of said auxiliary surfactant is from about 25 to about 200 percent by weight based on the weight of said coating aid surfactant.

4. A photographic material characterized in that a support having thereon at least one layer comprising a dried coating composition of Claim 1.

5. A method for preparation of a photographic material, said method characterized in that coating a layer having the composition of Claim 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 42 0480

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	US-A-3 507 660 (FUJI FILM) 21 April 1970 * whole document *	1-5	G03C1/38
A	PATENT ABSTRACTS OF JAPAN vol. 4, no. 149 (P-032)21 October 1980 & JP-A-55 098 746 (MITSUBISHI PAPER MILLS LTD) 28 July 1980 * abstract *	1-5	
P,A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 323 (P-1386)15 July 1992 & JP-A-4 095 948 (KONICA CORP.) 27 March 1992 * abstract *	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	04 MARCH 1993	GUILLEMOIS F.S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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