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HARDENERS FOR PHOTOGRAPHIC PROCESSING SOLUTIONS

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9 Claims. (Cl. 95—88)

This invention relates to photographic materials and particularly to hardening photographic gelatin or emulsions by adding certain hardening agents to photographic processing solutions.

The use of hardening agents to prevent the softening or swelling of photographic emulsion layers during processing, particularly at high temperatures, is well known. Hardening agents used for this purpose have been incorporated either in the emulsion layer or in the photographic developer used to develop the exposed emulsion. Not all hardening agents, however, are equally suitable for use in the emulsion and in the developer. In Staud and Briggs U. S. Patent 2,063,351, granted December 8, 1936, diketone hardening agents are described for use in emulsion layers. Of the diketone compounds described in this patent, we have found that the aromatic diketones are unsuitable for incorporation in developers or prebaths because of incompatibility with the developer or because of lack of hardening action.

It is, therefore, an object of the present invention to provide hardening agents suitable for incorporation in photographic developers or prebaths. Other objects will appear from the following description of our invention.

These objects are accomplished, according to the present invention, by the incorporation of dialkyldiketones in photographic developing solutions or prebaths used to treat the exposed emulsion layer before development.

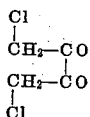
According to our invention the dialkyldiketone hardener is added to an ordinary photographic developing solution or is made up as a separate solution to treat the exposed emulsion before development. A separate solution of the hardener is preferably made up with a small volume of solvent such as water or methyl alcohol and this solution is then diluted to the desired concentration in the developing solution.

Hardening agents of the dialkyldiketone class which we have found suitable for use in this way are the following:

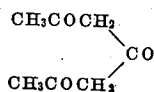
Diacetyl



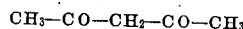
Sym.-dichlorodiacetyl



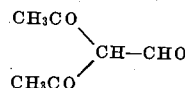
Diacetyl acetone



Acetyl acetone



Formyl diacetyl methane



Our hardening agents and method have been found especially suitable for, although not limited to, use with the process of multi-color development described in Mannes, Godowsky and Wilder U. S. Patent 2,252,718, granted August 19, 1941. In the process of that application a photographic film having three superposed emulsion layers sensitive to different regions of the visible spectrum thereon, is exposed and developed in a black and white developer, then selectively exposed to the colors to which the layers are sensitive and developed in a color forming developer after each exposure. In this process there is some tendency for the top emulsion layer to soften during the black and white development step and later to peel from the other emulsion layers. We have found that by incorporating a hardening agent such as that described in the present application in the first color developer, the softening and peeling of the outer emulsion layer is decreased or overcome. Under the conditions of development used in this processing, that is 10 to 12 minutes at 70° F., diacetyl and other dialkyldiketones were found to be effective in producing sufficient hardness of the top emulsion layer to prevent peeling. This hardening effect was produced without interfering with the developing action.

The hardening agents which we employ may be used in amounts ranging from 0.15 to 1.5% by weight of the developing solution, the preferred range being from 0.25 to 0.5%.

The following example of a hardening developer is illustrative:

Solution A

45	P-Aminodiethylaniline hydrochloride	grams	2
	Sodium sulfite	do.	6
	Sodium carbonate	do.	50
	Potassium bromide	do.	5
50	Potassium thiocyanate	do.	1
	Diacetyl	do.	1.5
	Water to	cc.	950

Solution B

55	o-Hydroxydiphenyl	grams	3
	Sodium hydroxide	do.	5
	Water to	cc.	50

(Solution B is added to Solution A.)

The hardening agents which we use result in overcoming the softening of the emulsion layer

during development and the tendency of the emulsion layer to reticulate, frill or peel is thereby overcome. In addition to this function, the use of hardening agents according to our invention has been found in some cases to improve the resolving power of emulsions after processing.

Our hardening method may be used not only with sensitive photographic emulsions but may also be used to harden non-sensitive photographic gelatin layers, such as overcoating and backing layers and gelatin layers coated on various supports such as film, paper or cloth.

It is to be understood that our invention is susceptible of modifications within the scope of the disclosure and claims and that the examples are to be taken as illustrative only.

We claim:

1. The method of hardening a photographic gelatin layer of an exposed photographic element including a silver halide layer which comprises treating said gelatin layer with a solution containing a dialkyl diketone.

2. The method of hardening an exposed gelatino-silver halide emulsion layer which comprises treating said layer with a solution containing a diacetyl.

3. The method of hardening an exposed gelatino-silver halide emulsion layer which comprises treating said layer with a solution containing diacetyl.

4. The method of hardening an exposed gelatino-silver halide emulsion layer which comprises treating said layer with a solution containing symmetrical dichloro diacetyl.

5. The method of hardening an exposed gelatino-silver halide emulsion layer which comprises treating said layer with a solution containing an acetyl acetone.

6. The method of hardening an exposed gelatino-silver halide emulsion layer which comprises treating said layer with a solution containing diacetyl acetone.

7. The method of hardening an exposed gelatino-silver halide emulsion layer which comprises developing said layer in a photographic developing solution containing a dialkyl diketone.

8. A hardening photographic developing solution comprising an aqueous solution of a photographic developer containing a dialkyl diketone.

9. In the treatment of an exposed multi-layer photographic element having a plurality of differentially-sensitive gelatino-silver halide emulsion layers on one side of a support, the step of hardening and preventing peeling of the outermost emulsion layer from the underlying emulsion layers, which comprises developing said element in a solution of a developing agent and a dialkyl diketone.

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