Patented Feb. 8, 1949

2,461,476

UNITED STATES PATENT OFFICE

2,461,476

GELATIN SUBBING COMPOSITIONS CONTAINING LACTONES OR HYDROXY LACTONES

Frank J. Kaszuba, Binghamton, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application December 18, 1946, Serial No. 717,096

8 Claims. (Cl. 106—135)

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This invention relates to photographic film and particularly to subbing compositions therefor.

It is known that a gelatino silver-halide emulsion will not adhere to an untreated film base. An intermediate or subcoating layer is necessary to prevent frilling of the gelatin layer when wet, or stripping when dry. Since hardened gelatin, as used for glass plates does not adhere to a film base, it is necessary to use a mixture of gelatin with an organic solvent for the material of the film base, such as acetone, ethyl acetate, an alcohol-ether or an alcohol-acetone mixture. Gelatin is insoluble in these organic solvents and the film base is insoluble in water, but it is possible to prepare dispersions consisting of gelatin in a mixture of one of the organic solvents and water with a volatile organic acid, such as acetic acid, and the like, as a dispersing agent.

Many volatile and non-volatile organic acids have heretofore been used as dispersing agents for the gelatin in subbing compositions. It has been found, however, that the use of these acids causes a decrease in sensitivity and artificial ageing of the gelatino silver-halide emulsion layer. This effect is due primarily to the acidic nature of the dispersing agent. Moreover, subbing solutions containing a dispersing agent possessing acidic characteristics have a tendency to corrode the film-making machinery and the solvent recovery system which is customarily a part thereof.

The present invention has as an object to overcome the above-mentioned difficulties and to provide a method of dispersing gelatin in a subbing composition by means of dispersing agents, which will not desensitize and artificially age the gelatino silver-halide emulsion layer and which will not corrode the film-making machinery or solvent recovery system connected therewith.

Another object is to provide a non-desensitizing, non-corrosive dispersing agent for gelatin in subbing compositions.

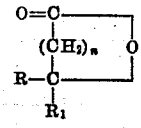
A further object is to provide a new type of gel solution in which the gelatin is dispersed by means of a non-desensitizing, non-corrosive dispersing agent, which has no adverse effect upon photographic gelatino silver-halide emulsions.

Other objects will appear from the following description.

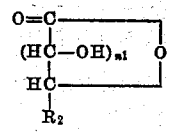
These objects are accomplished by the use, as dispersing agents in gelatin subbing compositions,

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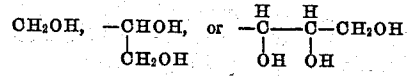
of lactones and hydroxy lactones, characterized by the following general formulae:



and



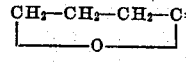
wherein R represents either hydrogen, methyl or ethyl, R_1 represents either hydrogen or methyl, R_2 represents hydrogen,



n represents a positive integer from 2 to 4, and n_1 represents a positive integer from 2 to 3.

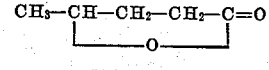
Typical lactones and hydroxy lactones corresponding to the foregoing general formulae, which are included within the scope of this invention, are as follows:

(1)



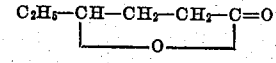
Butyrolactone

(2)



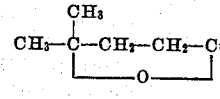
γ-Valerolactone

(3)



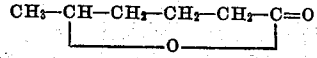
γ-Caprolactone

(4)



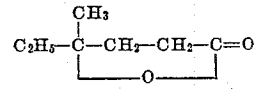
Isocaprolactone

(5)



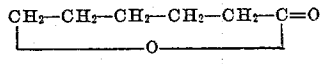
δ-Caprolactone

(6)



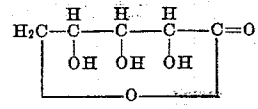
γ-Methyl-γ-caprolactone

(7)



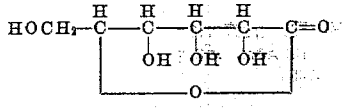
ε-Caprylolactone

(8)



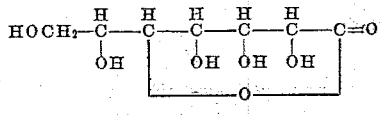
δ-Arabinolactone

(9)



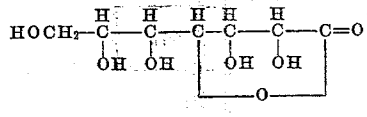
δ-Gluconolactone

(10)



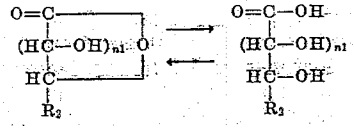
δ-Glucoheptonolactone

(11)



γ-Glucoheptonolactone

When the hydroxy lactones are dissolved in water, especially in the presence of gelatin, the lactone bridge usually opens, forming a free carboxyl group with an ionizing hydrogen atom. The carboxylated compound stabilizes the formation of the gelatin dispersion. Upon evaporation of the gelatin dispersion, any excess carboxylated compound is reconverted to a hydroxy lactone with the elimination of deleterious effects which might be caused by the hydrogen ions. Thus, in aqueous solution the hydroxy lactone exists in equilibrium with the carboxylated form which ionizes to yield hydrogen ions.



The amount of the above-mentioned lactones and hydroxy lactones, which may be employed as dispersing agents, may vary over a small range, such as, for example, from about 0.05% to 1%, and preferably from 0.1% to 0.3%. The gelatin may range from about 0.5% to 1.5% and preferably from 0.5% to 1.0%, and the water from about 1.0% to 3.0%, the balance being substantially an organic solvent or mixture of such solvents may range from 94.5% to 98.5%. All proportions are by weight.

The subbing compositions are made by mixing the components to form a free flowing composition which dries or sets within a reasonable length of time and forms a thin layer on a film base. In general, it is desirable to dissolve the lactone or hydroxy lactone (dispersing agent) in water and add to it the gelatin until the gelatin is dispersed. Slight warming and agitation will facilitate the dispersion of the gelatin in the aqueous solution of the lactone or hydroxy lactone. The organic solvent or mixtures thereof are then mixed with the aqueous dispersion of

gelatin, and the solution thus obtained is deposited on a film base in any convenient manner, such as by beading, immersion, roll application, or otherwise, the subbing operation preferably being carried out in connection with, or as a part of, the process of making the film support itself. The subbing solutions made up as above described are clear dispersions of gelatin in the solvent mixture.

The film bases used in accordance with this invention are the cellulose derivatives, e. g., cellulose nitrate, cellulose acetate, and other lower fatty acid esters of cellulose including simple and mixed esters, such as cellulose propionate, cellulose butyrate, cellulose acetate-propionate, cellulose acetate-butyrate and the like, ethers of cellulose, such as the ethyl ether, benzyl ether, and the like, or of any film-forming polymer or resin, such as polyvinyl chloride, copolymers of polyvinyl chloride and vinyl acetate, copolymers of polyvinyl chloride and vinylidene chloride, and the like, superpolymers as described in United States Patents 2,071,250-2-3 and 2,130,948.

It will be appreciated that each different type of cellulose ester, ether and mixtures thereof, including the synthetic linear superpolymers, requires a slightly different solvent or solvent combination. The solvent or solvent mixture employed does not dissolve gelatin, but must be such that it will have a solvent or at least a softening or swelling action on the film base, so as to stick or anchor the gelatin upon the area of the base which has been softened or swollen, and the term "solvent" as used in the claims should be so construed. For example, with a cellulose acetate or a superpolymer base glycerol-α-chlorohydrin, a low molecular weight alcohol, e. g., methanol, ethanol, and the like, or a ketone, such as acetone, or a mixture of glycerol-α-chlorohydrin, alcohol and acetone may be employed. The ratio of alcohol to acetone ranges from about 30-60% to 75-25%, respectively. With cellulose acetate-propionate film base, an alkyl ester, such as, for example, methyl acetate, ethyl acetate, butyl acetate, and the like, either alone or with methanol, glycerol-α-chlorohydrin or 1.4-dioxane, may be effectively employed. The weight of glycerol-α-chlorohydrin employed may vary from 1% to 5%. It may be pointed out at this point that the nature of the organic solvent or solvent mixture is immaterial so long as it wets or bites into the cellulose derivative and superpolymer film base material, and the term "solvent" as used in the claims should be so construed. Since the materials suitable for film base and their solvent properties are known, no difficulty is presented in selecting a suitable solvent or solvent mixture for use in the subbing compositions.

The invention will be further illustrated but is not intended to be limited by the following examples.

Example I

A film base of cellulose acetate was coated with the following subbing solution:

	Parts
Gelatin	1.0
Water	2.0
Butyrolactone	0.3
Glycerol-α-chlorohydrin	2.7
Methanol	32.0
Acetone	62.0

After the subbing layer had dried, the usual light-sensitive emulsion layer was coated directly

on it. After exposure and processing the emulsion adhered tenaciously to the cellulose acetate film support.

Example II

A film base of cellulose acetate-propionate having an acetyl content of 30% was coated with the following subbing solution:

	Parts
Gelatin	0.7
Water	2.1
γ-Caprolactone	0.2
Glycerol-α-chlorohydrin	2.0
Methanol	40.0
Acetone	55.0

After the subbing layer had dried, the usual light-sensitive emulsion layer was coated directly on it. After exposure and processing the emulsion adhered tenaciously to the cellulose acetate-propionate film support.

Example III

A film base prepared from poly(vinyl chloride-vinyl acetate) was coated with the following subbing solution:

	Parts
Gelatin	1.0
Water	2.7
δ-Arabinolactone	0.3
Glycerol-α-chlorohydrin	3.0
Methanol	40.0
Acetone	53.0

After the subbing layer had dried, the usual light-sensitive emulsion layer was coated directly on it. After exposure and processing, the emulsion adhered tenaciously to the synthetic linear superpolymer film support.

The specific coating solutions set forth in the above examples may be substituted by the following:

Example IV

	Parts
Gelatin	0.5
Water	1.3
δ-Glucanolactone	0.2
Ethanol	75.0
Acetone	23.0

Example V

	Parts
Gelatin	1.0
Water	2.7
Isocaprolactone	0.3
Methanol	60.0
Acetone	36.0

The photographic film bases produced according to the present invention were found to be entirely satisfactory and to give the customary physical requirements, such as, extreme strength, flexibility, and good water-resistance.

The small quantity of lactone or hydroxy lactone, which may remain with the gelatin after evaporation of the water and organic solvent from the subbing composition, has no adverse effect upon the light-sensitive emulsion layer, nor has the subbing composition any adverse effect upon the containers in which it is stored, or upon the coating equipment employed.

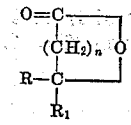
It will be understood that wherein the claims appended hereto, the term "subbing" is used, that such is intended to include the operation of applying a subbing layer from any one of the subbing compositions prepared in accordance with the present invention.

While the present invention has been described in considerable detail with reference to certain preferred procedures, materials, and uses, it is understood that the class of lactones and hydroxy lactones and their use as dispersing agents for gelatin is not limited thereto and that numerous variations and modifications described in the foregoing specification may be made. As for example, a mixture of two or more of the lactones and/or hydroxy lactones may be employed as dispersing agents.

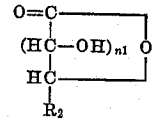
It is also understood that all the broad examples of the present invention include the preparation of gelatin solutions in general, in which the gelatin is dispersed in the solvent by means of lactones and hydroxy lactones, or mixtures thereof. All such modifications and variations are within the scope of the invention as defined by the appended claims.

I claim:

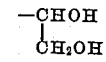
1. A gelatin composition suitable for the subbing of a photographic film support, which comprises from 0.5% to 1.5% of gelatin dispersed in from 94.5% to 98.5% of a solvent for said support by means of from 0.05% to 1.0% of a compound selected from the class consisting of those of the following formulae:



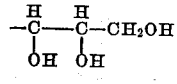
and



wherein R is a member of the group consisting of H, CH_3, and C_2H_5, R_1 is a member of the class consisting of H and CH_3, R_2 is a member of the group consisting of H,



and



n represents a numeral from 2 to 4, and n_1 represents a numeral from 2 to 3.

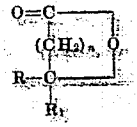
2. A gelatin composition suitable for the subbing of a photographic film support, which comprises from 0.5% to 1.5% of gelatin dispersed in from 94.5% to 98.5% of a solvent for said support by means of from 0.05% to 1.0% of butyrolactone.

3. A gelatin composition suitable for the subbing of a photographic film support, which comprises from 0.5% to 1.5% of gelatin dispersed in from 94.5% to 98.5% of a solvent for said support by means of from 0.05% to 1.0% of γ-caprolactone.

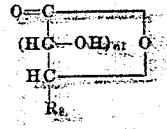
4. A gelatin composition suitable for the subbing of a photographic film support, which comprises from 0.5% to 1.5% of gelatin dispersed in from 94.5% to 98.5% of a solvent for said support by means of from 0.05% to 1.0% of δ-arabinolactone.

5. A gelatin composition suitable for the subbing of a cellulose derivative film support which comprises from 0.5% to 1.5% of gelatin dispersed in from 94.5% to 98.5% of a mixture of

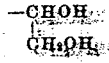
actone and methyl alcohol, and from 1.0% to 3.0% water, by means of from 0.5% to 1.0% of a compound selected from the class consisting of those of the following formulae:



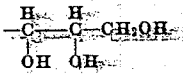
and



wherein R is a member of the group consisting of H, CH_3, and C_2H_5, R_1 is a member of the class consisting of H and CH_3, R_2 is a member of the group consisting of H,



and



n represents a numeral from 2 to 4, and n_1 represents a numeral from 2 to 3.

6. A gelatin composition suitable for the subbing of a cellulose acetate photographic film support, which comprises 1.0% of gelatin dispersed in a mixture of 62.0% of acetone, 32.0% of methyl alcohol, and 2.0% of water, by means of 0.3% of butyrolactone.

7. A gelatin composition suitable for the subbing of a cellulose acetate-propionate photographic film support, which comprises 0.7% of gelatin dispersed in a mixture of 55.0% of acetone, 40.0% of methanol, and 2.1% of water by means of 0.2% of γ-caprolactone.

8. A gelatin composition suitable for the subbing of a poly(vinyl chloride-vinyl acetate) film support, which comprises 1.0% of gelatin dispersed in a mixture of 53.0% of acetone, 40.0% of methyl alcohol, and 2.7% of water, by means of 0.3% of δ-arabinolactone.

FRANK J. KASZUBA.

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The following references are of record in the file of this patent:

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Number	Name	Date
2,313,570	Nadeau et al.	Mar. 9, 1943
2,341,877	Middleton et al.	Feb. 15, 1944

Certificate of Correction

Patent No. 2,461,476. February 8, 1949.

FRANK J. KASZUBA

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 7, line 2, claim 5, for "0.5%" read *0.05%*;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of August, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.