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ANTIFADING BATHS FOR PHOTOGRAPHIC BLACK AND WHITE MATERIALS

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6 Claims. (Cl. 95—88)

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This invention relates to photographic black and white negatives and prints, and particularly to antifading baths employed in the treatment of black and white photographic taking and printing materials.

It is known that open chain and cyclic amides containing at least one methylol radical attached directly to the amide nitrogen atom have been suggested for the production of silver images having a blue-black image tone. These compounds may be added to silver halide emulsions, subbing layers or backing layers or may be used in the developer solution to achieve the desired blue-black toning effect.

Photographic negative and positive prints having a metallic silver image, particularly those negatives and prints which have a warm image tone and are characterized by a small particle size of metallic silver, show under certain conditions of storage, a propensity to fade, i. e., lose density and change the color of the silver image. This susceptibility is most marked when the negative or print is exposed to an atmosphere containing gaseous products of the oxides of nitrogen, oxides of sulfur, and reactive sulfiding compounds, such as hydrogen sulfides (H_2S) and the like, which are frequently encountered in ore smelting, soft coal burning and artificial gas burning areas.

The utilization of the open chain and cyclic methylol amides as suggested by the prior art is ineffective in alleviating the fading problem since the various processing steps to which the photographic material is subjected, wash out the methylol amides. As a consequence, there are none left after the final washing treatment. Moreover, the presence of the methylol amides during the development step favors the formation of blue-black tones and precludes the obtainment of pictures having a warm image tone.

It is an object of the present invention to eliminate the fading and change of the color of the silver image in black and white negatives and prints upon exposure to the atmosphere.

Other objects and advantages will appear hereinafter.

I have discovered that the above objects are accomplished by treating a photographic black and white material subsequent to exposure and development with a bath of an aqueous solution containing a water-soluble addition product of formaldehyde and urea. The ureas which readily

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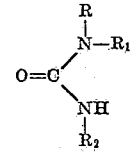
react with formaldehyde are characterized by the following general formula:



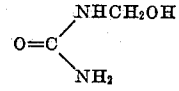
wherein R, R_1, and R_2 are members selected from the class consisting of hydrogen and lower alkyls, such as methyl, ethyl, propyl, allyl, butyl, and wherein R_2 is always hydrogen when both R and R_1 are alkyl.

The following are examples of suitable ureas which may be reacted with formaldehyde:

Urea	N,N-dimethylurea
N-methylurea	N,N'-dimethylurea
N-ethylurea	N,N-diethylurea
N-propylurea	N,N'-diethylurea
N-butylurea	

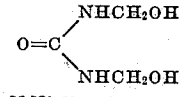
The following compounds are illustrative of the reaction products of formaldehyde and a urea compound which may be employed as fading inhibitors:

(1) Ber. 41, 26



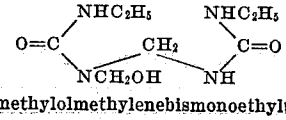
N-methylolurea

(2) Ber. 41, 26



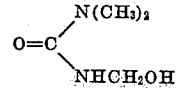
N,N'-dimethylolurea

(3) Annalen 361, 134



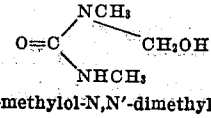
N-methylolmethylenebismonoethylurea

(4) Annalen 361, 135



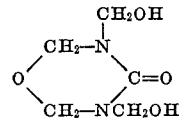
N'-methylol-N,N-dimethylurea

(5) Annalen 361, 157



N-methylol-N,N'-dimethylurea

(6) C. A. 30, 5944



N,N'-dimethyloluron

By utilizing a bath containing the addition products, the tendency of the developed silver images in black and white negatives, positives and prints to fade and change in tone or color upon storage or exposure to an atmosphere containing the aforementioned gases is completely eliminated for an indefinite period of time. The exact operation of the addition products upon the developed silver images is still unknown. It is believed for the sake of temporary explanation that the particles of the addition products protect the silver images from the attack of the aforementioned gases without adversely affecting the silver images.

In preparing the antifading baths of the present invention, the addition product is simply dissolved in water and the resulting solution utilized in the treatment of the photographic material subsequent to exposure and development. The concentration of the addition product is not critical and varies within a wide range. The actual concentration employed will depend upon the type of emulsion used in the photographic black and white material and varies between 0.5 and 20%. For practical purposes, concentrations ranging between 2 and 10% are preferred.

To facilitate the penetration of the addition product into the silver halide emulsion layer subsequent to exposure and development, it may be desirable to incorporate a surface active agent, such as the formaldehyde condensation product of naphthalene sulfonic acid sold under the trade name of "Tamol NNO," the sodium sulfonate of hexylsuccinate, the sodium sulfonate of butylnaphthalene and the like.

The black and white photographic materials which may be treated subsequent to exposure and development are contact printing paper, projection printing paper, ordinary black and white film which may be a positive or negative and motion picture film.

The following examples will serve to illustrate the methods for accomplishing the above objects but are not to be construed as limiting the invention.

Example I

A black and white negative was printed by projection on two 5 x 7 sheets of black and white chlorobromide projection paper. The exposed sheets were developed for 1 to 2 minutes at 20° C. in a warm tone developer of the following composition.

	Gms.
p-Monomethylaminophenol sulfate	0.8
Sodium sulfite	12.0
Hydroquinone	3.3
Sodium carbonate (monohydrate)	12.0
Potassium bromide	1.4

Water to make 1 liter.

The developed papers were shortstopped for 2 minutes in a shortstop bath of the following composition:

Acetic acid, 45.0 cc.
Water to make 1 liter.

The prints were then washed for 2 minutes in running water and hardened for 5 minutes in an acid hardening fix of the following composition:

Sodium thiosulfate	gms	240.0
Sodium sulfite	gms	15.0
Acetic acid 28%	cc	45.0
Potassium alum	gms	15.0

Water to make 1 liter.

In preparing the above fixing solution, the sodium thiosulfate is separately dissolved in a sufficient amount of water and then added to a solution of the remaining ingredients and brought up to volume. After fixing, the prints were washed for 10 minutes in running water at 20° C.

After the final washing, one print was set aside while the other was rinsed for 3 minutes in an aqueous solution containing 4.3% of N,N'-dimethylolurea and then dried. At this point, both prints appeared identical and were characterized by a warm image tone. The prints were then stored in an atmosphere containing the combustion product of an unvented burner utilizing natural gas. The print rinsed in the solution containing the N,N'-dimethylolurea showed no fading or change of color in the silver image, whereas the untreated print showed considerable fading and discoloration.

Example II

Example I was repeated with the exception that 4 grams of N,N'-dimethylolurea were replaced by 5 grams of N-methylolmethylenebismonoethylurea. The black and white print washed in plain water and exposed for several days to an atmosphere containing oxides of nitrogen showed considerable fading and change of color in the silver image, whereas the print washed with the aqueous solution containing the formaldehyde urea addition product showed no fading or change of color.

Example III

Example I was again repeated with the exception that 4 grams of N,N'-dimethylolurea were replaced by 10 grams of N,N'-dimethyloluron. The results obtained were identical with those of Example I.

Example IV

Example I was again repeated with the exception that 4 grams of N,N'-dimethylolurea were replaced by 5 grams of a water-soluble resinous condensation product of formaldehyde and urea, prepared in accordance with the procedure described on page 631 of Carleton Ellis' book "The Chemistry of Synthetic Resins," (Reinhold Publishing Corp., New York, N. Y., 1935). The results obtained were identical with those of Example I.

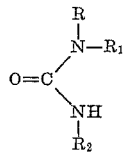
The treating baths which I have described and employed may be used in treating various kinds of silver halide emulsions, such as chloride, bromide, chlorobromide, bromoiodide, or chlorobromoiodide emulsions subsequent to exposure and development.

Various modifications of this invention will occur to persons skilled in the art and it is, therefore, understood that the patent granted shall only be limited by the appended claims.

I claim:

1. In the process of producing silver images in a silver halide emulsion layer by exposing the emulsion, developing, fixed and washing the same, the improvement which comprises preventing the fading and change of color of

the silver images upon exposure to the atmosphere by treating the emulsion layer subsequent to development with an aqueous solution containing a water-soluble addition product of formaldehyde and a urea selected from the class consisting of those having the following formula:



wherein R, R_1 and R_2 each represent a member selected from the class consisting of hydrogen and lower alkyl, and wherein R_2 is always hydrogen when both R and R_1 are lower alkyl.

2. The process according to claim 1 wherein the addition product is N,N'-dimethylolurea.

3. The process according to claim 1, wherein the addition product is N-methylolmethylenebismonoethylurea.

4. The process according to claim 1, wherein the addition product is N,N'-dimethyloluron.

5. The process according to claim 1, wherein the addition product is a water-soluble, resinous condensation product of formaldehyde and urea.

6. The process according to claim 1, wherein the addition product is N'-methylol-N,N-dimethylolurea.

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No references cited.