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PHOTOGRAPHIC FIXING PROCEDURE AND BATHS

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This invention relates to improved photographic procedure for the treatment of non-gelatin emulsion photographic elements and in particular to improved procedure for fixing such photographic elements. The invention also pertains to improved fixing compositions for such photographic elements.

Various non-gelatin materials have been used heretofore as protective colloids or carriers as a substitute for gelatin in photographic silver halide emulsions. Thus, resins such as cellulose nitrate, acetate, acetate-butyrate; polyvinyl acetals such as polyvinyl acetaldehyde acetal and polyvinyl butyraldehyde acetal; cold water soluble polyvinyl acetaldehyde acetal, polyvinyl alcohol and polyvinyl esters such as hydrolyzed polyvinyl acetate have been used for this purpose. These substitutes are superior to gelatin in many respects but it has been noted that they frequently are not satisfactorily permeated by fixing solutions so that the removal of silver halide by conventional fixing solutions has in many cases been incomplete or required an inordinately long period of time.

This invention has for its object to provide improved procedure for the fixing of photographic elements bearing a non-gelatin emulsion. Another object is to provide improved fixing compositions which permit rapid fixing of non-gelatin emulsions, and especially those which have limited permeability to water or to the usual fixing baths. Other objects are to improve the state of the art.

These and other objects are accomplished by our invention which includes immersing a photographic element, which comprises a non-gelatin layer containing a developed silver halide photographic image, in a bath which contains a simple salt of hydrogen iodide such as an alkali metal or ammonium iodide and a member of the group consisting of thiourea and thiocyanate as the essential fixing constituents.

In the following examples and description we have given several of the preferred embodiments of our invention, but it is to be understood that these are set forth for the purpose of illustration and not in limitation thereof.

Examples of suitable iodides are sodium and potassium and ammonium iodide. Examples of thiocyanates which may be used are sodium, potassium and ammonium thiocyanate; organic thiocyanates such as thiocyanocatechol may be used, but we prefer to use inorganic thiocyanates.

The iodide-thiourea mixtures are preferably used in aqueous solutions containing between

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about 8% and 25% iodide to between about .25 and 8% thiourea. The amount of iodide in the iodide-thiocyanate mixture is somewhat more critical, and we prefer to use about 25% iodide to between about 5% and 25% thiocyanate. When using amounts in the upper portion of the ranges given for one agent it is preferable to use amounts in the lower portion of the range for the other fixing agent. Fixing baths containing the above-noted proportions of the essential fixing constituents have been tested and in each case have been found to give a fixing time of three to three and one-half minutes or less. The exact proportions and quantities used depend upon the composition of the non-gelatin carriers which have been produced with sufficient variation in structure to require fixing baths embodying all of the proportions given above. Proportions somewhat outside the ranges or amounts given can be used with satisfactory results if slower fixing times can be tolerated. In general the higher the concentration of both of the constituents the shorter will be the fixing time. Proportions in the higher ranges are not ordinarily used except for non-gelatin emulsions which are very impermeable. The concentrations indicated give a completely clear film free of silver halide in three to three and one-half minutes. Similar tests with a conventional fixing bath containing 30% hypo required an hour for a similar degree of fixing.

The invention is applicable to non-gelatin emulsions in general and will enable shorter fixing times with all such emulsions. It is of particular value in connection with those non-gelatin emulsions which have limited permeability to water.

What we claim is:

1. The process of permeating and fixing a photographic element which includes a non-gelatin layer having slight permeability to normal fixing solutions and containing a developed silver image which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents from 8% to 25% of a water soluble simple salt of hydrogen iodide and a member of the group consisting of thiourea in the amount of 0.25%–87% and a soluble thiocyanate in the amount of 5%–25%, in the latter case the amount of iodide being about 25%.

2. The process of permeating and fixing a photographic element which includes a non-gelatin layer having slight permeability to normal fixing solutions and containing a developed

silver image which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents between about 8% and 25% alkali metal iodide and between about 0.25% and 8% thiourea.

3. The process of permeating and fixing a photographic element which includes a non-gelatin layer having slight permeability to normal fixing solutions and containing a developed silver image, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituent between about 8% and 25% potassium iodide and between about 0.25% and 8% thiourea.

4. The process of permeating and fixing a photographic element which includes a non-gelatin layer having slight permeability to normal fixing solutions and containing a developed silver image which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents about 25% alkali metal iodide and between about 5% and 25% thiocyanate.

5. The process of permeating and fixing a photographic element which includes a non-gelatin layer having slight permeability to normal fixing solutions and containing a developed silver image, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents about 25% potassium iodide and between about 5% and 25% thiocyanate.

6. The process of permeating and fixing a photographic element which includes a non-gelatin layer containing a developed silver image and requiring approximately one hour for penetration by a normal fixing solution which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents from 8% to 25% of potassium iodide and a member of the group consisting of thiourea in the amount of 0.25%–8% and a soluble thiocyanate in the amount of 5%–25%, in the latter case the amount of iodide being about 25%.

7. The process of permeating and fixing a photographic element which includes a non-gelatin layer containing a developed silver image and requiring approximately one hour for penetration by a normal fixing solution which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents between about 8% and 25% potassium iodide and between about 0.25% and 8% thiourea.

8. The process of permeating and fixing a photographic element which includes a non-gelatin layer containing a developed silver image and requiring approximately one hour for penetration by a normal fixing solution which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents about 25% potassium iodide and between about 5% and 25% thiocyanate.

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