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SURFACE-ACTIVE COMPOUNDS USED AS COATING AIDS IN FILM-FORMING COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Coating compositions including a hydrophilic colloid and at least one compound of the formula:

$$R(—OCH_2CH_2)_m—X—A—SO_3M$$

wherein:

M stands for hydrogen, an alkali metal atom, ammonium or organic ammonium,
X stands for oxygen or sulphur,
A stands for alkylene comprising at least 3 C-atoms or for aralkylene,
R stands for a branched-chain aliphatic group of 10 to 20 carbon atoms, and
m stands for 0 to 30,

are described. The coating compositions are particularly useful in the formation of photographic silver halide materials and the layers coated therefrom do not exhibit hydrophobic areas leading to repellency spots or comets.

This invention relates to surface active compounds suitable for use as coating aids for film-forming coating compositions comprising a hydrophilic colloid, and to hydrophilic colloid compositions comprising said coating aids.

In the application of film-forming coating compositions comprising a hydrophilic colloid to surfaces, particularly in the photographic industry, it is desirable to apply such coating compositions uniformly and at good production speeds. In many cases it is even desirable to apply such coatings over other previous layers, which are either wet or dry.

It is necessary, in the photographic industry, that colloid compositions ready for coating are entirely hydrophilic in order to obtain a uniform layer therewith comprising no hydrophobic inclusions leading to repellency spots or comets in the said layer. Moreover, the entire surface of a layer formed from such colloid compositions should be hydrophilic so that said layer can be rewet readily either by the processing solutions if said layer is the top layer of a photographic material to be processed, or by the coating composition which will be applied to said layer for forming a next layer. Indeed, during processing, air-bubbles are more easily carried along by a hydrophobic surface than by a hydrophilic surface, which air-bubbles will manifest themselves as small undeveloped areas in the processed material; moreover, when the material comprises hydrophobic inclusions whereby its surface is not entirely hydrophilic but shows hydrophobic areas, water will not uniformly wet the said surface in that it is repelled on the hydrophobic areas and form drops thereon and therefore, after processing such like materials cannot be uniformly dried and show a poor retouchability when it is desired to retouch such like materials.

In the case wherein the layer formed from the said colloid composition is overcoated with a following layer, the maximum speed of the moving layer to be overcoated

at which no repellency occurs can be increased when and to the extent that the surface to be overcoated is more hydrophilic; local hydrophobic areas at the surface of the layer to be overcoated can give rise to the formation of so-called repellency spots or comets in the said next layer.

Thus, in order to eliminate all these possible coating defects such as air bubbles, repellency spots or "comets" the use of coating aids has been widely adopted.

Saponin in conventionally used as coating aid for coating compositions comprising hydrophilic colloids. Though this product excels by its favorable "anticomet" action, it may vary markedly from batch to batch and is much more expensive than synthetic coating aids.

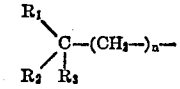
A number of synthetic surface active agents has been proposed for use as coating aids in order to improve coating of compositions comprising hydrophilic colloids more particularly gelatin layers. However, most of these coating aids, while improving some properties of the layer, also adversely affect other desired properties. For instance, hydrophilic colloid layers comprising coating aids, which prevent the formation of "comets" in the said layers, may have an inadequate rewettability which causes difficulties in the processing of photographic elements or it may be difficult to overcoat such layers when in wet state which is quite undesirable especially in simultaneous multilayer applications. In order to overcome these disadvantages it has been proposed to use mixtures of coating aids having different properties.

It has now been found that surface active compounds corresponding to the following general formula:

$$R—(OCH_2CH_2)_m—X—A—SO_3M$$

wherein:

M stands for hydrogen, an alkali metal atom such as lithium, sodium and potassium, ammonium or organic ammonium e.g. diethanol ammonium, triethanol, ammonium, triethyl ammonium and morpholinium,
X stands for oxygen or sulphur,
A stands for alkylene comprising at least 3 C-atoms, preferably a tri- or tetramethylene group, which may be substituted e.g. by hydroxyl or alkyl or for aralkylene,
R stands for a branched-chain aliphatic group of 10 to 20 carbon atoms, preferably an aliphatic group of the formula



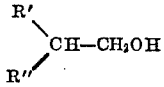
wherein *n* is 0 or 1, R_3 stands for hydrogen, or when $n=1$ may be alkyl such as methyl and each of R_1 and R_2 stands for a straight-chain or branched-chain alkyl group or together represent the atoms necessary to close an alicyclic ring structure, and
m stands for 0 to 30,

are excellent inexpensive coating aids for use in coating compositions comprising a hydrophilic film-forming colloid such as gelatin.

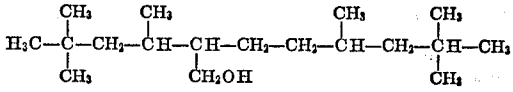
The surface-active compounds according to the invention and corresponding to the above general formula can be very easily prepared as illustrated below. The coating aids of the invention corresponding to the above formula wherein X is oxygen can be prepared by reaction of alicyclic alcohols or branched-chain alcohols ($m=0$) or such ethoxylated alcohols ($m=1$ to 30), with sultones such as 1,3-propane sultone, 1,4-butane sultone, 1,3-butane sultone, 2,4-butane sultone, 2-methyl-2,4-pentane sultone and o-toluene sultone, etc. The coating aids according to the above general formula wherein X is sulphur can be prepared e.g. by reaction of the corresponding thiols with a chloro-alkane sulphonic acid.

As an example of an alicyclic alcohol from which coating aids according to the invention can be prepared hydroabietyl alcohol may be mentioned.

Examples of branched-chain alcohols that can be used are branched-chain aliphatic secondary alcohols such as the commercially available isotetradecyl alcohol i.e. 2-methyl-7-ethyl-4-undecanol and the widely known branched-chain primary oxo-alcohols having at least 10 C-atoms such as isodecylalcohol, isotridecylalcohol, isohexadecylalcohol and isooctadecylalcohol. Isodecylalcohol is a commercial material prepared from C_9-olefins (tripropylene) by means of the oxo-synthetsis (cf. H. Römp-Chemie Lexikon-Franck-sche Verlag, Stuttgart, West Germany) and is a mixture of primary branched-chain C_{10}-alcohols. Isotridecyl alcohol is a commercial material prepared from C_{12}-olefins (triisobutylene, tetrapropylene, or di(2-methyl-1-pentene)) by means of the oxo-reaction and is a mixture of primary branched-chain C_{13}-alcohols. Isohexadecylalcohol and isooctadecylalcohol are commercial materials prepared by aldol-condensation of C_8- or C_9-aldehydes formed by oxo-synthesis; isohexadecylalcohol is a mixture of branched-chain primary C_{16}-alcohols mainly consisting of alcohols as represented by the formula



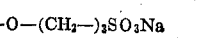
wherein R'=dimethylbutyl and R''=dimethylhexyl whereas isooctadecylalcohol is a branched-chain alcohol for which the following formula is given:

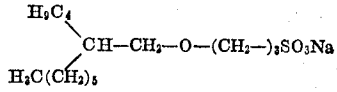


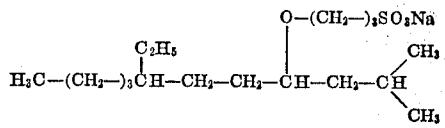
Other branched-chain alcohols from which the coating aids of the invention can be derived are the branched-chain alcohols prepared by alkaline condensation using catalytic amounts of alkali such as potassium hydroxide at temperatures comprised between 200 and 300° C. (known as Guerbet-reaction—see e.g. Fette-Seifen-Anstrichmittel, 71, No. 3, pp. 215–218 (1969)) of a branched-chain or straight-chain alcohol with the same or other branched-chain or straight-chain alcohol.

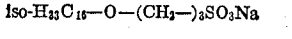
More details regarding the preparation, the composition and properties of branched-chain oxo-alcohols which can be used to form the coating aids according to the present invention can be found in Fortschr. Chem. Forsch. Bd 11/1, pp. 121–134.

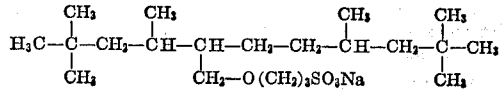
Examples of coating aids suitable for use according to the present invention can be represented by the following formulae:

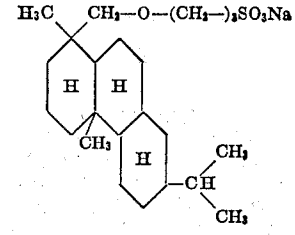
(1) 

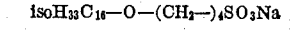
(2) 

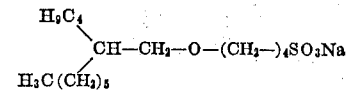
(3) 

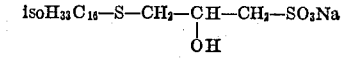
(4) 

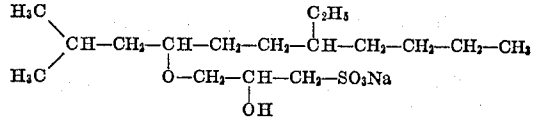
(5) 

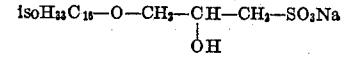
(6) 

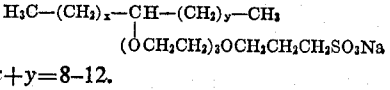
(7) 

(8) 

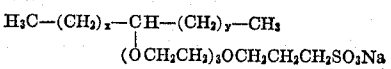
(9) 

(10) 

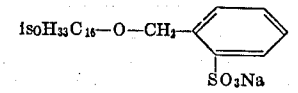
(11) 

(12) 

wherein $x+y=8–12$.

(13) 

wherein $x+y=8–12$.

(14) 

These compounds are prepared as is illustrated by the preparations below.

COMPOUND 1

A mixture of 50 g. of isotridecyl alcohol, 13.5 g. of sodium carbonate and 30.5 g. of propane sultone was heated for 9 h. at 150° C. whilst stirring, so that a viscous paste was obtained. The reaction product was cooled, mixed with acetone and kneaded therewith. Subsequently, it was filtered off with suction and dissolved in anhydrous methanol. The sodium salt of hydroxypropane sulphonic acid formed, was filtered off and the methanol solution was concentrated by evaporation. Yield: 68 g.

COMPOUND 2

A mixture of 46.5 g. of 2-butyloctanol, 13.25 g. of sodium carbonate and 30.5 g. of propane sultone was heated for 9 h. at 150° C. whilst stirring, so that a thick paste was obtained. The reaction product was then treated in the same way as Compound 1. Yield: 54 g.

COMPOUND 3

A mixture of 53.5 g. of isotetradecylalcohol (i.e. 2-methyl-7-ethyl-4-undecanol), 13.25 g. of sodium carbonate, and 30.5 g. of propane sultone was heated for 9 hours at 150° C. whilst stirring, so that a thick paste was obtained. The reaction product was then treated in the same way as Compound 1, with the difference, however, that anhydrous isopropanol was used instead of methanol. Yield: 35 g.

COMPOUND 4

A mixture of 60.5 g. of isohexadecylalcohol (commercially available e.g. from Esso Belgium N.V., Antwerp, Belgium), 13.25 g. of sodium carbonate, and 30.5 g. of

propane sultone was heated for 9 h. at 150° C. whilst stirring, so that a thick paste was obtained. The reaction product was then treated in the same way as Compound 1, with the difference however, that anhydrous ethanol was used instead of methanol. Yield: 70 g.

COMPOUND 5

A mixture of 67.5 g. of isooctadecylalcohol (commercially available e.g. from Farbwerke Hoechst A.G., Frankfurt am Main, Höchst, West Germany), 13.25 g. of sodium carbonate and 30.5 g. of propane sultone was heated for 9 h. at 150° C. whilst stirring, so that a thick paste was formed. The reaction product was treated in the same way as Compound 1, with the difference however, that anhydrous ethanol was used instead of methanol. Yield: 63 g.

COMPOUND 6

A mixture of 73 g. of hydroabietylalcohol, 13.25 g. of sodium carbonate, and 30.5 g. of propane sultone was heated for 9 h. at 150° C. whilst stirring, so that a thick paste was formed. The reaction product was treated in the same way as Compound 1, with the difference however, that anhydrous ethanol was used instead of methanol. Yield: 53 g.

COMPOUND 7

A mixture of 60.5 g. of isohexadecylalcohol, 13.25 g. of sodium carbonate, and 34 g. of butane sultone was heated for 13 h. at 150° C. whilst stirring, so that a thick paste was formed. The reaction product was treated in the same way as Compound 1, with the difference, however, that anhydrous ethanol was used instead of methanol. Yield: 70 g.

COMPOUND 8

A mixture of 46.5 g. of 2-butyloctanol, 13.25 g. of sodium carbonate and 34 g. of butane sultone was heated for 16 h. at 150° C. whilst stirring, so that a thick paste was formed. The reaction product was treated in the same way as Compound 1, with the difference, however, that anhydrous ethanol was used instead of methanol. Yield: 45 g.

COMPOUND 9

To a suspension of 56.2 g. of the sodium salt of isohexadecyl mercaptan in 300 ml. of dimethylformamide, 39.2 g. of the sodium salt of 2-hydroxy-3-chloropropane sulphonic acid was added. The mixture was refluxed for 8 h. and then cooled. The resulting sodium chloride was filtered with suction and the dimethylformamide solution was concentrated by evaporation. The residue was washed with acetone and recrystallized from dichloroethane. Yield: 40 g.

Isohexadecyl mercaptan can be prepared as follows:

(a) Isohexadecylbromide

At a temperature of 70° C., hydrogen bromide was introduced into 914 g. of isohexadecylalcohol until the solution was saturated. The water formed was isolated and the oil taken up in ether. The ether layer was washed till neutral, dried over sodium sulphate and concentrated by evaporation. The residue was distilled. Boiling point: 140° C./4 mm. Yield: 1092 g.

(b) Isohexadecyl isothiouronium bromide

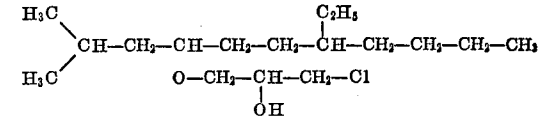
305 g. of isohexadecyl bromide and 76 g. of thiourea in 600 ml. of ethanol were refluxed for 16 hours. The clear solution was concentrated by evaporation and the residue recrystallized from acetonitrile, cooled, filtered by suction and dried at 50° C. Yield: 316 g.

(c) Isohexadecyl mercaptan

To 228 g. of isohexadecyl isothiouronium bromide in 420 ml. of water and 420 ml. of ethanol under a nitrogen atmosphere, 36 g. of sodium hydroxide were added with stirring. The mixture was then refluxed for 2 hours and cooled. The solution was acidified with 150 ml. of 5 N sulphuric acid, poured into 900 ml. of water and extracted with 300 ml. of methylene chloride. The methylene chloride solution was isolated, dried over magnesium sulphate and concentrated by evaporation. The residue was distilled. Boiling point: 125° C./0.3 mm. Yield: 150 g.

COMPOUND 10

This product was prepared according to the method described in Tenside 5, 1968, 43 starting from the compound with formula:

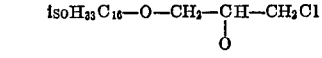


which was prepared as follows:

To 85.6 g. of isotetradecyl alcohol, 36.8 g. of epichlorohydrin was added dropwise at 60° C. in 2 hours while introducing boron trifluoride. When all epichlorohydrin was added the mixture was stirred for 5 hours at 60° C. and then kept for 3 hours at 70° C. under vacuum in order to distill off the residual epichlorohydrin. Yield: 122 g.

COMPOUND 11

This compound was prepared according to the method described in Tenside 5, 1968, 43 starting from the compound with formula:



which was prepared as follows:

To 121 g. of isohexadecylalcohol, 46 g. of epichlorohydrin was added dropwise at 60° C. in 2 hours, while introducing boron trifluoride. When all epichlorohydrin was added the mixture was stirred for 5 hours at 60° C. and then kept for 3 hours under vacuum at 70° C. in order to distill off the residual epichlorohydrin. Yield: 166 g.

COMPOUND 12

A mixture of 40.2 g. of an ethoxylated secondary synthetic C_{11}–C_{15} aliphatic alcohol containing 3 ethylene oxide units per molecule and commercially available from Union Carbide and carbon under the trade name Tergitol 15–S–3, 6.3 g. of sodium carbonate and 12.2 g. of propane sultone was heated for 7 hours at 150° C. while stirring. Acetone was then poured on the cooled viscous paste, which was then kneaded therewith. Subsequently, the reaction product was filtered with suction and then dissolved in anhydrous isopropanol. The sodium salt of hydroxypropane sulphonic acid formed, was filtered off and the isopropanol solution was concentrated by evaporation. Yield: 14 g.

COMPOUND 13

A mixture of 66.6 g. of an ethoxylated secondary synthetic C_{11}–C_{15} aliphatic alcohol containing 9 ethylene oxide units per molecule and commercially available from Union Carbide and carbon under the trade name Tergitol 15–S–9, 6.3 g. of sodium carbonate, and 13.4 g. of propane sultone was heated for 8 h. at 150° C. while stirring, whereby a viscous paste was formed. Acetone was poured on the cooled reaction product, which was then kneaded theerwith. Subsequently, the reaction product was filtered with suction and dissolved in a mixture of equal volumes of anhydrous dioxane and anhydrous ethanol. The sodium salt of hydroxypropane sulphonic acid formed, was filtered with suction and the solution was concentrated by evaporation. Yield: 20 g.

COMPOUND 14

A mixture of 60.5 g. of isohexadecyl alcohol, 13.25 g. of sodium carbonate, and 42.5 g. of o-toluene sultone was heated with stirring for 8 hours at 140° C., whereby a

viscous paste was formed. The reaction product was cooled and taken up in anhydrous acetone, whereupon the solution was filtered over active charcoal. The filtrate was concentrated by evaporation and the residue taken up in water. The aqueous layer was extracted with ethyl acetate whereupon the aqueous layer was concentrated by evaporation. Yield: 35 g.

The coating aids according to the present invention promote the uniformity of coating and markedly reduce the tendency of repellency spots formation. Coating compositions containing the coating aids of use according to the invention can be applied to dry surfaces as well as to wet surfaces and form layers that can be easily overcoated in wet as well as in dry state, the said layers being either light-sensitive layers or not. Light-sensitive hydrophilic colloid materials comprising these coating aids also show improved wettability by photographic processing liquids.

It may sometimes be advisable to use blends of two or more coating aids according to the present invention. Indeed it is frequently observed that one coating aid according to the invention performs best in one respect e.g. as regards its anticomet properties, while another is definitely superior in a different effect e.g. promoting uniformity of coating. These blends provide the major effects required and can often show characteristics superior to either coating aid alone. These effects may also result with blends of the coating aids of use according to the present invention with known coating aids such as saponin and other synthetic coating aids.

The coating aids of the present invention have also favorable properties for dispersing or emulsifying substances in hydrophilic colloid compositions, which as a result of the presence of said coating aids also show improved coating characteristics. For instances, they are suitable as dispersing agent or emulsifying agent for substances that are to be incorporated into layers comprising a hydrophilic colloid and that would give rise to the formation of repellency spots in said layers when no compounds according to the invention are present.

Although the coating aids according to the present invention are mainly intended for use in coating compositions comprising gelatin as hydrophilic colloid, they can also be used as coating aid for coating compositions comprising other hydrophilic colloidal materials or mixtures of them, e.g. hydrophilic natural colloids, modified hydrophilic natural colloids or synthetic hydrophilic polymers. More particularly these colloids may be selected of such film-forming natural or modified natural hydrophilic colloids as e.g. glue, casein, zein, hydroxyethyl cellulose, carboxymethyl cellulose, methyl cellulose, carboxymethyl hydroxyethyl cellulose, gum arabic, sodium alginate and hydrophilic derivatives of such colloids. They may also be selected of such synthetic hydrophilic polymers as e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl amine, polyethylene oxide, polystyrene sulphonic acid, polyacrylic acid, and hydrophilic copolymers and derivatives of such polymers. In this connection reference is made e.g. to United Kingdom Patent Specification 1,139,891 and to French Patent Specification 1,507,874 which relate among others to heat- and/or pressure-sensitive materials comprising a recording layer mainly consisting of a dispersion of hydrophobic thermoplastic polymer particles in a hydrophilic colloid binder.

It has been found that coating aids according to the present invention improve the coating characteristics of coating compositions already at a concentration as low as 0.01% by weight relative to the weight of dry colloid. Larger concentrations, however, can also be used but generally the concentration is not higher than 5% by weight based on the weight of dry colloid.

The coating aids according to the invention are particularly suitable for use in a coating composition comprising gelatin as hydrophilic colloid, 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 materials therein, a silver halide such as silver bromide, silver chloride, silver iodide, or mixtures thereof or another light-sensitive substance. The emulsion may contain other added substances such as sensitizing dyes, hardeners, stabilizers, pH-adjusting compounds, color couplers, antifogging agents, development accelerators, thickening agents, developing agents, softening agents, or the like. For instance, the coating aids of the invention are useful in gelatin photographic emulsions, not only those which are non-optically sensitized, but also in orthochromatic and panchromatic emulsions. This also includes gelatin emulsions intended for color photography such as those containing color forming couplers and fine-grain emulsions of the Lippmann-type.

The coating aids of use according to the present invention and their mixtures with other coating aids are also very useful in various other types of coating compositions in which gelatin is an important constituent, for example, in gelatin coating compositions to be applied as antihalation layer to the back or front of the base in a photographic material, as protective layer, as filter layer, as intermediate layer, as anticurling layer, etc., which layers can also contain all kinds of other ingredients such as filling agents, hardening agents, antistatic agents, antifriction agents, or in any type of gelatin layer, which is coated from a composition comprising an aqueous solution of gelatin.

The coating compositions in accordance with our invention may be coated on a transparent support e.g. of glass, cellulose esters, polyethylene terephthalate or a non-transparent reflecting material such as of paper or an opaque cellulose ester. It is often desirable first to coat a subbing layer to the support, this practice of subbing being well known in the art.

The coating procedure may comprise any of the standard procedures employed in industry, such as roller coating, brush coating, dip-coating, spraying, using a doctor blade or an air blade to control the thickness and distribution of the coating composition.

The following examples illustrate the present invention.

Example 1

A series of three aqueous gelatin solutions comprising per kg. 50 g. of gelatin were prepared.

To each of these gelatin compositions a certain amount of coating aid was added as listed in the table below.

After having been coated on a conventional subbed cellulose triacetate support the number of repellency spots in the layer formed was counted.

The results found are listed in the following table.

Coating aid used per kg. gelatin solution:	Repellency spots per sq. m.
15 ml. of a 12% aqueous solution of saponin (A)	18
(A)+10 ml. of a 5% aqueous solution of Compound 1	10
(A)+10 ml. of a 5% aqueous solution of Compound 2	12

Example 2

Example 1 was repeated with the difference that now the coating aids listed in the following table were used.

Coating aid used per kg. gelatin solution:	Repellency spots per sq. m.
15 ml. of a 12% aqueous solution of saponin (A)	14
(A+10 ml. of a 5% aqueous solution of Compound 4	4
(A)+10 ml. of a 5% aqueous solution of Compound 5	6

We claim:

1. A photographic element comprising a support and one or more water-permeable hydrophilic colloid layers

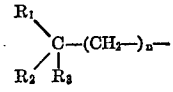
including light-sensitive silver halide emulsion layers wherein one or more of said layers comprises a compound corresponding to the formula:

$$R—(OCH_2CH_2)_m—X—A—SO_3M$$

wherein:

M stands for hydrogen, an alkali metal atom, ammonium or organic ammonium,
A stands for alkylene comprising at least 3 C-atoms, or aralkylene,
X stands for oxygen or sulphur,
R stands for a branched-chain aliphatic group of 10 to 20 carbon atoms, and
m stands for 0 to 30.

2. A photographic element according to claim **1**, wherein in the said formula R stands for the group of the formula:



wherein:

n is 0 or 1,
R_3 stands for hydrogen or when $n=1$ may be alkyl, and each of R_1 and R_2 stands for a straight-chain or branched-chain alkyl group or together represent the atoms necessary to close an alicyclic ring structure.

3. A photographic element according to claim **1**, wherein the said compound is present in the said layer(s) in an amount of from 0.01 to 5% by weight based on the weight of dry colloid in the said layer(s).

4. A photographic element according to claim **3**, wherein the said colloid is gelatin.

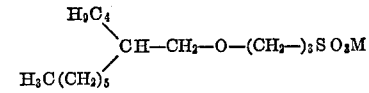
5. A photographic element according to claim **1**, wherein said colloid layer comprising the said compound is a light-sensitive silver halide emulsion layer.

6. A photographic element according to claim **1**, wherein the said colloid layer comprisnng the said compound is a protective hydrophilic colloid layer coated over a silver halide emulsion layer.

7. The photographic element of claim **1** wherein said compound is:

$$isoC_{13}H_{27}—O—(CH_2—)_3SO_3M$$

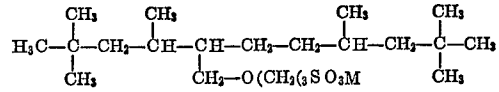
8. The photographic element of claim **1** wherein said compound is:



9. The photographic element of claim **1** wherein said compound is:

$$iso—H_{33}C_{16}—O—(CH_2—)_3SO_3M$$

10. The photographic element of claim **1** wherein said compound is:



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96—94 R, 114.5, 114.7