

UNITED STATES PATENT OFFICE

2,396,830

PHOTOGRAPHIC PROCESS AND
COMPOSITION FOR FIXING

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No Drawing. Application January 8, 1944,
Serial No. 517,550

11 Claims. (Cl. 95—88)

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 hydrolized 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 ethylenediamine and a member of the group consisting of trimethylol amino methane; 2,4,6-triamino toluene trihydrochloride; 6 methyl-2-amino benzo-thiazolium p-toluene sulfonate and thiourea 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.

For the ethylenediamine-trimethylol amino methane mixtures we prefer to use between about 4 and 50 grams ethylenediamine to between about 9 and 2 grams of trimethylol amino methane in 100 cc. of aqueous solution. For the ethylenediamine-2,4,6 triamino toluene trihydrochloride mixtures we prefer to use between about 1 and

50 grams of ethylenediamine to between about 10 and 2 grams of 2,4,6 triamino toluene trihydrochloride in 100 cc. of aqueous solution. For the ethylenediamine-6 methyl-2-amino benzo-thiazolium p-toluene sulfonate mixture we prefer to use between about 1 and 50 grams of ethylenediamine to between about 1 and .2 gram of 6-methyl-2-amino benzo-thiazolium p-toluene sulfonate in 100 cc. of aqueous solution. For the ethylenediamine-thiourea mixture we prefer to use between about 1 and 50 grams of ethylenediamine to between about 8 and 1 grams of thiourea in 100 cc. of aqueous solution.

When using amounts in the upper portion of the ranges given for the ethylenediamine it is preferable as indicated above 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 usually 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 fixing a photographic element which includes a non-gelatin layer containing a developed silver image which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents ethylenediamine and a member of the group consisting of trimethylol amino methane; 2,4,6-triamino toluene trihydrochloride; 6 meth-

yl-2-amino benzothiazolium p-toluene sulfonate; and thiourea.

2. The process of fixing a photographic element which includes a non-gelatin layer containing a developed silver image, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents ethylenediamine and thiourea.

3. The process of fixing a photographic element which includes a non-gelatin layer containing a developed silver image, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents ethylenediamine and trimethylol amino methane.

4. The process of fixing a photographic element which includes a non-gelatin layer containing a developed silver image, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents ethylenediamine and 6-methyl-2-amino benzothiazolium p-toluene sulfonate.

5. The process of fixing a photographic element which includes a non-gelatin layer containing a developed silver image and having but limited permeability to water, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents between about 1 and 50 grams of ethylenediamine and between about 1 and 8 grams of thiourea per 100 cc. of aqueous solution.

6. The process of fixing a photographic element which includes a non-gelatin layer containing a developed silver image, and having but limited permeability to water, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents between about 4 and 50 grams of ethylenediamine and between about 2 and 9 grams of trimethylol amino methane per 100 cc. of aqueous solution.

7. The process of fixing a photographic element

which includes a non-gelatin layer containing a developed silver image and having but limited permeability to water, which process comprises immersing said photographic element in a bath which contains as the essential fixing constituents between about 1 and 50 grams of ethylenediamine and between about .2 and 1 gram of 6-methyl-2-amino benzothiazolium p-toluene sulfonate per 100 cc. of aqueous solution.

8. A fixing composition adapted to rapidly fix a photographic element which includes a non-gelatin layer containing a developed silver image which composition comprises a mixture of ethylenediamine and a member of the group consisting of trimethylol amino methane, 2,4,6-triamino toluene trihydrochloride, 6-methyl-2-amino benzothiazolium p-toluene sulfonate and thiourea.

9. A fixing composition adapted to rapidly fix a photographic element which includes a non-gelatin layer containing a developed silver image, which composition comprises between about 1 and 50 grams of ethylenediamine and between about 1 and 8 grams of thiourea per 100 cc. of aqueous solution.

10. A fixing composition adapted to rapidly fix a photographic element which includes a non-gelatin layer containing a developed silver image, which composition comprises between about 4 and 50 grams of ethylenediamine and between about 2 and 9 grams of trimethylol amino methane per 100 cc. of aqueous solution.

11. A fixing composition adapted to rapidly fix a photographic element which includes a non-gelatin layer containing a developed silver image which composition comprises between about 1 and 50 grams of ethylenediamine and between about .2 and 1 gram of 6-methyl-2-amino benzothiazolium p-toluene sulfonate per 100 cc. of aqueous solution.

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