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GELATIN SUBBING COMPOSITIONS CONTAINING A MIXTURE OF FORMAMIDE AND GLYCEROL- α -CHLOROHYDRIN

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This invention relates to the subbing of photographic film, and more particularly to the preparation of gelatin subbing compositions in which the gelatin is dispersed therein by means of a mixture of formamide and glycerol- α -chlorohydrin.

In the manufacture of photographic film, it is necessary to affix a photo-sensitive layer to a suitable support. Usually, the support is prepared from a cellulose derivative, or from some other flexible thermoplastic material coated with a discreet layer of a cellulose derivative. Whatever its composition, the support is hydrophobic. On the other hand, the colloidal carrier in the photo-sensitive layer is usually some hydrophilic substance, such as gelatin. When gelatin is coated on a film base, it is found that there is little or no adhesion between the two. As a matter of fact, the hydrophilic layer can be peeled from the support with complete ease.

In order to insure adequate adhesion between the two layers, it is necessary to impart a hydrophilic nature to the surface of the film base. This is accomplished by treating the support with what is known to the art as a "subbing solution." This is merely an organosol of gelatin or some other water sensitive substance. It is believed that the organic solvents in the subbing solution soften the surface of the film base so that the hydrophilic material is simultaneously deposited in the said surface. Thus, when a "subbed" support is coated with a photo-sensitive layer excellent adhesion results between the two.

Hitherto, gelatin organosols were prepared according to the following formula:

	Grams
Gelatin	1.00
Water	4.00
Acid (acetic acid, and the like as a dispersing medium)	2.00
Methanol	43.00
Acetone	50.00

Although excellent adhesion is obtained by the use of a subbing solution of this type, it frequently gives rise to serious desensitization of the silver-halide photographic emulsions, especially when these emulsions are of the type which are highly sensitive to actinic rays.

This defect is apparently caused by the acid present in the sub layer; yet if the acid is left out of the composition, the gelatin cannot be dispersed in the organic solvents in a sufficient quantity to effect suitable adhesion in the finished film. Moreover, the presence of an acid has the disadvantage in that it volatilizes during the sub-

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bing operation and corrodes 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 difficulty and to provide an improved method of dispersing gelatin in a subbing composition by means of dispersing agents which will not adversely affect the properties of the finished film, nor corrode the film-making machinery or solvent recovery system connected therewith.

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

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

Other objects and advantages will appear hereinafter.

These objects are accomplished by the use of a mixture of formamide and glycerol- α -chlorohydrin as the gelatine-dispersing medium. It has been found that if the water and organic acid in a typical gelatin subbing composition are replaced by the said mixture, excellent dispersions of gelatin are obtained, which serve as suitable subbing compositions, giving satisfactory adhesion without desensitization of the silver-halide emulsion layer during storage and prolonged ageing.

During the experimentation which led to my invention, I found that acetamide could not be substituted for the formamide due to the fact that the former is a solid at room temperature and its use is impractical. Various dichlorohydrins were also considered as possible substitutes for the glycerol- α -chlorohydrin, but were found to be of too limited stability. Glycerol, glycols, ethylene chlorohydrin, and the like, were also tried, but none of them possessed the necessary solvent action that glycerol- α -chlorohydrin exerts on cellulose derivatives and other water-insoluble film-forming materials. When formamide was used alone, such a large quantity was necessary that drying difficulties were encountered after the subbing operation. Formamide with glycerol, or with a glycol, was found to be inoperative. On the other hand, when glycerol- α -chlorohydrin is used alone, the gelatin is dispersed very slowly, since chlorohydrin is not efficient as a dispersing medium in the presence of large amounts of organic solvents.

The amount of the foregoing mixture, which may be employed as a dispersing agent, may vary over a small range such as, for example, from about 5% to 20% and preferably from 8% to 15% of a 1:1 or 1:2 mixture of formamide and glycerol- α -chlorohydrin, respectively. The gelatin may range from about 0.5% to 1.5% and preferably from 0.5% to 1%. The phase in which the gelatin is dissolved consists substantially of an organic solvent or a mixture of such solvents. All proportions are by weight.

The subbing compositions are made by mixing the components in various ways in proportions so as 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 gelatin in a 1:1 or 1:2 mixture of formamide and glycerol- α -chlorohydrin, respectively, and add to it the necessary solvent until the gelatin is completely dispersed therein. Slight warming and agitation will facilitate the dispersion of the gelatin in the dispersion mixture. The organic solvents such as alcohol, acetone, ethylene dichloride, methyl cellosolve, or other solvents normally employed in subbing compositions, or mixtures thereof, are then mixed with the dispersion of gelatin and the solution thus obtained is coated on the film base in any convenient manner.

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 photographic film support, 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 application of the subbing solution according to the present invention may be carried out in any manner well-known to those skilled in the art, such as by beading, immersion, roll application, etc. The film base or support may be any cellulose organic derivative composition usually used for this purpose. It may consist of a simple ester such as cellulose acetate, cellulose triacetate, a mixed ester such as cellulose acetate-propionate, cellulose butyrate, cellulose acetate-butyrate, ethers of cellulose, such as the methyl ether, ethyl ether, and the like, or of any film-forming polymer or resin such as polyvinyl chloride, copolymers of polyvinyl chloride-vinyl acetate, copolymers of polyvinyl chloride-vinylidene chloride, superpolymers as disclosed in United States Patents 2,071,250 and 2,071,252, and the like.

It will be appreciated that each different type of cellulose ester, ether and mixtures thereof, including the synthetic polymer, requires a slightly different solvent or solvent combination. The solvent or solvent mixture employed must be such that it will have a solvent, or at least a softening or swelling action on the cellulose derivative and the synthetic polymer support, so as to stick or anchor the gelatin upon the area of the support which has been softened or swollen. For example, with a cellulose acetate or a superpolymer base a low molecular weight alcohol, e. g., methanol, ethanol, and the like, or a ketone, such as acetone or a mixture of alcohol or acetone, may be employed. The average ratio of alcohol to acetone ranges from about 50-50% to 75-25%, respectively. The most practical results, however, may be determined by a few simple experi-

ments. 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 1,4-dioxane, may be effectively employed.

The gelatin subbing compositions, prepared in accordance with the present invention, may be applied to one or both sides of a suitable photographic film support.

The method of subbing a photographic film base is conveniently illustrated by the following examples, it being understood that they are illustrative only and should not be construed as limitative of the present invention.

Example I

A gelatin solution was made up having the following composition:

	Parts
20 Gelatin -----	1.0
Formamide -----	5.0
Glycerol- α -chlorohydrin -----	10.0
Methanol -----	42.0
Acetone -----	42.0

The formamide and glycerol- α -chlorohydrin were added to the gelatin and the mixture stirred until solution was effected. Gentle warming accelerates the process. After mixing thoroughly, it is slowly added to the mixture of acetone and methanol with adequate stirring.

The subbing composition thus obtained is a clear dispersion in which the gelatin is completely dispersed.

A film support of cellulose acetate was led through an immersion type hopper containing the foregoing solution. The support, after leaving the subbing apparatus, was led through an appropriate drying apparatus maintained at a temperature of 120-200° F., where the solvents were evaporated from the surface of the support.

Example II

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

	Parts
Gelatin -----	1.0
Formamide -----	4.0
50 Glycerol- α -chlorohydrin -----	4.0
Methanol -----	45.5
Acetone -----	45.5

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 a poly (vinyl chloride-vinyl acetate) was coated with the following subbing composition:

	Parts
Gelatin -----	1.0
65 Formamide -----	4.5
Glycerol- α -chlorohydrin -----	9.0
Methanol -----	34.0
Ethylene dichloride -----	51.5

When 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 photographic film bases produced accord-

ing 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 the mixture of formamide and glycerol- α -chlorohydrin, which may remain with the gelatin after evaporation of the solvent or solvent mixture from the subbing composition, has no adverse effect upon the light-sensitive emulsion layer nor has the subbing composition any adverse effect upon the container 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 dispersing a subbing layer from any one of the subbing compositions prepared in accordance with the present invention.

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 an organic solvent for said support by means of from 5 to 20% of a mixture of formamide and glycerol- α -chlorohydrin in the ratio ranging from 1:1 to 1:2 respectively.

2. A gelatin composition suitable for the subbing of a cellulose acetate photographic film support which comprises from 0.5% to 1.5% gelatin dispersed in a mixture of methanol and acetone, by means of from 5 to 20% of a mixture of formamide and glycerol- α -chlorohydrin in the ratio ranging from 1:1 to 1:2 respectively.

3. A gelatin composition suitable for the subbing of a photographic film support which consists of the following constituents:

Parts by weight

	Gelatin	1.0
	Formamide	5.0
	Glycerol- α -chlorohydrin	10.0
5	Methanol	42.0
	Acetone	42.0

4. A gelatin composition suitable for the subbing of a photographic film support which consists of the following constituents:

Parts by weight

	Gelatin	1.0
	Formamide	4.0
	Glycerol- α -chlorohydrin	4.0
15	Methanol	45.5
	Acetone	45.5

5. A gelatin composition suitable for the subbing of a photographic film support which consists of the following constituents:

Parts by weight

	Gelatin	1.0
	Formamide	4.5
	Glycerol- α -chlorohydrin	9.0
25	Methanol	34.0
	Ethylene dichloride	51.5

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REFERENCES CITED

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

UNITED STATES PATENTS

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