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PROCESSING OF CERTAIN NONGELATIN EMULSIONS

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This invention relates to improved procedure for the processing of photographic elements which include an emulsion layer of a polyvinyl resin which is not readily permeable to processing baths.

It is known to substitute polyvinyl resins for the gelatin in photographic emulsions. Polyvinyl acetals such as polyvinyl acetaldehyde acetal, polyvinyl propionaldehyde acetal and polyvinyl butyraldehyde acetal; polyvinyl esters such as partially hydrolized polyvinyl acetate and mixed polyvinyl acetal-esters are examples of polyvinyl resins which have been used for this purpose. See, for instance, Fordyce 2,211,323, Aug. 13, 1940; Lowe 2,253,078, Aug. 19, 1941; Lowe 2,276,322, Mar. 17, 1942; Lowe 2,276,323, Mar. 17, 1942, and Lowe 2,286,215, June 16, 1942. It will be noted that these patents specify certain ranges of vinyl alcohol content which are most permeable to photographic processing baths. These patents also indicate that outside these ranges, and in certain cases inside certain portions of these ranges, difficulty is encountered in connection with lack of permeability to conventional processing baths.

This invention has for its object to provide improved methods for processing polyvinyl resin photographic emulsions. Another object is to provide improved processing baths for photographic elements which include a layer of a polyvinyl resin which contains a silver salt and which is not readily permeable to usual processing baths. A still further object is to provide a method for treating an exposed photographic element which includes a layer of a polyvinyl resin containing a silver salt whereby its permeability to the processing bath is increased and whereby the processing time is substantially reduced. Other objects will appear hereinafter.

These and other objects are accomplished by our invention which includes treating an exposed photographic element including a layer of a polyvinyl resin which contains a silver salt and which is not sufficiently permeable to the usual processing baths with a processing bath which contains a thiocyanate. It has been found that the rate of penetration is greatly increased by the presence of this material in the processing bath and that the speed of development, fixation, etc. is correspondingly increased.

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.

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Organic thiocyanates such as thiocyanocatechol may be employed but we prefer to use inorganic thiocyanates. Examples of the most satisfactory thiocyanates which we have tried are sodium, potassium and ammonium thiocyanate. The thiocyanate can be added to any photographic processing bath utilized to treat the photographic element containing the vinyl resin as above specified. Thus it can be added to the conventional developing or fixing bath. On the other hand, it can be used as a fixing agent per se, and in such case a conventional fixing agent is unnecessary.

As indicated above our invention is applicable to polyvinyl resin-containing emulsions generally. However, it is of particular advantage in connection with the processing of polyvinyl resin emulsions which have poor permeability to processing baths. Thus polyvinyl esters which contain above about 71% of polyvinyl ester are slowly penetrated. Other polyvinyl resins such as the acetaldehyde, butyraldehyde etc. acetals are in certain cases, especially in the higher acetal content range, impermeable or slowly permeable to processing baths. Our invention is, therefore, of particular advantage in connection with the treatment or processing of such emulsions. However, it is applicable to emulsions which can be processed with conventional processing baths since the thiocyanate will increase the rate of penetration and rate of developing or fixation. Therefore, it is to be understood that the foregoing resins which are slowly or incompletely penetrated constitute the preferred embodiment of our invention.

The thiocyanates can be added to the developing and fixing baths in greatly varying amounts depending upon the degree of permeability and speed of penetration desired. For most purposes between about one and one hundred grams per liter of processing solution will be found to be satisfactory. For developing solutions we prefer to add about one to fifty grams of thiocyanate per liter of developer. For purposes of fixation one to one hundred grams per liter are generally useful, but we prefer to employ thiocyanate in the upper portion of the range mentioned; i. e., about fifty to one hundred grams per liter of fixing solution.

In some cases it may be advantageous to add an amine such as ethanol amine, triethanol amine to the baths especially the fixing bath, to avoid or prevent opalescence in the dried film.

Example I

A silver halide emulsion was prepared by dispersion of the halide in a polyvinyl acetaldehyde acetal which contained about 35 per cent unreacted polyvinyl alcohol and this emulsion was coated upon a flexible film base in known manner and photographically exposed. When treated in a conventional developer such as diluted D–72 (diluted 1 part developer to 2 parts water) the development took place in ten minutes with poor contrast. The same film exposed in the same way was developed in D–72 developer (diluted 1:2) to which had been added 10 grams per liter of sodium thiocyanate. The development in this solution took place in two minutes and the contrast was markedly improved. D–72 developer is manufactured by Eastman Kodak Company and is made up of the following:

Water, 50° C	cc..	500
Monomethyl-paraminophenolsulfate	grams..	3.1
Sodium sulfite (des.)	do....	45
Hydroquinone	do....	12
Na_2CO_3 (des.)	do....	67.5
KBr	do....	1.9
Water to make	liter..	1

Example II

Film carrying the emulsion described in Example I was exposed, developed and then fixed in a simulated conventional fixing bath containing 30 per cent hypo. The rate of fixation was 2 hours and 30 minutes. Addition of 100 grams of sodium thiocyanate per liter of the 30 per cent hypo reduced the time of fixation to 3 minutes.

Example III

Five grams of sodium thiocyanate per liter of diluted developer D–72 (diluted 1:2) developed the photographic film described in Example I in 2 minutes at 70° F. The developed film had good contrast. The film so developed was fixed in 3 minutes by treatment with a bath containing 100 grams sodium thiocyanate and 100 cc. of ethanolamine per liter of 30 per cent hypo.

Example IV

Five grams of sodium thiocyanate per liter of diluted D–16 developer (diluted 1:2) developed the photographic film described in Example I in 2 minutes at 70° F. The film had good contrast and was fixed in 3 minutes by treatment with a bath containing 100 grams of sodium thiocyanate and 100 cc. of ethanolamine per liter of 30 per cent hypo.

D–16 developer is manufactured by Eastman Kodak Company and is made up of the following:

Water, 50° C	cc..	750
Monomethyl-paraminophenolsulfate	grams..	.31
Sodium sulfite (des.)	do....	39.6
Hydroquinone	do....	6
Na_2CO_3 (des.)	do....	18.7
KBr	do....	.86
Citric acid	do....	.68
Potassium metabisulfite	do....	1.5
Cold water to make	liter..	1

What we claim is:

1. The method of treating an exposed photographic element which comprises immersing the element including a layer of a polyvinyl resin which contains a silver salt and which is not readily permeable to processing baths, in a processing bath which contains an inorganic thiocyanate and ethanolamine.

2. The method of treating an exposed photographic element which comprises immersing the element including a layer of a polyvinyl resin which contains a silver salt and which is not readily permeable to processing baths, in a processing bath which contains an inorganic thiocyanate and an ethanolamine.

3. The method of developing an exposed photographic element which comprises immersing the element including a layer of a polyvinyl acetal resin which contains a silver salt and which is not readily permeable to developing baths, in a developing bath which contains an inorganic thiocyanate and ethanolamine.

4. The method of fixing an exposed and developed photographic element which comprises immersing the element including a layer of polyvinyl acetal resin which contains a silver image and a silver salt and which is not readily permeable to fixing baths in a fixing bath which contains an inorganic thiocyanate and ethanolamine.

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