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DIFFERENTIAL FIXING SOLUTION

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This invention relates to photographic fixing and more particularly to a method for differentially fixing out silver halide.

The principle of photographic fixation depends upon the solubility of silver halides in solvents such as sodium thiosulfate. In photographic processes there has been little need for a solvent solution which will dissolve one or more silver halides and leave another unaffected. However, in the field of color photography and in the reversal processes for the production of colored images there is now a need for such a method. Likewise, in the direct positive processes of black-and-white photography a method for differential fixation would be useful.

One object of the present invention is to provide a method for differentially fixing out silver halides. Another object is to describe the application of the method to color photography and black-and-white photography. Other objects appear hereinafter.

These objects are accomplished by a fixing solution containing a sufficient amount of halide that only the more soluble of a group of silver halides is soluble in the solution.

The solutions which are used contain certain well-known solvents for silver halides such as ammonia, sodium chloride, sodium thiocyanate, sodium sulfite, sodium bisulfite and mixtures of these. In addition to these, in the manner of my invention, a halide such as potassium bromide or a silver halide is added to prevent the solution of one or more silver halides. A consideration of solubility principles involving the solubility of silver halides will more fully describe my invention.

Some salts difficultly soluble in water can be dissolved in certain salt solutions due to the formation of a complex ion composed of the cation of the difficultly soluble salts and one of the constituents of the solvent solution. Thus, silver bromide is soluble in a hypo solution due to the formation of the silver thiosulfate complex ion, or in a thiocyanate solution due to the formation of silver thiocyanate complex. The extent to which a difficultly soluble salt can be dissolved in such a solution is dependent on the solubility product of the salt and on the dissociation constant for the complex. Now if the dissociation constant of the complex is smaller than the solubility product, the concentration of the silver ions in the equilibrium with the silver thiosulfate complex ions is much smaller than the silver ion concentration in equilibrium with bromide ion, and if the silver bromide is put into a thiosulfate ion solution, the silver thiosulfate complex ion is formed until the silver ion concentration is in equilibrium both with the bromide ion and the silver thiosulfate complex ion. If the solubility product is smaller than the dissociation constant of the complex, very little of the difficulty soluble salt will be dissolved by the solution containing the complex forming ion. Such is the case for silver bromide and ammonium hydroxide, in which silver ammonia complex is formed.

In the case of two different difficultly soluble salts of the same cation, whose solubility products are quite different, such as silver bromide and silver chloride, much more of the more soluble salt will be dissolved by a complex-forming solution such as ammonium hydroxide. Now if the solvent solution is saturated with the more difficultly soluble salt, the less difficultly soluble salt can still be dissolved in the solution and a differential solution of a mixture of the two salts can be affected, leaving the less soluble salt practically unaffected.

This method of differentially dissolving certain salts of the same cation has a wide application and can be specifically applied to photographic processes in which three different salts of silver are used, such as silver chloride, silver bromide, and silver iodide. For example, if an ammonium hydroxide solution or a saturated sodium chloride solution is saturated with silver bromide, this solution can be used for fixing out a silver chloride emulsion in the presence of a silver bromide emulsion without appreciable effect on the latter. Or, by saturating a solution of hypo, potassium thiocyanate, or sulfite with silver iodide, the solution can be used for fixing out a silver bromide or silver chloride emulsion in the presence of a silver iodide emulsion.

The above-mentioned solvent solutions can be generalized into any solution having an ion which forms a soluble complex with silver ion and from which the dissociation constant of the complex is of the same order of magnitude as the solubility product of silver chloride or silver bromide. In addition, silver halide solvent solutions may contain halides of metals other than silver such as potassium bromide or potassium iodide, in an amount sufficient to give the concentration of halogen ions which would be obtained if the halide were the less soluble of a group of silver halides. For example, silver chloride may be fixed out in the presence of silver bromide or silver iodide by adding to a solvent solution containing ammoniacal bisulfite the correct amount

of potassium bromide; but this solution would not fix out silver bromide in the presence of silver iodide. When to a solvent solution containing sodium thiosulfate the correct amount of iodide is added, both silver chloride and silver bromide may be fixed out in the presence of silver iodide.

These methods of differential fixation have special application in photographic reversal color processes such as disclosed in Mannes and Godowsky, Patent No. 2,252,718, granted August 19, 1941. In this process of color development an exposed multi-layer color film is given negative development and in a subsequent step in the processing treatment, the negative silver image is removed by the use of oxidizing agents. The differential fixation process of the invention may be used instead of the powerful oxidizing agents such as acid permanganate or chromate for the removal of this silver. The silver images may be first bleached with a less powerful oxidizing solution to silver halide, preferably silver chloride or silver bromide, by well-known methods, and then treated with the differential fixing solutions of the invention whereby the silver halide corresponding to the silver of the negative image is removed without affecting the silver halide to be used for the development of the positive image in color.

In a direct positive process for the production of positive photographic images by the reversal method, a negative image is recorded upon a sensitive material and after negative development, according to my invention, the negative silver image may be bleached to silver halide different than that of the original emulsion and removed in the presence of the original emulsion by application of a differential fixing solution of the invention. The positive image may be then produced in the usual manner from the sensitive silver halide remaining in the positive image area.

The following examples serve to illustrate the differential fixing solutions of my invention.

Example 1

Silver chloride may be fixed out in the presence of silver bromide by treatment with the following solution.

	Cubic centimeters
Ammonium hydroxide (conc.)	50
Water to	1,000

Saturated with silver bromide.

Example 2

Silver chloride may be fixed out in the presence of silver bromide or silver iodide by treatment with the following solution.

Ammonium hydroxide (conc.)	cc.	40
Potassium bromide	gm.	0.25
Sulfuric acid (conc.)	cc.	3
Sodium bisulfite	gm.	15
Water to	cc.	1,000

It is to be understood that the disclosure herein is by way of example and that I consider as included in my invention all modifications and equivalents falling within the scope of the appended claims.

What I claim as new and wish to secure by Letters Patent of the United States is:

1. A method for differentially fixing out silver halides which comprises saturating an ammonia solution with silver bromide and then treating a photographic element containing silver bromide and silver chloride with said solution whereby silver chloride may be fixed out in the presence of silver bromide.

2. A method for differentially fixing out silver halides which comprises adding silver iodide to a thiosulfate solution in an amount sufficient that a more soluble silver halide may be fixed out in the presence of silver iodide and then treating a photographic element containing a group of silver halides including silver iodide with said solution whereby a more soluble silver halide is fixed out in the presence of silver iodide.

3. A method for differentially fixing out silver halides which comprises adding silver iodide to a thiosulfate solution in an amount sufficient that silver bromide may be fixed out in the presence of silver iodide and then treating a photographic element containing silver bromide and silver iodide with said solution whereby silver bromide is fixed out in the presence of silver iodide.

4. A method for differentially fixing out silver halides which comprises saturating a thiosulfate solution with silver iodide and then treating a photographic element containing silver bromide and silver iodide with said solution whereby silver bromide may be fixed out in the presence of silver iodide.

5. A method for differentially fixing out silver halides which comprises adding potassium bromide to an ammoniacal bisulfite solution in an amount sufficient that silver chloride may be fixed out in the presence of silver bromide and then treating a photographic element containing silver chloride and silver bromide with said solution whereby silver chloride is fixed out in the presence of silver bromide.

6. A method for differentially fixing out silver halides which comprises adding to a silver halide solvent solution a halide having an anion in common with the less soluble of the group of silver halides in an amount sufficient to render the less soluble silver halide insoluble in said solution, and then treating a photographic element containing said group of silver halides with said solution whereby a more soluble silver halide of anion other than in said solution is fixed out in the presence of a less soluble silver halide of said group of silver halides.

7. A method for differentially fixing out silver halides which comprises adding a halide having an anion in common with the less soluble of a group of silver halides to an ammonia solution in an amount sufficient to render the less soluble silver halide insoluble in said solution, and then treating a photographic element containing said group of silver halides with said solution whereby a more soluble silver halide of anion other than in said solution is fixed out in the presence of a less soluble silver halide of said group of silver halides.

8. A method for differentially fixing out silver halides which comprises adding a halide having an anion in common with the less soluble of a group of silver halides to a thiosulfate solution in an amount sufficient to render the less soluble silver halide insoluble in said solution, and then treating a photographic element containing said group of silver halides with said solution whereby a more soluble silver halide of anion other than in said solution is fixed out in the presence of a less soluble silver halide of said group of silver halides.

9. A method for differentially fixing out silver halides which comprises adding a halide having an anion in common with the less soluble of a

group of silver halides to an ammoniacal bisulfite solution in an amount sufficient to render the less soluble silver halide insoluble in said solution, and then treating a photographic element containing said group of silver halides with said solution whereby a more soluble silver halide of anion other than in said solution is fixed out in the presence of a less soluble silver halide of said group of silver halides.

10. A method for differentially fixing out silver halides which comprises treating an exposed, developed, and bleached multilayer color film containing a group of silver halides with a solvent solution for silver halide containing a halide having an anion in common with the less soluble of said group of silver halides in an amount sufficient to render the less soluble silver halide insoluble in said solution, and then treating said photographic element with said solution whereby a more soluble silver halide of anion other than in said solution is fixed out in the presence of a less soluble silver halide of said group of silver halides.

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