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PHOTOGRAPHIC GELATIN LAYER CONTAINING A N-ACYLATED AMINO ACID

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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 gelatino-silver-halide layers and, in fact, the spreading of any 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 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 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 water-soluble N-acylated aliphatic amino carboxylic acids and their salts, in which the acyl radical is the radical of an acid selected from the group consisting of the aliphatic acids of from 8 to 18 carbon atoms and the alicyclic acids. In the term "aliphatic amino carboxylic acids" I mean to include not only the simple amino-acids, but the polypeptides, whether they be prepared synthetically or by the degradation of natural proteins. In the term "salts" I mean to include not only the inorganic salts, such as the sodium salts, but the organic salts, such, for instance, as the ethanolammonium salts, the trimethylammonium salts, the trimethylol-methyl ammonium salts, and the methyldimethylol-methyl ammonium salts: that is to say, the salts formed with the organic bases ethanolamine, trimethylamine, amino trimethylol methane and 2-methyl 2-amino propanediol. Among the aliphatic amino carboxylic acids, I may mention, by way of example, glutamic acid, glycylglycine, glycylalanine, and the mixtures of polypeptides and/or simple amino acids obtained by the hydrolysis of proteins, for instance, casein, gelatin, and zein. Among the aliphatic acids of from 8 to 18 carbon atoms and the alicyclic acids I may mention, by way of example, lauric, myristic, pelargonic, oleic, ricinoleic, naphthenic, abietic and hydroabietic acids, and the mixture of acids obtained from coconut oil. The preparation of N-acylated aliphatic amino carboxylic

acids and their inorganic salts is described in U. S. Patents 2,015,912 of F. Sommer, 2,063,987 of H. Dreyfus, and 2,113,819 of N. B. Tucker, and in British Patents 425,370 and 435,481. The organic salts may be prepared by dissolving the sodium salt of the N-acylated aliphatic amino carboxylic acid in water, precipitating the free N-acylated aliphatic amino carboxylic acid by means of 1:1 hydrochloric acid, separating by decantation and redissolving in water containing the organic base. The salt is obtained as a gummy material by evaporation of the liquid in vacuo at 50° C.

These N-acylated aliphatic amino carboxylic acids or their salts 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 0.001 to 0.5 part of spreading agent per 100 parts by weight of wet emulsion. This gives a spreading agent content of 0.01% to 5% in the dried emulsion layer. They have not 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 N-acylated aliphatic amino carboxylic acids or their salts, above 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 glycollic, 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.

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 0.01% to 5% of a compound selected from the group consisting of the water-soluble N-acylated aliphatic amino carboxylic acids and their salts, in which the acyl radical is the radical of an acid selected from the group consisting of the aliphatic acids of from 8 to 18 carbon atoms and the alicyclic acids.

2. Photographic sensitive material comprising a gelatin layer containing from 0.01% to 5% of a compound selected from the group consisting of the water-soluble N-acylated aliphatic amino carboxylic acids and their salts, in which the acyl radical is the radical of an acid selected from the group consisting of the aliphatic acids of from 8 to 18 carbon atoms and the alicyclic acids.

3. Photographic sensitive material comprising a base and two superposed gelatin layers, in which the gelatin layer nearer the base contains from 0.01% to 5% of a compound selected from the group consisting of the water-soluble N-acylated aliphatic amino carboxylic acids and their salts, in which the acyl radical is the radical of an acid selected from the group consisting of the aliphatic acids of from 8 to 18 carbon atoms and the alicyclic acids.

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 0.01% to 5% of a compound selected from the group consisting of the water-soluble N-acylated aliphatic amino carboxylic acids and their salts, in which the acyl radical is the radical of an acid selected from the group consisting of the aliphatic acids of from 8 to 18 carbon atoms and the alicyclic acids.

5. Photographic sensitive material comprising a gelatin layer containing from 0.01% to 5% of the sodium salt of the N-lauroyl compound of the hydrolysis products of casein.

6. Photographic sensitive material comprising a gelatin layer containing from 0.01% to 5% of the sodium salt of the N-lauroyl compound of the hydrolysis products of gelatin.

7. Photographic sensitive material comprising a gelatin layer containing from 0.01% to 5% of the sodium salt of the N-lauroyl compound of the hydrolysis products of zein.

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