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SUBBING SOLUTION FOR PHOTOGRAPHIC **FILMS**

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This invention relates to the manufacture of photographic materials, and more particularly to the preparation of gelatin subbing solutions in which the gelatin is dispersed therein by meansof various easily decomposable tetraalkyl ammonium hydroxides.

In the manufacture of photographic film it is necessary to deposit on the usual cellulose derivative support or film base an extremely thin coating of gelatin in order to prepare the sur- 10 face of the material for the permanent adhesion of the light-sensitive emulsion thereto. It is known that the keeping qualities and other properties of the finished film are dependent to a very great extent upon the nature of the gel sub 15 and the manner in which it is applied to the support. It is accordingly a matter of prime importance that the gelatin be uniformly dispersed in the subbing solution and that the dispersing agent be of such nature that it will not adversely 20 near or equal to that of the emulsion. affect the properties of the finished film, nor interfere with the process of manufacture. Many different dispersing agents have heretofore been used for this purpose, but all have possessed certain serious drawbacks which have 25 made their use inconvenient or expensive. For example, the use of volatile acids has been suggested, but it is found that they are disadvantageous because of the fact that they volatilize during the subbing operation and corrode the film 30 making machinery and the solvent recovery system which is customarily a part thereof. In order to overcome this difficulty it has been proposed to use certain non-volatile acids, but the use of such agents has the serious disadvantage 35 that the acid remains in the gel sub and exerts a destructive or desensitizing action on the sensitive emulsion.

The present invention has as an object to overcome the above-mentioned prior art difficulties 40 and to provide a method of dispersing gelatin in a subbing solution by means of dispersing agents which will not corrode the film-making machinery or solvent recovery system connected therewith and which will not remain as such in the 45 support and contaminate or desensitize the photographic emulsion. Another object is to provide a non-volatile and easily decomposable agent for dispersing gelatin in a solution or dispersion thereof. A further object is to provide a new type of gel solution in which the gelatin is dispersed by means of a non-volatile, non-corrosive dispersing agent which has no adverse effect upon photographic emulsions. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broader aspects, comprises the use as dispersing agents in gel subbing solution of various tetraalkyl ammonium hydroxides which, although stable at ordinary room temperatures, are, nevertheless, easily decomposable into volatile or non-volatile, non-corrosive compounds at temperatures generally employed in the manufacture and the subbing of photographic film support and makes possible the preparation of a sub whose pH is near or equal to that of the emulsion for which the base is intended. Among these hydroxides may be mentioned trimethyl benzyl ammonium hydroxide and tetramethyl ammonium hydroxide. The decomposition products are tertiary amines and alcohols, none of which affect the sensitivity of emulsions in contact with them and in addition they maintain the pH level of the subbing layer

In the following examples and descriptions we have set forth several of the preferred embodiments of our invention, but they are included merely for purposes of illustration and not as a limitation thereof.

Our invention may be conveniently illustrated by the subbing of a cellulose acetate support. For this purpose we make up a gel subbing solution as follows:

Example 1

		r cent
	Gelatin	1.0
	Trimethyl benzyl ammonium hydroxide	
	Water	5.0
)	Acetone	65.95
	Methanol	28.0

This solution is applied to the cellulose acetate support 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. It is found that a subbing solution made as above described is a clear water-white liquid in which the gelatin is completely dispersed. After the application of the subbing solution to the film support, the support is subjected to a temperature of about 180-260° F. The effect of temperature is to decompose the trimethyl benzyl ammonium hydroxide into a tertiary amine and an alcohol a portion of which though retained in the gelatin layer laid down on the film has no desensitizing or other adverse action on the emulsion which is 55 subsequently applied to the film. After the subbing operation is completed, the subbed support is coated with the light sensitive emulsion in the usual manner.

Other gelatin solutions suitable for the subbing of cellu.ose acetate and other types of cellulose derivative supports are as follows:

Example 2

Per cent	
Gelatin 1.0	
Tetramethyl ammonium hydroxide 0.0	5
Water 9.8	
Acetone 30.1	
Methanol 59.0	5

Example 3

Pe	rcent
Gelatin	1.0
Tetramethyl ammonium hydroxide	
Water	
Methanol	89.0

While we have found it convenient to illustrate our invention by reference to gelatin solutions suitable for the subbing of cellulose acetate film support, our invention is in no sense limited to the subbing of this particular type of support, 25 as it may be applied with equal success to the treatment of almost any type of cellulose derivative material, providing the necessary adjustments in the proportion and kind of solvent constituents used in the subbing solution are made. 30 As is well known to those skilled in the art, each different type of cellulose derivative, in general, requires a slightly different solvent combination. It may be pointed out at this point that the gel subbing solution is of a somewhat different nature than a gelatin emulsion, in that it must contain components that have a solvent or at least a softening or swelling action on the cellulose derivative material of the support, that is, these solvent components must wet and "bite into" the 40 cellulose derivative, as otherwise it would be impossible to anchor or stick the gelatin to the support. These solvent components comprise a wide range of solvents, typical examples being acetone, methyl alcohol, ethyl alcohol, methyl cellosolve and others. We generally employ an amount of tetralkyl ammonium hydroxide equal to 5-10% of the weight of gelatin in the subbing solution.

It will be evident that our invention has completely solved the extremely troublesome problem of obtaining the necessary degree of dispersion of gelatin in subbing solutions without the deleterious effects heretofore resulting from the use of corrosive volatile acids, or non-corrosive, non-volatile acids, or decomposable organic acids. On the contrary, no material such as an acid which would lower the emulsion pH comes in contact with the emulsion.

The decomposition products of the hydroxides which may remain in the film are of such a nature that either they are neutral or slightly basic and do not adversely affect the light sensitive layer. In fact it is believed that during the curing of the subbing layer, the decomposition products are substantially totally volatilized.

The use of tetralkyl ammonium hydroxides is intended in no way to simulate the activities of buffers since no appreciable regulation of the emulsion pH is possible with slightly basic ter-70 tiary amines which may remain in the sub layer after decomposition of the quaternary ammonium hydroxides.

The tetralkyl ammonium hydroxides are typical of the easily decomposable basic compounds 75

which will disperse gelatin in the manner described in our invention. However, there are other quaternary hydroxides such as tetralkyl phosphonium hydroxides, tetralkyl arsonium hydroxides, and tetralkyl stilbonium hydroxides which are comparably basic in nature and are contemplated for use in our invention in the manner described. These are decomposable with heat in a manner similar to the quaternary am-

By "alkyl" as used herein we mean to include substituted alkyls such as benzyl.

While our invention is best illustrated by reference to the preparation of gelatin solutions suitable for the subbing of photographic film support, it is understood that it is not limited to this particular application, as in its broader aspects it includes the preparation of gelatin solutions in general in which the gelatin is dispersed in the solvent by means of the tetralkyl ammonium hydroxides described herein.

What we claim is new and desire to secure by Letters Patent is:

- 1. A gelatin solution suitable for the subbing of photographic film support which comprises gelatin dispersed in an organic solvent solution by means of a tetralkyl ammonium hydroxide decomposable into non-corrosive compounds at temperatures of 180-260° F.
- 2. A gelatin solution suitable for the subbing of photographic film support which comprises gelatin dispersed in an organic solvent solution by means of a tetralkyl ammonium hydroxide selected from the group consisting of trimethyl benzyl ammonium hydroxide and tetramethyl ammonium hydroxide.
- 3. A gelatin solution suitable for the subbing of photographic film support which comprises gelatin dispersed in an organic solvent solution by means of trimethyl benzyl ammonium hydroxide.
- 4. A gelatin solution suitable for the subbing of photographic film support which comprises gelatin dispersed in an organic solvent solution by means of tetramethyl ammonium hydroxide.
- 5. A gelatin solution suitable for the subbing of a cellulose derivative photographic film support which comprises gelatin dispersed in a mixture of acetone, methyl alcohol, and water by means of a tetralkyl ammonium hydroxide selected from the group consisting of trimethyl benzyl ammonium hydroxide and tetramethyl ammonium hydroxide.
- 6. A gelatin solution suitable for the subbing of a cellulose acetate photographic film support which comprises gelatin dispersed in a mixture of acetone, methyl alcohol, and water by means of trimethyl benzyl ammonium hydroxide.
- 7. A gelatin solution suitable for the subbing of a cellulose acetate photographic film support which comprises gelatin dispersed in a mixture of acetone, methyl alcohol, and water by means of tetramethyl ammonium hydroxide.
- 8. The method of subbing a photographic film support which comprises applying thereto an organic solvent solution of gelatin in which the gelatin is dispersed by means of a dispersing agent selected from the group consisting of trimethyl benzyl ammonium hydroxide and tetramethyl ammonium hydroxide, subjecting the film to a temperature of 180–260° F., whereby the solvents and volatile constituents are removed from the deposited layer and the dispersing agent is decomposed into non-corrosive compounds.
 - 9. The method of subbing a photographic film

support which comprises applying thereto an organic solvent solution of gelatin in which the gelatin is dispersed by means of trimethyl benzyl ammonium hydroxide, subjecting the film to vents and volatile constituents are removed from the deposited layer and the dispersing agent is decomposed into non-corrosive compounds.

10. The method of subbing a photographic film support which comprises applying thereto an 10 organic solvent solution of gelatin in which the gelatin is dispersed by means of tetramethyl ammonium hydroxide, subjecting the film to a temperature of 180-260° F., whereby the solvents and

volatile constituents are removed from the deposited layer and the dispersing agent is decomposed into non-corrosive compounds.

11. The method of subbing a photographic film a temperature of 180-260° F. whereby the sol- 5 support which comprises applying thereto an organic solvent solution of gelatin in which the gelatin is dispersed by means of a tetralkyl ammoniuim hydroxide, treating the film at a temperature at which the dispersing agent is decomposed into non-corrosive compounds and the solvents and volatile constituents are removed from the layer.

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