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SENSITIZING AGENT FOR PHOTOGRAPHIC EMULSIONS

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8 Claims. (Cl. 95—7)

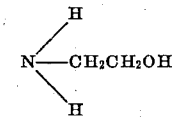
This invention relates to a material and method for sensitizing photographic films, and particularly to a substance and method useful for hypersensitizing color-sensitized film.

In our co-pending application Serial No. 371,713, filed June 17, 1929, we have disclosed the usefulness of triethanolamine as a sensitizer for light sensitive silver halide emulsions. The present application covers the use of this substance and its equivalents and is to that extent a continuation of said application.

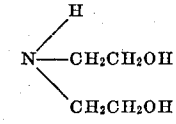
Previous work in this field has consisted largely of the development of various color-sensitizing dyes, of various substances whose presence in the emulsion enhances sensitivity, and of the methods of so-called hypersensitizing consisting of bathing plates or film, especially panchromatic materials. The use of the words "sensitizing" and "hypersensitizing" may at times have been confusing. By derivation they are scarcely capable of clear differentiation. We, however, prefer to use them in the following sense. By a "sensitizer" we imply any substance which, added to the emulsion, confers on it a range of sensitivity not already inherent in such emulsion. By a "hypersensitizer" we indicate a substance which, introduced into the emulsion at any stage, either at the time of making or later, as for instance by bathing, enhances the sensitivity, or increases it in the same range as previously present. Therefore, a sensitizer, for example, produces a sensitivity to a certain band of the spectrum or wave length range, which the emulsion would not otherwise have possessed. The emulsion may have been relatively insensitive to any or all wave lengths without the addition of the sensitizer. On the other hand a hypersensitizer increases the total sensitivity of the emulsion but in the sense in which we use this term, it does not usually change or extend the sensitivity range. That is, while the spectral range to which the emulsion is sensitive remains the same, the sensitivity in this range is usually greatly increased.

As indicated above triethanolamine is a compound not hitherto known for the purpose and useful as a hypersensitizer and sensitizer and one which moreover confers valuable properties on an emulsion. Equivalent substances are the other substituted ammonia compounds in which one or more of the hydrogen atoms in ammonia is replaced by a hydroxyalkyl group and the other nitrogen bonds not so satisfied join the nitrogen atom to hydrogen or an alkyl group. These substances may be more tersely described as alkyl amines containing one or more hydroxyalkyl groups. This classification will include the hydroxyalkyl amines and alkyl amino alcohols. Examples of this group are: Monoethanolamine, diethanolamine, β-diethylamino ethyl alcohol, β-diethylamino propyl alcohol, and λ-diethylamino propyl alcohol. The chemical structure of these substances follows:

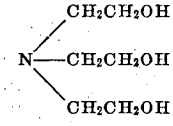
1. *Monoethanolamine*



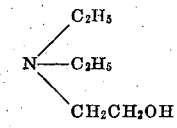
2. *Diethanolamine*



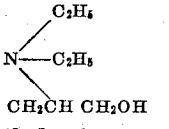
3. *Triethanolamine*



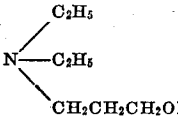
4. *β-Diethylamino ethyl alcohol*



5. *β-Diethylamino propyl alcohol*



6. *λ-Diethylamino propyl alcohol*



We may use these substances in one of three ways.

1. The substance may be added to or incorporated in the ingredients of the support. This method has been disclosed in our co-pending application and is particularly useful where the substance is also of value in the support itself. This

is true, for example, of triethanolamine, which renders a support of cellulose acetate or cellulose nitrate more flexible. When such a substance is incorporated in the base, the action appears to be that when the support has been coated with a light sensitive emulsion the emulsion will gradually be sensitized or hypersensitized upon standing by the gradual transfusion of some of the hypersensitizer into the emulsion coating of the film.

2. The substance may be introduced into the emulsion by bathing. We have also disclosed this method in our previous application. To carry out this method it is only necessary to prepare a solution of the hypersensitizer in distilled water, bathe the plate or film in this solution for a short time, and then dry it.

3. The substance may be incorporated in the emulsion. This will be valuable in certain cases for hypersensitizing, and in certain others will be more valuable for the improvement of other physical characteristics.

Our invention is more specifically carried out as follows:

Method 1.—Fifty grams of acetone soluble cellulose acetate are dissolved in a mixture of 215 cc. of acetone and 10 cc. of triethanolamine for the production of a good acetate dope giving a film of a high degree of flexibility. After forming, this support is then dried and coated with the desired emulsion. A satisfactory support may also be produced by dissolving 50 grams of acetone soluble cellulose acetate in a mixture of 225 cc. of acetone and 2.5 cc. of triethanolamine.

Method 2.—For the ordinary purposes of hypersensitizing, as for example, hypersensitizing panchromatic film by bathing, the procedure is as follows: A solution of the hypersensitizer of about the concentration range 0.2 to 0.5% in distilled water is made. To this solution it may be desirable to add about 1% of Ethyl Alcohol if the solution is not perfectly clear. In this solution the panchromatic film is bathed for approximately two minutes at 45 degrees Fahrenheit. After bathing the film is squeegeed with moist cotton and dried at 70 degrees Fahrenheit with air circulated by an electric fan. It will be obvious that in this method the concentration of the hypersensitizing bath and the time of bathing are variable and may be adjusted to give most satisfactory results.

Method 3.—The substance may be incorporated in the emulsion. In carrying out this method many variable enter and it will be necessary to adjust the procedure to every individual case to obtain a satisfactory result. The method is, of course, especially useful with panchromatic emulsions containing dyes which sensitize more strongly to the red, especially dyes of the type more recently made available. The addition of the hypersensitizer is made directly to the emulsion at the time of making, and before coating, and the amount added will be of about the order of 0.5% of the weight of the emulsion.

These materials may, however, be added to emulsions at any time and in other proportions, for purposes other than hypersensitizing. It is thus found that the addition of small quantities of triethanolamine to an emulsion will produce a more flexible and pliable coating, and the substance may be added therefore with this object alone. It will be found, however, that the general sensitivity of the emulsion is enhanced by the addition of one of these substances.

Substances of the type we have disclosed have marked advantages over the type of hypersensitizers as heretofore employed. The compounds previously used have in general had a very strong and unpleasant odor. The substances which we disclose on the other hand are odorless, give a considerable amount of plasticity to the dried emulsion of the film, are powerful hypersensitizing agents, and produce a minimum of fog.

An additional and important advantage of the hypersensitizers here described is the fact that plates or films treated with them may be kept a relatively long time before use. Heretofore hypersensitized plates could be used only a short time immediately after the hypersensitizing step. Plates or films prepared according to this invention are useful for weeks.

As some of the compounds specified herein have individually valuable properties, when used in photographic emulsions, in addition to those which we have pointed out, we consider as included in our invention the use of the class of compounds mentioned and of the individual members of that class, for whatever purpose in connection with photographic emulsions, particularly in gelatino-silver-halide emulsions, and we consider as included in our invention all modifications and equivalents properly falling within the terms of the appended claims.

What we claim is:

1. A photographic sensitive element including a silver halide emulsion layer which contains an alkyl amine containing one or more hydroxyalkyl groups.

2. A photographic sensitive element comprising a support and a silver halide layer containing an alkyl amine having one or more hydroxyalkyl groups.

3. A photographic sensitive element comprising a silver halide emulsion layer and a support containing a cellulose derivative and an alkyl amine having one or more hydroxyalkyl groups, at least a portion of which has diffused into the emulsion.

4. A photographic sensitive element including a silver halide emulsion layer which contains a substituted ammonia compound in which one or more of the hydrogen atoms in ammonia is replaced by a hydroxyalkyl group and the other nitrogen bonds not so satisfied join the nitrogen atom to hydrogen or an alkyl group.

5. A photographic sensitive element comprising a silver halide emulsion layer, said emulsion containing triethanolamine.

6. A photographic sensitive element comprising a silver halide emulsion layer, and a support containing a cellulose derivative and triethanolamine, at least a portion of which has diffused from the support into the emulsion layer.

7. A photographic sensitive element including a silver halide emulsion layer which contains a sensitizing dye and an alkyl amine containing one or more hydroxy alkyl groups.

8. A photographic sensitive element including a silver halide emulsion layer which contains a sensitizing dye and triethanolamine.

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Certificate of Correction

Patent No. 1,925,508. September 5, 1933.

CYRIL J. STAUD ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 61, for "λ-diethyl-" read *γ-diethyl-*; line 96, last line of formula 5, for "CH_2CHCH_2OH" read CH_3CHCH_2OH; and line 97, formula 6, for "λ-Diethylamino" read *γ-Diethylamino*; page 2, line 54, for "variable" read *variables*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 31st day of October, A.D. 1933.

[SEAL]

F. M. HOPKINS,
Acting Commissioner of Patents.