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PHOTOGRAPHIC GELATIN LAYER CONTAINING A DI-(POLYALKYLENE GLYCOXY) ALKANE

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This invention relates to photographic light-sensitive materials, such as sensitized film, plates, and paper, comprising layers in which sensitive silver salts are suspended or dispersed in gelatin or other suitable vehicle, and optionally comprising other layers as well. More particularly, it relates to the use of certain agents to facilitate the spreading of gelatin or other hydrophilic colloid layers which are deposited from a predominantly aqueous medium and used in such photographic materials.

My invention perhaps finds its greatest usefulness in the manufacture of photographic film in which a sensitive gelatin emulsion layer is applied to the film base, set by chilling, and then, without drying, is overcoated with a protective gelatin layer, the sensitive gelatin emulsion layer containing such a spreading agent. The general process of coating film base with a sensitive gelatin emulsion layer, setting by chilling, and overcoating with a protective gelatin layer, is fully set forth in U. S. Patent No. 1,699,349 of William B. Dailey.

If a sensitive gelatino-silver-halide emulsion is coated on a film base (which has usually first been coated with a thin layer or sub-stratum of gelatin or other colloid and dried) without the addition of a suitable spreading agent, difficulty is experienced in that the emulsion will spread unevenly. Moreover, if the emulsion, while still in a wet, chilled condition, is overcoated with a protective gelatin coating, air bubbles form between the emulsion layer and the protective layer. Either of these defects, of course, greatly impairs the quality of the photographic film.

It has, therefore, been customary in the art to add certain agents, such, for instance, as saponin, to the sensitive emulsion in order to avoid these defects as far as possible. Saponin has surface-active properties, and not only acts as a spreading agent for gelatin, but by some mechanism not clearly understood, it prevents the formation of air bubbles between the gelatin layers when a wet, chilled gelatin emulsion layer containing the proper concentration of saponin is overcoated with a warm gelatin solution.

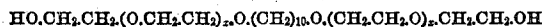
However, saponin, being a naturally occurring material of vegetable origin, is of varying quality, and synthetic agents are to be preferred because of their more constant and controlled properties. Because of its varying quality, some batches of

ment in spreading. This is true whether the saponin be employed in the emulsion layer or in the protective overcoating or other layer.

Other surface-active materials have been tried in place of saponin, but many of them, while they may act to some extent as spreading agents for gelatin, have been found to be entirely ineffective for preventing the formation of air bubbles when a wet, chilled gelatin emulsion containing them is overcoated with a warm gelatin solution, and many of them are objectionable from the standpoint of fogging or desensitizing the emulsion.

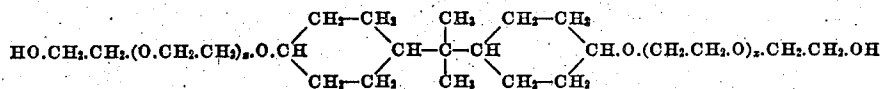
I have found a class of surface-active compounds which are not only excellent spreading agents for gelatin and other hydrophilic colloid layers which are deposited from a predominantly aqueous medium and used in photographic films, plates, and paper, but which, when incorporated in layers such as sensitive gelatin emulsions, are superior to saponin in the prevention of bubble formation when the wet, chilled emulsion layer is overcoated with a warm gelatin solution or other hydrophilic colloid of the type which is deposited from a predominantly aqueous medium. These compounds are the di-(polyalkylene glycoxy) alkanes in which the alkenyl radical is selected from the group consisting of the aliphatic alkenyl radicals containing from 8 to 18 carbon atoms and the di-cyclohexenyl dialkyl methanes in which each alkyl radical contains less than 3 carbon atoms, each polyalkylene glycoxy chain contains from 5 to 20 alkylene glycol radicals, and the alkylene radical is selected from the group consisting of ethylene and propylene.

The di-(polyalkylene glycoxy) alkanes in which the alkenyl radical is an aliphatic alkenyl radical of from 8 to 18 carbon atoms, e. g. di-(polyethylene glycoxy) decane,



may be prepared in a manner similar to that shown in British Patent 443,559, by condensing ethylene oxide or propylene oxide with dihydric alcohols of from 8 to 18 carbon atoms, e. g. decamethylene glycol.

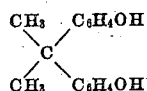
The di-(polyalkylene glycoxy) alkanes in which the alkenyl radical is a di-cyclohexenyl dialkyl methane, e. g. 4:4'-di-(polyethylene glycoxy-cyclohexyl) dimethyl methane



saponin may cause an increase in fog or a decrease in sensitivity in the sensitive emulsion, and in some cases may produce little or no improve-

ment may be prepared as follows: Phenol is reacted with acetone (or diethyl ketone or methyl ethyl ketone) as described in U. S. Patent 1,225,748 of

Wallace A. Beatty, to give the compound diphenylol dimethyl methane,



(or the corresponding diethyl or methyl ethyl compound). This compound is hydrogenated as described in British Patent 274,439, to give the corresponding dicyclohexylol dialkyl methane. This is then condensed with ethylene oxide or propylene oxide, in a manner similar to that shown in British Patent 443,559. Such compounds are mentioned in French Patent 772,302.

Any of these di-(polyalkylene glycoxy) alkanes may be incorporated in the sensitive gelatin emulsion at any point in its manufacture such that they will be present during its coating, in the proportion of from 0.075 to 1 part of the compound per 100 parts by weight of wet emulsion. This gives a content of the compound 0.75% to 10% in the dried emulsion layer. These compounds have no detrimental effect upon the photographic properties of the emulsion, but, on the contrary, improve them. It is believed that the property of the spreading agent which prevents the formation of air bubbles when a wet, chilled gelatin emulsion is overcoated with a warm gelatin solution, also tends to prevent the formation of air bubbles, repellent spots, etc., on the surface of a sensitive emulsion containing such a spreading agent, when that emulsion, coated on a film, plate, paper, etc., is immersed in a developer.

As above pointed out, the di-(polyalkylene glycoxy) alkanes defined may be used in any one or more of the colloid layers used to build up a photographic sensitive element upon a base such as film, glass, paper, etc., which layers consist of gelatin or other hydrophilic colloid which is deposited from a predominantly aqueous medium, i. e., a medium used as the solvent for such materials in which water predominates, the remainder of the medium contributing to give a good dispersion of the colloid. If two superposed colloid layers are present, either, neither or both of which may be photographically sensitive, the spreading agent may be used in either layer or in both layers. However, where a wet, chilled light-sensitive gelatin or similar layer is to be overcoated with a warm solution or emulsion of gelatin or similar material, the presence of the spreading agent in the wet, chilled layer is essential for preventing the formation of air bubbles between the layers. Examples of such hydrophilic colloids other than gelatin, which are useful as layers in photographic films, plates, paper, etc., are the water-soluble cellulose derivatives such as well hydrolyzed cellulose acetate (described in U. S. Patent No. 2,110,491 of Salo) and cellulose esters of hydroxy monocarboxylic acids, such as lactic or glycolic, and salts of cellulose esters of dicarboxylic acids, such as phthalic (described in U. S. Patent No. 2,127,573 of Sheppard and U. S. Patent No. 2,127,621 of Staud), as well as polyvinyl alcohol and hydrolyzed polyvinyl acetate (described in applications of Wesley G. Lowe, Serial Nos. 318,559 and 318,560, filed February 12, 1940) and water-soluble polyvinyl acetals (described in an application of Charles R. Fordyce, Serial No. 221,584, filed July 27, 1938, Patent No. 2,211,323). When colloids other than gelatin are used, it may be desirable to coat them at different temperatures. 75

In the claims appended hereto, where a "hydrophilic colloid depositable from a predominantly aqueous medium" is referred to, it will be understood to mean any hydrophilic colloid which can be deposited from a medium which is predominantly aqueous, the remainder of the medium being an organic solvent which contributes to the dispersibility of the colloid; examples of such organic solvents for this purpose are acetone, ethyl alcohol, ethylene glycol, monoacetin and pyridine.

What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. Photographic sensitive material comprising a layer of a hydrophilic colloid depositable from a predominantly aqueous medium, said layer containing from 0.75% to 10% of a di-(polyalkylene glycoxy) alkane in which the alkenyl radical is selected from the group consisting of the aliphatic alkenyl radicals containing from 8 to 18 carbon atoms and the di-cyclohexenyl dialkyl methanes in which each alkyl radical contains less than 3 carbon atoms, each polyalkylene glycoxy chain contains from 5 to 20 alkylene glycol radicals, and the alkylene radical is selected from the group consisting of ethylene and propylene.

2. Photographic sensitive material comprising a gelatin layer containing from 0.75% to 10% of a di-(polyalkylene glycoxy) alkane in which the alkenyl radical is selected from the group consisting of the aliphatic alkenyl radicals containing from 8 to 18 carbon atoms and the di-cyclohexenyl dialkyl methanes in which each alkyl radical contains less than 3 carbon atoms, each polyalkylene glycoxy chain contains from 5 to 20 alkylene glycol radicals, and the alkylene radical is selected from the group consisting of ethylene and propylene.

3. Photographic sensitive material comprising a base and two superposed gelatin layers, in which the gelatin layer nearer the base contains from 0.75% to 10% of a di-(polyalkylene glycoxy) alkane in which the alkenyl radical is selected from the group consisting of the aliphatic alkenyl radicals containing from 8 to 18 carbon atoms and the di-cyclohexenyl dialkyl methanes in which each alkyl radical contains less than 3 carbon atoms, each polyalkylene glycoxy chain contains from 5 to 20 alkylene glycol radicals, and the alkylene radical is selected from the group consisting of ethylene and propylene.

4. Photographic sensitive material comprising a base; a photo-sensitive gelatin emulsion layer and a gelatin overcoating on the emulsion, in which the photo-sensitive gelatin emulsion layer contains from 0.75% to 10% of a di-(polyalkylene glycoxy) alkane in which the alkenyl radical is selected from the group consisting of the aliphatic alkenyl radicals containing from 8 to 18 carbon atoms and the di-cyclohexenyl dialkyl methanes in which each alkyl radical contains less than 3 carbon atoms, each polyalkylene glycoxy chain contains from 5 to 20 alkylene glycol radicals, and the alkylene radical is selected from the group consisting of ethylene and propylene.

5. Photographic sensitive material comprising a gelatin layer containing from 0.75% to 10% of a di-(polyethylene glycoxy) decane.

6. Photographic sensitive material comprising a gelatin layer containing from 0.75% to 10% of a 4:4'-di-(polyethylene glycoxy-cyclohexyl) dimethyl methane.

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