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PHOTOGRAPHIC FIXING METHOD

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7 Claims. (Cl. 95—88)

This invention relates to an improved photographic fixing bath, and more particularly to a fixing bath which is adapted for use at abnormally high temperatures and which can be used after the use of a highly alkaline developer without causing reticulation.

The usual types of fixing baths are either practically neutral or are somewhat acid and include, in addition to the sodium thiosulphate, which dissolves the undeveloped silver salts, an acid sodium salt or similar acidifying agent and a hardening agent. If a film has been developed in a highly alkaline developer or has been developed at an unusually high temperature so that the gelatine is considerably softened and it is then placed in such a fixing bath, the sudden hardening of the surface accompanied by the acidifying thereof which causes a sudden contraction of the surface layer of the gelatine in relation to the lower layers has a tendency to cause reticulation. I find, however, that if the developed film is placed in a fixing bath having an alkalinity approaching that of the developer, no such reticulation occurs and a correspondingly improved photographic image results.

If an appropriate alkali is added to a sodium thiosulphate solution of ordinary concentration, it tends to soften the emulsion and render the film liable to damage in handling, and reticulation is likely to occur when the film is placed in the succeeding wash. The addition of an ordinary hardening agent to such a fixing bath does not prevent this difficulty, since the softening of the gelatine occurs before the hardening agent has time to become effective.

I secure the necessary degree of alkalinity without the foregoing objections and with a hardening, instead of a softening of the gelatine by balancing the alkali with alum. The alum reacts with the alkali to first form aluminum hydroxide, which tends to be precipitated and to then form an aluminate which remains in solution, but which has a hardening action on the gelatine. If the alkali is used up by oxidation, or otherwise, a corresponding amount of aluminum hydroxide is precipitated, thereby maintaining the alkalinity of the bath constant.

One object of the present invention is to provide an improved method for fixing photographic emulsions.

Another object of the invention is to provide a fixing method which may be used at relatively high temperatures.

Another object of the invention is to provide a fixing method which will prevent reticulation of the emulsion when either the developer or fixing bath is used at high temperatures.

Another object of the invention is to provide a fixing method which will automatically recover the dissolved silver.

Other and incidental objects of the invention will be apparent to those skilled in the art from a reading of the following specification.

In my improved fixing method I use the usual sodium thiosulphate as a fixer, and I may also add paraformaldehyde to the fixing bath as an additional hardener. The balancing of the alkali and alum may be accomplished as described and claimed in my U. S. Patents 2,199,903 and 2,199,904 of May 7, 1940, which describe such a balanced solution of alkali and alum applied to a developer where the alum acts as a buffer to the alkali.

This application is a division of my application Serial No. 306,71, filed November 30, 1939, Patent 2,321,347, in which my improved fixing bath itself is claimed, a typical formula for which is as follows:

Sodium thiosulphate		400
Alum		40–26
Sodium hydroxide		30–20
Para-formaldehyde	grams	20
Water	cc	1000

The proportion of alum and sodium hydroxide is, as indicated above, in the general ratio of 4:3. The quantity of sodium hydroxide, however, is determined by the alkalinity of the developer which preceded the fixing bath. If the developer is highly alkaline, the fixing bath should have substantially the same alkalinity which can be determined as usual by the pH value. Since there is no change in the alkalinity of the solution in which the film is immersed, there is then no tendency toward reticulation in passing the film from one solution to the other, while the hardening action of the fixing bath is sufficient to prevent any tendency toward reticulation when the film is immersed in the subsequent wash water.

There is a tendency for the alkali in the fixing bath to be gradually converted to the carbonate by the carbon dioxide in the air in contact with the surface thereof, and particularly when used for developing motion picture film, by the carbon dioxide in the air carried into the bath by the film, and this reaction releases a corresponding amount of aluminum hydroxide from the solution or in other words the alum buffers the alkali.

This aluminum hydroxide settles out in the form of a gelatinous precipitate.

The fixing bath is alkaline and not acid, and it therefore does not suddenly stop the action of the developer in the emulsion, as would an acid fixing bath. The consequence of this is that any developer in the emulsion goes into solution in the fixing bath and reduces the dissolved silver in the fixing bath. This reduced silver, which is practically in colloidal form, is precipitated with the aluminum hydroxide and the silver may be readily recovered from the resulting sludge. A further result of this action is that the fixing bath does not become saturated with silver salts and maintains its original activity over a relatively long time. If an insufficient quantity of developer to accomplish the regeneration of the fixing bath is carried over by the film, small additional quantities of developer may be added to the fixing bath for this purpose, and partly spent developer may be used, thereby recovering not only the silver in solution in the fixing bath, but also that in solution in the developer.

It will be apparent to those skilled in the art that the proportion of sodium thiosulphate or "hypo" in the solution may be varied according to the requirements of the work at hand, and it will be also apparent that not only should the alkalinity be varied as pointed out, but that the quantity of paraformaldehyde should be varied according to the degree of hardening desired. Ordinary formaldehyde may, of course, be added to the bath instead of the paraformaldehyde, but there is no point to such a procedure since the formaldehyde is converted into the paraformaldehyde, and this procedure has the disadvantage that the hardening action varies according to the degree to which the polymerization has occurred.

I claim as my invention:

1. The method of preventing reticulation of photographic emulsions including a silver halide, comprising the steps of fixing the image in a fixing bath having an alkalinity substantially the same as that of the alkaline developer in which the film was developed and an amount of alum sufficient to buffer the alkali.

2. The photographic method including the steps of developing the emulsion including silver halide in an alkaline developer and thereafter fixing in a fixing bath having substantially the same alkalinity as the developer and an amount of alum sufficient to buffer the alkali.

3. The photographic method including the steps of developing the emulsion including silver halide in an alkaline developer having a comparatively high alkalinity and thereafter fixing and hardening in a fixing bath having substantially the same alkalinity as the developer and an amount of alum sufficient to buffer the alkali.

4. The photographic method of treating an emulsion including silver halide which has been developed in an alkaline developer having a comparatively high alkalinity including fixing the emulsion in a fixing bath having substantially the same alkalinity as the developer and an amount of alum sufficient to buffer the alkali.

5. The photographic method of treating a silver halide emulsion which has been developed in a highly alkaline developer including the step of fixing and hardening the emulsion in a fixing bath having substantially the same alkalinity as the developer and an amount of alum sufficient to buffer the alkali.

6. The method of preventing reticulation of photographic emulsions including a silver halide, comprising the steps of fixing the image in a fixing bath having an alkalinity substantially the same as that of the highly alkaline developer in which the film was developed and an amount of alum sufficient to buffer the alkali.

7. The method of treating a photographic emulsion which includes a silver salt and has been developed in an alkaline developer, including the step of fixing the emulsion in a separate fixing bath which has (*a*) substantially the same alkalinity as the developer and (*b*) an amount of alum sufficient to buffer the alkali.

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