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Willems

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[54] **HYDROPHILIC FILM-FORMING COLLOID COMPOSITION**

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[58] **Field of Search** ..... 96/114.5, 114, 67, 96/50 PL

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[57] **ABSTRACT**

Coating compositions are described which comprise a hydrophilic colloid and an ester of the sulphonate derivative of an unsaturated polycarboxylic acid material comprising more than three carboxylic acid equivalents with at least one non-ionic surface active hydroxy compound, at least one of the carboxylic acid groups being stronly with the said non-ionic surface active compound and the remaining unesterified carboxylic acid groups being in acid form, in salt form or esterified with one or more compounds containing hydroxy group(s). These coating compositions are particularly useful in the formation of photographic silver halide elements. The layers coated from these compositions show a reduced formation of comets or repellency spots and can be overcoated easily with other hydrophilic colloid layers.

8 Claims, No Drawings

HYDROPHILIC FILM-FORMING COLLOID COMPOSITION

This invention relates to film-forming coating compositions comprising a hydrophilic colloid and novel coating aids for said compositions.

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, so as to obtain a uniform layer therewith, which comprises no hydrophobic inclusions that may give rise to repellency spots or comets. 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 carried along more easily 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 so that its surface is not entirely hydrophilic but shows hydrophobic areas, water will not uniformly wet the said surface in that it is repelled at the hydrophobic areas and form drops thereon. Therefore, after processing suchlike materials cannot be dried uniformly and they show a poor retouchability.

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.

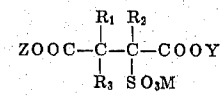
Thus, in order to eliminate all these possible coating defects such as air-bubbles, repellency spots, or "comets" and unevenesses the use of coating aids has been widely adopted.

So far saponin is widely used as a coating aid for coating compositions comprising hydrophilic colloids. This product, however, may vary markedly from batch to batch and is much more expensive than synthetic coating aids. Moreover, it may adversely affect the photographic properties of an emulsion containing it.

A number of synthetic coating aids have been proposed to improve coating of compositions comprising hydrophilic colloids, more particularly gelatin layers. However, most coating aids, while improving some properties of the layer, also adversely affect other desired properties. For instance, some coating aids prevent the formation of comets in gelatin layers. Yet, it is difficult to overcoat layers containing such coating aids when in wet state. Moreover, suchlike coating aids will tend to form air-bubbles on the surface of a photographic emulsion layer during processing in automatic machines and prevent uniform drying of the layer after processing. To overcome these disadvantages it has been proposed to combine coating aids having different properties.

In accordance with the present invention novel coating aids for hydrophilic colloid coating compositions are provided wherein said coating aids are esters of the sulphonate derivative of an unsaturated aliphatic polycarboxylic acid material comprising more than three carboxylic acid equivalents, with a non-ionic surface-active agent containing at least one hydroxy group, the said unsaturated polycarboxylic acid material being prepared according to a process, which comprises heating an alkaline-earth metal salt of citric acid at a temperature within the range of 230° to 400°C until an increase in titratable alkalinity of the reaction mixture is obtained and until not more than 32 % by weight, preferably not more than 5 % by weight of the original citric acid salt remains. At least one of the carboxylic acid groups of the polycarboxylic acid material has been esterified and the remaining carboxylic acid groups may be in the acid form, may be provided with a salt-forming cation, which may be an alkaline metal or alkaline-earth metal, ammonium, organic ammonium, etc., or may be esterified (before, during, or after the esterification with the said non-ionic surfactant) with one or more compounds containing (a) hydroxy group(s) e.g. monohydric or polyhydric alcohols. The coating aids of use according to the invention therefore may be in the form of a simple ester, which may be a full, partial and/or mixed ester or it may be in the form of complex esters, in which two or more polycarboxylic acid residues are ester-linked to each other by a polyhydroxy compound, e.g. ethylene glycol, polyethylene glycol, propylene glycol, or polypropylene gylcol.

The water-soluble coating aids for hydrophilic colloid coating compositions according to the present invention may be represented by the following schematic general formula :

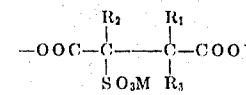


wherein :

M stands for hydrogen or a salt-forming cation, e.g. an alkaline or alkaline-earth metal such as potassium, sodium, lithium, and calcium, ammonium, organic ammonium, e.g. diethanolammonium, triethanolammonium , and morpholinium,

Z stands for the ester-linked residue of a non-ionic surface-active hydroxy compound containing in the original molecule at least one hydroxy group,

Y stands for hydrogen, a group M as defined above, a group Z as defined above, alkyl, hydroxyalkyl or a group



ester-linked by a polyhydroxy e.g. dihydroxy compound, and

each of R_1, R_2, and R_3, the same or different, stands for hydrogen, alkyl comprising from one to three C-atoms or a group CH_2COOX, at least two of R_1,

R_2, and R_3 being a group CH_2COOX, wherein X has one of the significances given for Y.

The above schematic general formula is representative of the esterified sulphonate derivative of the unsaturated polycarboxylic acid material described above.

A wide variety of non-ionic surface-active hydroxy compounds are suitable for being ester-linked to the sulphonated polycarboxylic acid material and include those described in "Non-ionic Surfactants" by M.J. Schick — 1967 — Marcel Dekker Inc., New York.

Examples of non-ionic surface-active hydroxy compounds, are alkoxylated hydroxy compounds e.g. the reaction product of an alcohol or phenol with more than one mole, preferably 3 to 50 moles, of ethylene oxide. Other non-ionic surface-active compounds are the polyoxy alkylene esters of fatty acids e.g. the reaction product of a C_{12}–C_{18} aliphatic carboxylic acid such as myristic acid, palmitic acid, stearic acid, and oleic acid with more than more mole, preferably 3 to 50 moles of ethylene oxide. Suitable alcohols, which may be alkoxylated include C_6–C_{24} aliphatic alcohols, oleyl alcohols, alkylated-β-naphthol, oxo alcohols, the so-called Ziegler alcohols, alcohols obtained by oxidation of paraffins, ether alcohols, secondary alcohols e.g. (but not exclusively) made by reduction of the ketones obtained by pyrolysis of synthetic paraffin wax fatty acids, polyalkyl cyclohexanols made by the reduction of the corresponding isophorones, sod-oil, alkylphenols, complex phenols derived from condensation of a simple phenol with an aldehyde or ketone e.g. phenol with an alkyl-cyclohexanone, etc.

A particularly useful class of non-ionic surfactants that can be used for esterification are polyalkoxylated e.g. polyethoxylated alkylphenols, such as phenols carrying one or more C_6–C_{14} alkyl substituents, that may be linear or branched such as isooctyl-phenol, nonylphenol and diisobutyl-phenol, and made to react with ethylene oxide, three to 50 ethylene oxide molecules forming the alkoxylated chain.

Another useful class of non-ionic surfactants are alkoxylated e.g. ethoxylated aliphatic monohydric alcohols, particularly C_6–H_{24} primary or secondary alcohols that may contain from three to 50 ethoxy groups in the alkoxy chain.

Provided the final coating aid for use in hydrophilic colloid coating compositions remains water-soluble, the ethylene oxide chain of the non-ionic surfactant to be ester-linked with the polycarboxylic acid material may include also isopropylene oxide units.

The examples of alkoxylated hydroxy compounds and polyoxyalkylene esters of fatty acids that are suitable for esterification with the polycarboxylic acid material to form the coating aids according to the present invention, can be represented by the following general formula :

$$RO\left[(CH_2CH_2O)_n(CHCH_2O)_p\right](CH_2CH_2O)_mH$$
$$\qquad\qquad\qquad\quad CH_3$$

wherein :

R stands for an aliphatic carboxylic acyl group preferably comprising from 12 to 18 C-atoms, a hydrocarbon group or a substituted hydrocarbon group, especially an aliphatic straight-chain or branched-chain hydrocarbon group and in particular an alkyl or alkenyl group with six to 24 carbon atoms, or an alkaryl group, in which the aryl group may be mononuclear or multinuclear e.g. an alkylated phenyl or naphthyl group, in which the alkyl group(s) preferably contain(s) from four to 10 C-atoms when the aryl group is naphthyl and from six to 14 C-atoms when the aryl group is phenyl,

each of n and m stands for 0 to 50,

p stands for 0 to 25, and

q is such that $p \times q$ is at most 25,

the total number of recurring ethylene oxide units i.e. $(n \times q) + m$ being at least 3 and at most 50 and the ratio of ethylene oxide recurring units to isopropylene oxide recurring units (if any) i.e. $[(n \times q) + m/p \times q]$ being at least 2.

As mentioned above, the polycarboxylic acid material, from which the coating aids according to the invention are derived, is a carboxylic acid material obtained by the controlled pyrolysis of an alkaline-earth metal salt of citric acid, i.e. by heating the said alkaline-earth metal salt for a period of time and at a temperature preferably not less than 230°C, more preferably in the range of 250°C to 400°C, and particularly in the range 300° to 375°C, until an increase in titratable alkalinity is obtained, and until not more than 32 %, preferably not more than 5 % by weight, of the original citric acid salt remains. Such acid materials and their preparation are described in United Kingdom Patent Specification 1,082,179 (= U.S. Pat. application Ser. No. 563,816). The product is then hydrolyzed, either before or after sulphonation, by conventional hydrolysis techniques for the production of acids from their corresponding salts.

The chemical identity of the said unsaturated acid material has not been determined precisely although it is different from, although it may contain, aconitic acid, which may be removed from the material if desired either before or after the hydrolysis step, together if desired with any inorganic salt generated during the controlled pyrolysis. From analysis carried out on the pyrolysis product it appears that the unsaturated acid component is a derivative of an as yet unidentified unsaturated acid containing more than three carboxylic acid groups per molecule.

The water-soluble coating aids according to the invention contain at least one sulphonate group, which is preferably an alkali metal, alkaline-earth metal, or ammonium sulphonate group.

The said sulphonate group(s) may be incorporated either by sulphonating ethylenically-unsaturated linkages in the esterified acid and subsequently neutralizing the resulting sulpho-derivative, or by sulphonating the not yet esterified acid material and effecting neutralization after the esterification.

The said acid material may be sulphonated by bringing a solution of the said material in contact with hydrogen sulphite ions under acid conditions. Thus a hydrogen sulphite or sulphite compound may be introduced into the said compound, or SO_2 injected into the said solution, to produce a corresponding sulphopolycarboxylic acid material.

Thus, during the esterification reaction, the polycarboxylic acid derived from the controlled pyrolysis of the citric acid salt may be in the unsaturated state or in the form of its sulphoderivative. If unsaturated acids are used for esterification, the esters are subsequently sulphonated. In either instance, the sulpho-esters are neutralized to form the corresponding sulphonate salts as described hereinbefore.

The esterification of the polycarboxylic acid or its sulphonated derivative is carried out in conditions well known to those skilled in the art, by condensation of the (sulpho-) acid material with the non-ionic surface-active hydroxy compound. During esterification the water formed in the course of the esterification process may be removed by distillation, preferably under reduced pressure. After the desired degree of esterification has been reached the remaining acid can be neutralized by the addition of a suitable base.

Suitable neutralizing agents are sodium hydroxide, or bases of other alkali metals such as potassium or lithium, alkaline-earth metal bases, such as e.g. calcium, magnesium, and zinc, or trivalent metal bases such as aluminum oxide or hydroxide. It is also possible to neutralize the acid by means of ammonia, or organic bases containing basic amino groups e.g. lower and higher amines, and the amino alcohols such as mono- , di- and triethanolamine.

In the process in which the esterification process precedes the hydrogen sulphite reaction, a concentrated solution of a water soluble hydrogen sulphite is added gradually to the ester material with continuous stirring. The reaction is carried out preferably in a closed vessel to facilitate the addition reaction of the hydrogen sulphite. The reaction time is dependent upon the speed, at which the hydrogen sulphite is added to the reaction mixture and upon the reaction temperature, which usually is about 100°C.

In the process, in which the hydrogen sulphite addition reaction precedes the esterification reaction, which method is the preferred method, the sulpho-acid material is subject to esterification. Any of the known esterification techniques apply. Usually no catalyst is needed, because the strongly acidic sulphonic acid group present in the sulpho-acid material will in most instances catalyse the reaction sufficiently, so that no further catalyst is needed. If in some instances, the reaction velocity is too low, it may be advantageous to convert the sulpho-acid material into an even more reactive form, such as the chloride, prior to esterification.

As noted above, the sulphonate esters of the polycarboxylic acid material for use according to the present invention may also be complex esters in which at least two polycarboxylic acid residues are ester-linked through a polyhydroxy compound, or mixed esters in which remaining carboxylic acid groups have been esterified with other non-ionic surfactants containing (a) hydroxyl group(s), or with monohydric or polyhydric alcohols. The formation of such a complex ester or mixed ester structure may be effected either before, during, or after the unsaturated polycarboxylic acid material(or the corresponding sulpho-acid material) has been esterified partially with the non-ionic surfactant containing (a) hydroxyl group(s).

At the end of the esterification reaction, neutralization of the remaining acid may be carried out as described hereinbefore.

For more details regarding the techniques of sulphonation of the esterified or not yet esterified polycarboxylic acid material and the techniques of esterification of the polycarboxylic acid material or its sulpho derivative there can be referred to the United Kingdom Patent Specification 1,082,179 and Belgian Patent Specification 717,565.

Coating compositions containing the coating aids according to the present invention can be applied to dry surfaces as well as to wet surfaces and form layers that can be overcoated easily in wet as well as in dry state, the said layers being either light-sensitive layers or not. The coating aids according to the present invention have good anti-comet properties and thus prevent the formation of repellency spots. Though they comprise a sulphonate group, the coating aids of the invention give less rise to frothing and resulting air-bubbles than saponin and other conventional synthetic coating aids comprising sulphate or sulphonate groups.

The coating aids of use according to the present invention can be used also in combination with other coating aids e.g. coating aids that strongly reduce repellency spots but that render the layer containing them difficult to overcoat. By the presence of the coating aids according to the present invention the latter disadvantage is overcome and the mentioned strong reduction of repellency spots formation is maintained. Moreover, the coating aids according to the present invention have also favourable dispersing or emulsifying properties so that they can be used 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 instance 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 were present. Other properties of the coating aids according to the present invention will appear hereinafter.

Although the coating aids according to the present invention are intended mainly 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 among such film-forming natural or modified natural hydrophilic colloids as, e.g., glue, casein, zein, hydroxyethylcellulose, carboxymethylcellulose, methylcellulose, 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 French Patent Specification 1,507,874, which relate i.a. 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.

The coating aids according to the present invention are good coating aids for use in coating compositions as defined above either alone or in admixture with non-ionic surface-active compounds such as those referred to above or with other anionic surface-active agents e.g. dialkyl sulphosuccinic acid salts and salts of alkyl sulphuric acids, salts of alkyl sulphonic acids, salts of alkylaryl polyether sulphuric acids and salts of alkylaryl polyether sulphonic acids. It has been found that coating aids according to the present invention improve the

coating characteristics of coating compositions even at a concentration as low as 0.01 by weight relative to the weight of solids. Larger concentrations, however, can also be used but generally the concentration is not higher than 5 % by weight based on the weight of solids. In coating compositions intended for being coated as hydrophilic colloid layers in photographic silver halide materials said coating aids are generally present in amounts from 0.01 to 2 % 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 material therein, a silver halide e.g. silver bromide, silver chloride, silver iodide, or mixtures thereof or another light-sensitive substance. The emulsion may contain other additives e.g. sensitizing dyes, hardeners, stabilizers, pH-adjusting compounds, colour 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 colour photography suc as those containing colour forming couplers.

The coating aids of the 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, e.g. in gelatin coating compositions to be applied as an antihalation layer to the back or front of the base in a photographic material, as a photographic material, as a protective layer, as a filter layer, as an intermediate layer, as an anticurling layer, etc., which layers can also contain all kinds of other ingredients e.g. 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 on a non-transparent reflecting material e.g. of paper or an opaque cellulose ester. It is often desirable first to coat a subbing layer on 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 favourable effect of the coating aids according to the present invention.

EXAMPLE 1

To a series of gelatin silver bromoiodide emulsions comprising per kg 80 g of dry gelatin and 1.75 g of saponin a certain amount of coating aid was added as listed in the table below. The emulsion samples were then coated on a subbed film support and overcoated while still wet with a protective gelatin layer comprising 30 g of gelatin per litre and containing an antistatic agent and sodium diisooctyl sulphosuccinate as coating aid.

In each case the "critical speed" for applying the protective layers on the wet emulsion layers was determined and the number of repellency spots i.e. comets per sq.m. were counted for each material.

By critical speed is understood the maximum speed of the moving base to be coated, at which the composition for forming the protective layer can be coated yet. Indeed, the layers of air carried along by the moving base are capable, at a certain speed, of preventing in large areas, contact of the protective coating composition with the wet emulsion layer, whereby uncoated portions remain on the moving emulsion layer. If the speed of coating is reduced, the contact of the emulsion layer with the protective gelatin layer takes place over the entire area, the instability of the coated layer, because of the incomplete wetting of the base, does not occur and univormity of the layer thickness is maintained.

The results attained are listed in the following table.

Coating aid used in the emulsion per kg (in addition to the saponin)	Critical speed in m/min	Repellency spots per sq. m.
none	11	20
0.2 g of sodium oleyl methyl tauride	32	26
12 ml of a 5 % aqueous solution of the product of preparation 1 below	>40	2
12 ml of a 5 % aqueous solution of the product of preparation 2 below	>40	4
12 ml of a 5 % aqueous solution of the product of preparation 3 below	>40	4
12 ml of a 5 % aqueous solution of the product of preparation 4 below	>40	4
12 ml of a 5 % aqueous solution of the product of preparation 5 below	>40	14

From the above results the following can be learned. Sodium oleyl methyl tauride has a favourable effect on the critical speed, which means that the emulsion layer can be overcoated easily with the gelatin antistress layer. However, the number of repellency spots in the case sodium oleylmethyl tauride is used, remains high. As can be seen, by the use of coating aids according to the present invention the critical speed is increased yet while the number of comets is also reduced markedly.

EXAMPLE 2

A series of three photographic gelatino silver halide emulsions all having the same composition, were prepared. To each of these emulsion samples a certain amount of coating aid was added as listed in the table below.

After coating on a conventional subbed cellulose triacetate support the number of repellency spots in the layers formed was counted.

The results found were listed in the following table.

Coating aid used in the emulsion layer per kg emulsion comprising 80 g of gelatin	Repellency spots per sq.m.
15 ml of a 12 % aqueous solution of saponin (A)	26

(A) + 17 ml of a 5 % aqueous solution of the product of preparation 6 below (B)	12
(A) + (B) + 2.5 ml of a 5 % aqueous solution of the ethoxylated nonylphenol used in preparation 6	6

The above results show the favourable effect of the use of a non-ionic surface-active material in addition to the coating aids of the invention.

The coating aids according to the invention referred to in the above examples were prepared as follows.

Preparation 1

Thirty-eight litres of an aqueous solution of sulpho-acid material, having an acid concentration of 12,500 milliequivalents per litre, obtained by the controlled pyrolysis of calcium citrate at a temperature of from 250° to 350°C for three hours, followed by hydrolysis and sulphonation of the resulting acid material and 48.9 kg of an ethoxylated mixture of C_6–C_{14} linear synthetic alcohols obtained by making react 3 moles of ethylene oxide per hydroxyl equivalent and having a hydroxyl value of about 215, were introduced into a reaction vessel provided with an agitator.

The sulpho-acid material and the ethoxylated alcohols were made to react with stirring at a temperature comprised between 60° and 100°C under a reduced pressure of about 150 mm Hg. Water was distilled off continuously under vacuum and after about 3 hours water evolution ceased. The reaction mixture was heated under reduced pressure until the acidity of the product formed was reduced to about 80 % of the original acidity.

The remaining sulphonic and carboxylic acid functions were neutralized by means of a diluted aqueous solution of sodium hydroxide.

Preparation 2

In a similar way as described in preparation 1 a same amount of sulpho-acid material was esterified with 59.4 kg of an ethoxylated mixture of C_6–C_{14} linear synthetic alcohols obtained by making react 5 moles of ethylene oxide per hydroxyl equivalent and having a hydroxyl value of about 177.

The sulpho-acid material and the ethoxylated alcohols were made to react as described in preparation 1 until the acidity of the product formed was reduced to about 60 % of the original acidititiy.

The remaining sulphonic and carboxylic acid functions was neutralized by means of a diluted aqueous solution of sodium hydroxide.

Preparation 3

Five hundred ml of an aqueous solution of sulpho-acid material having an acid concentration of 12,500 milliequivalents per litre, obtained by the controlled pyrolysis of calcium citrate at a temperature of 250° to 350°C in about 3 hours, followed by hydrolysis and sulphonation of the resulting acid material and 126.5 g of diethylene glycol were introduced into a reaction vessel provided with an agitator and therein made to react with stirring at a temperature between 60° and 100°C under a reduced pressure of about 150 mm Hg.

Water was distilled off continuously and after about 2 hours the evolution of water ceased. The contents of the reactor were then kept under reduced pressure and heated until the remaining acidity had fallen to about 60 % of its initial value.

Six hundred twenty-seven g of an ethoxylated mixture of C_1–C_{15} secondary synthetic alcohols obtained by making react 7 moles of ethylene oxide per hydroxyl equivalent and having a hydroxyl value of about 110.4 were the introduced into the reactor. The contents were again made to react under reduced pressure of about 150 mm Hg at a temperature of from 90° to 100°C for about 3 hours, until the remaining acidity had fallen to about 40 % of the initial value.

The remaining sulphonic acid and free carboxyl functions were then neutralized with dilute sodium hydroxide solution.

Preparation 4

36.4 litres of an aqueous solution of sulpho-acid material having an acid concentration of 11,000 milliequivalents per litre, obtained by the controlled pyrolysis of calcium citrate at a temperature of from 250° to 350°C for 3 hours, followed by hydrolysis and sulphonation of the resulting acid material, 40.2 kg of an ethoxylated mixture of C_{11}–C_{15} secondary synthetic alcohols obtained by making react 7 moles of ethylene oxide per hydroxyl equivalent and having a hydroxyl value of about 110.4 and 45 kg of n-butyl alcohol were introduced into a reaction vessel provided with an agitator. The contents were made to react with stirring at a temperature between 60° and 95°C under a reduced pressure of about 100 mm Hg.

An azeotropic mixture consisting of butyl alcohol and water was distilled off and collected in a water separator, the supernatant alcoholic layer being recycled continuously to the reaction vessel. After 8 hours the reaction was almost completed and then neutralized with a sodium hydroxide solution. The excess of alcohol was removed by distilling off of the azeotropic mixture under reduced pressure.

Preparation 5

In a similar way as described in preparation 1, a same amount of sulpho-acid material was esterified with 43.5 kg of an ethoxylated mixture of C_{12}–C_{14} linear synthetic alcohols obtained by making react 6 moles of ethylene oxide per hydroxyl equivalent and having a hydroxyl value of about 121.

Preparation 6

In a similar way as described in preparation 1, a same amount of sulpho-acid material was esterified with 55.8 kg of an ethoxylated nonylphenol obtained by making react 8.5 moles of ethylene oxide per hydroxyl equivalent and having a hydroxyl value of about 94.3.

We claim:

1. A photographic element comprising a support and one or more water-permeable colloid layers including light-sensitive silver halide emulsion layers wherein one or more of said layers comprise an ester of a sulphonate derivative of an unsaturated polycarboxylic acid material comprising more than three carboxylic acid equivalents and at least one non-ionic surface-active hydroxy compound, at least one of the carboxylic acid groups of said acid material being esterified with the said non-ionic surface-active compound and the remaining unesterified carboxylic acid groups being in acid form, in salt form, or esterified with one or more compounds containing at least one hydroxyl group wherein the said polycarboxylic acid material is a product of the process which comprises heating an alkaline-earth metal salt of citric acid at a temperature within the range of 230° to 400°C. until an increase of titratable alkalinity of the reaction mixture is obtained and until not more than 32% by weight of the original citric acid salt remains, and converting the product thereby obtained, before or

after sulphonation thereof, into the corresponding acid material.

2. A photographic element according to claim 1, wherein said non-ionic surface-active hydroxy compound is a polyalkoxylated alkylphenol.

3. A photographic element according to claim 1, wherein said non-ionic surface-active hydroxy compound is a polyalkoxylated aliphatic monohydric alcohol.

4. A photographic element according to claim 1, wherein said non-ionic surface-active hydroxy compound corresponds to the formula :

$$RO\left[(CH_3CH_2O)_n(\underset{CH_3}{CH}CH_2O)_p\right]_q(CH_2CH_2O)_mH$$

wherein :

R stands for a hydrocarbon group, or an aliphatic carboxylic acyl group,

each of n and m stands for 0 to 50,

p stands for 0 to 25, and

q is such that $p \times q$ is at most 25,

the total number of recurring ethylene oxide units being at least 3 and at most 50 and the ratio of ethylene oxide recurring units to isopropylene oxide recurring units (if present) being at least 2.

5. A photographic element according to claim 4, wherein R stands for alkyl or alkenyl comprising from six to 24 carbon atoms or for alkylated aryl, in which the alkyl contains from four to 14 carbon atoms.

6. A photographic element according to claim 1, wherein said ester is present in the said layer in an amount ranging from 0.01% to 2% by weight based on the weight of dry colloid present in the said layer.

7. A photographic element according to claim 1, wherein said colloid layer comprising the said ester is a light-sensitive hydrophilic colloid silver halide emulsion layer.

8. A photographic element according to claim 1, wherein the said colloid layer comprising the said ester is a protective hydrophilic colloid layer coated over a silver halide emulsion layer.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,762,928 Dated October 2, 1973

Inventor(s) Jozef Frans Willems

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Title page, in the Abstract, at line 7, "stronly" should read -- esterified --. Column 7, line 29, "suc as" should read -- such as --. Column 8, line 19, "univormity" should read -- uniformity --; Column 9, line 67, "C_1-C_{15}" should read -- C_{11}-C_{15} --. Column 12, line 4, claim 4, "(if present)" should read -- if present --; Column 12, after claim 8, insert claim 9 as follows:

-- 9. A photographic element according to claim 6,

wherein the said colloid is gelatin. --

Signed and sealed this 29th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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