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COMBINED DEVELOPER AND FIXER

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This invention relates to a developer-fixer for developing and fixing silver halide photographic emulsions. It relates more particularly to composite solutions which both develop and fix silver halide photographic emulsions, which are quite stable and retain their activity over relatively long periods of time, even when exposed in open tanks, and which give developed and fixed films substantially free from dichroic fog and with no more, or little more, development fog than is customarily obtained with ordinary developing and fixing procedures.

A number of attempts have been made heretofore to provide developing-fixing solutions. In general, these have involved the addition of sodium thiosulfate (hypo) to developing solutions, usually in rather large amounts, for example, 100 grams to 1,000 cc. of solution, although the use of lesser quantities has been proposed. To obtain reasonable densities with such solutions, it was found necessary to make them quite alkaline. While the increase in alkalinity did enable the production of stronger images, it introduced other difficulties including instability of the solution, the production of developed pictures having a relatively coarse grain, and the like. Attempts to stabilize the solution by the use of additives such as sugars or the like, while they resulted in increased stability, introduced difficulties because of their tendency to produce dichroic fog, as did attempts to make operable solutions of lower alkalinity through the use of lesser quantities of hypo.

Particular difficulties in the use of developer-fixers have been encountered in connection with such films as are used in microfilm work, which have very thin layers of emulsion.

The present invention provides improved composite developing and fixing solutions which are quite stable, that is, may be exposed even in open tanks for periods of weeks without substantial deterioration through oxidation, which give developed pictures having good contrast and desirable image density, with little if any more of the development fog than is obtained with the usual developing and fixing procedures and which are substantially free from dichroic fog.

The composite solutions of the invention contain an organic developing agent, usually a mixture of p-methylaminophenol and hydroquinone, a fixing agent, sodium thiosulfate, one or more alkaline salts, usually sodium carbonate, a preservative, usually sodium sulfite, and an alkali metal iodide, usually potassium iodide, the pH of the solution being carefully regulated and the

ingredients, particularly the sodium thiosulfate and the iodide, being present in carefully regulated amounts, with the result that the developing and fixing proceed with the production of developed pictures having good contrast and substantially free from objectionable fog. In some cases, it is desirable to include a relatively small quantity of alkali metal, usually potassium, bromide in the solution to reduce development fog, although with some films, such as dental film, such a constituent is not necessary.

The relative proportions of the reagents used, and the pH of the composite solutions, must be carefully controlled, as it is through the proper balance of the reagents and the control of the pH of the solutions used that the desirable results obtained with the solutions of the invention are possible.

With respect to pH, it is necessary that the solutions have a pH which does not exceed 9.5, and which is above about 8.0. Solutions with a pH in the range 8.3 to 9.0 give very good results. Particularly advantageous results are obtained with solutions having a pH of about 8.5. The pH of the solutions is controlled by the amount of alkaline salt, usually sodium carbonate, which is used.

The quantity of developing agent, e. g., Metol, hydroquinone, or other developing agent, such as glycine or chlorhydroquinone, is about in accordance with customary practice in developing solutions. Thus, using mixtures of Metol and hydroquinone, from 1 to 5 grams of Metol and 4 to 10 grams of hydroquinone, per 1,000 cc. of solution, may be used. For the treatment of such films as are used in microfilm work, it is best to use not more than 3 grams of Metol per 1,000 cc. of solution, and for such films, to use the Metol and hydroquinone in a ratio of about 1 to 4 or 1 to 5. With other films, such as X-ray films, a somewhat larger ratio of Metol to hydroquinone, such as 1 to 2, can be used with advantage.

The quantity of alkali salt, such as sodium carbonate, can be varied over a relatively wide range, all that is required being that the quantity be such as to impart to the solutions a pH within the range specified above. Ordinarily around 20 to 50 grams of sodium carbonate to 1,000 cc. of solution may be used, about 30 parts giving good results, such solutions having a pH of about 8.5.

Similarly, the amount of preservative or reducing agent, usually sodium sulfite, can be varied over a relatively wide range. It serves to protect the developer against oxidation when the solution is standing, and has some part in the devel-

opment. Thus the amount of sulfite may be as little as 20 grams per 1,000 cc. Too much sodium sulfite should not be used, as excessive concentration of salts in the solutions appears to have an adverse effect upon the quality of the pictures finally produced, and therefore it is not desirable to use more than about 50 to 60 grams of sodium sulfite to 1,000 cc. of solution.

The satisfactory results which are obtained with the developing-fixing solutions of the invention are largely attributable to the appropriate control of the quantities of sodium thiosulfate (hypo) and potassium iodide, coupled with the controlled pH and the limitations on the maximum quantities of other constituents discussed above. The quantity of potassium iodide for developing-fixing solutions of the invention may vary from 0.05 to 1.0 gram per 1,000 cc. (0.005 to 0.1%). Larger quantities introduce difficulties through failure of the film to fix properly. Smaller quantities result in the production of films exhibiting dichroic fog. With certain special films, having thin emulsions, as the film for microfilm work to which reference has been made, the limitation on the quantity of potassium iodide which may be used is even more severe, that is, it is limited to from 0.2 to 0.6 gram per 1,000 cc. of solution (0.02 to 0.06%), variation from this range either up or down introducing the same type of difficulties either with respect to dichroic fog or improper fixing. Instead of potassium iodide, sodium iodide may be used in equivalent quantities, but it is a somewhat more unpleasant material to handle than potassium iodide. The amount of potassium iodide used is quite independent of whether potassium bromide is or is not used in the solutions. That is, the potassium iodide used is in no way a substitute, in part or in whole, for potassium bromide, and the important functions which it performs in the specified quantities in these solutions cannot be performed by replacement of part or all of the potassium iodide by bromide.

The proportions of sodium thiosulfate (hypo) which may be used vary from about 12 to 30 grams (with 5 molecules of water of crystallization) to 1,000 cc. of solution (1.2 to 3.0%). Larger quantities introduce difficulties because pictures processed with solutions containing great concentrations of the hypo lack the contrast which is necessary. With smaller quantities, the solutions are not adequate fixing solutions, so that while development may be satisfactory, fixing is not.

Potassium bromide may, and for some purposes advantageously or necessarily is, included in the new solutions. For the development of ordinary films at temperatures of about 68° F., the amount of potassium bromide used may be 1 gram per 1,000 cc. or less, down to zero. If the solution is to be used at higher temperatures, for example, up to 85° F. the quantity of potassium bromide used may be increased, up to about 4 grams per 1,000 cc. With such films as are used in microfilm work, about 2 grams per 1,000 cc. of solution is sufficient even for temperatures up to 85° F. or even somewhat higher. The potassium bromide functions to cut down development fog. It is important, for this reason, in microfilm, and much other development work, but is not particularly important for the development of such films as dental X-ray films. It may be replaced

by sodium bromide, but sodium bromide is not as easy to handle as is potassium bromide.

The solutions may be provided in the form of concentrates, containing a good deal less water than is used in the developing solutions themselves, and which may be diluted for use. Alternatively, the dry reagents may be dissolved in water to form the developing solution in the usual way. Little difficulty is encountered in dissolving the reagents because of the relative diluteness of the solutions.

Other conventional ingredients, such as alcohol or the like, may be included in the developing solutions, particularly where they are provided in concentrated form.

In use, the developing-fixing solutions of the invention accomplish both the developing and fixing in a single operation, eliminating the need for care with respect to the time of treatment, as it is simply necessary to immerse the film in the solution for a sufficient period of time to permit the development and fixing to take place. It is not necessary to remove the film promptly after developing and fixing, because over-development does not take place. For this reason, the solutions are well adapted for use in apparatus for the mechanical processing of film, such as are used with advantage in microfilm work, for the development of dental or other X-ray pictures, etc.

The invention will be further illustrated by the following specific example, but it is not limited thereto.

Example.—A combined developing and fixing solution for use with microfilm is prepared from the following:

	Grams
Sodium sulfite	40
Sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)	30
Metol	1
Hydroquinone	5
Potassium bromide	2
Potassium iodide	.5
Hypo ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)	13

The solution is made up to 1,000 cc. It is effective for the developing and fixing of microfilm even at temperatures as high as 85° F. or somewhat higher.

I claim:

1. A combined developing and fixing solution for silver halide photographic emulsions including a developing agent, an alkaline salt, a preservative, and from 0.005 to 0.1% of alkali metal iodide and 1.2 to 3.0% of sodium thiosulfate (calculated as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), said solution having a pH between about 8.0 and about 9.5.

2. A solution as in claim 1 which in addition contains a small quantity of alkali metal bromide.

3. A developing and fixing solution for silver halide photographic emulsions including a developing agent, an alkaline salt, a preservative, from 0.02 to 0.06% of potassium iodide and from 1.2 to 1.8% of sodium thiosulfate (calculated as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), said solution having a pH between about 8.3 and about 9.0.

4. A solution as in claim 3 which in addition contains a small quantity, not in excess of about 0.2% of alkali metal bromide.

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