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ANTIFADING LAYERS FOR PHOTOGRAPHIC BLACK AND WHITE MATERIALS

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This invention relates to photographic black and white materials, and particularly to the prevention of fading of black and white photographs which are characterized by a warm image tone.

It is known that crystalline monomeric 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 pictures and particularly positive prints having a warm image tone and which are characterized by a small particle size of the 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 pronounced when the negative or print is exposed to an atmosphere containing gaseous products of the oxides of nitrogen, oxides of sulfur or reactive sulfiding compounds such as hydrogen sulfide (H_2S) and the like which are frequently encountered in areas where ore smelting is performed or where artificial gas or soft coal is used as a fuel.

The utilization of the monomeric, crystalline methylol amides as described by the prior art is ineffective in alleviating the fading problem encountered with warm tone silver images because the presence of the methylol amide during the development step favors the formation of a blue-black tone and precludes the obtainment of pictures having a warm image tone.

It is an object of the present invention to prevent the fading of warm tone black and white negatives and printing materials.

Other objects and advantages will appear hereinafter.

I have discovered that the above objects are accomplished by providing an emulsion capable of being developed into a silver image having a warm image tone with a colloidal surface coating comprising a colloidal carrier having dispersed therein, a water soluble, amorphous, resinous condensation product of formaldehyde and a urea. The ureas which are employed react readily with formaldehyde and are characterized by the following general formula:

$$R—NH—CO—NH_2$$

wherein R is hydrogen, lower alkyl such as methyl, ethyl, propyl, butyl, tert.-butyl, tert.-amyl, tert.-hexyl, lower hydroxyalkyl, e. g., hydroxyethyl, hydroxypropyl, hydroxybutyl, hydroxyamyl or lower acyl such as acetyl or propionyl.

The following are examples of suitable ureas which can be reacted with formaldehyde to yield the water soluble, amorphous, resinous condensation products: urea, N-methylurea, N-ethylurea, N-propylurea, N-(tert.-butyl)urea, N-(tert.-amyl)urea, N-(tert.-hexyl)urea, N-β-hydroxyethyl)urea, N-(γ-hydroxypropyl)urea, N-isobutylurea, N-acetylurea and N-propionylurea.

The water soluble, amorphous, resinous condensation products are prepared by reacting one molar equivalent of a urea with approximately from 1.1 to 3.0 molar equivalents of an aqueous formaldehyde solution in the presence of a suitable condensing agent. Among the suitable alkaline condensing agents are the alkali hydroxides, e. g., sodium hydroxide, potassium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, freshly precipitated calcium carbonate, aqueous ammonia solutions, water soluble organic bases, e. g., methylamine, dimethylamine, ethylamine, diethylamine, diethanolamine, trimethylamine, triethylamine, triethanolamine and morpholine. The condensation reaction is permitted to proceed until the desired degree of polymerization has been reached, whereupon further progress of the reaction is inhibited by cooling and/or by neutralization with a weak acid such as acetic acid.

The condensation can also be carried out in the presence of acidic condensing agents, provided the pH is suitably adjusted by appropriate buffers and the time of condensation is carefully controlled to prevent the formation of water insoluble products.

The water soluble, amorphous, resinous condensation products employed in accordance with this invention are B-stage condensation products having an average molecular weight of about 400 when the unsubstituted urea is used as a starting material. The median degree of polymerization may range from about 8 to 30.

The following patents are illustrative of the great number of publications in which the manufacture of water soluble, amorphous, resinous condensation products of urea and formaldehyde are described: United States Patents 1,460,606; 1,645,848; 1,676,543; 2,249,795; 2,275,821; 2,331,926; 2,348,686; 2,397,194; 2,406,217; 2,428,752; 2,456,191; 2,512,672 and 2,533,557.

By incorporating the water soluble, resinous, urea-formaldehyde condensation products into a solution of a colloidal carrier material which is coated over the silver halide emulsion layer, the tendency of the developed warm tone silver images in film negatives or positives and paper prints to fade and change color is substantially minimized and, in most cases, completely eliminated even when the film or paper print is exposed to an atmosphere containing the aforementioned gases which otherwise would give cause to fading or discoloration. The exact operation of the addition product upon the developed, warm tone silver images is still unknown. It is believed that the dispersed particles of the condensation product protect the developed warm tone silver images from the attack of these gases without adversely affecting the silver image. However, it is to be understood that this is offered as a theoretical explanation rather than as the description of the exact functioning of the condensation product.

For the preparation of a surface coating over the silver halide emulsion layer, the condensation product is incorporated in a finely divided form into an aqueous dispersion of a colloidal carrier or the condensation product is dissolved in water or aqueous alcohol and the solution added to an aqueous dispersion of a colloidal carrier. The colloidal carrier may be gelatin, a water soluble cellulose derivative such as hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, low acetyl value cellulose, polyvinyl alcohol, a partially hydrolyzed polyvinyl acetate, an acetal of polyvinyl alcohol, a copolymer of polyvinyl alcohol with ethylene, and the like.

The addition products incorporated as a supercoating over the emulsion layer are substantive to gelatin and other water permeable colloids and, as a consequence,

are non-diffusing in photographic processing baths. A surface active agent may be added to effect a smoother coating. It is to be noted, however, that any commercially available anionic, cationic or non-ionic surface active agent may be employed so long as it possesses the desired wetting, dispersing or emulsifying properties, is compatible with the formaldehyde-urea condensation product and its aqueous solutions are substantially colorless.

The proportions of the condensation product which may be incorporated into the colloidal surface coating or supercoat are not critical and the amounts employed will depend to an extent on the composition of the material used and the final thickness of the surface coating. For practical purposes, I have found that the proportions of the condensation product employed (based on the solid content if solutions are used) may range from 0.4 gram to 5 grams per liter of the 1.2 to 1.5 percent colloidal carrier solution or dispersion used in the preparation of the surface coating from 33 to 333 milligrams per gram of colloidal carrier, or from 6 milligrams to 90 milligrams of solid condensation product per gram of silver nitrate used in the preparation of the overcoated silver halide emulsion. In terms of overcoated areas, the amounts may range from approximately 3 milligrams to 35 milligrams of the condensation product based on its solid contents per square foot of overcoated emulsion.

Among the warm tone black and white photographic materials which can be protected by the colloidal surface layers containing the resinous condensation products are contact printing papers, projection printing papers and negative or positive films including motion picture films. The silver halides employed in the preparation of warm tone emulsions usually contain mixtures of silver halides such as silver chloro-bromides, silver bromo-iodides or silver chloro-bromo-iodides although some emulsions containing only one silver halide are also capable of being developed to a warm image tone. In general, silver chloro-bromide emulsions are preferred which contain approximately equal molar ratios of chlorine and bromine or a moderate excess of bromine, the latter not exceeding 70% based on the total halogen concentration. The preparation of these emulsions is well known to those skilled in the art and does not require further discussion. However, suitable emulsions capable of being developed to a warm tone image are described on pages 119 and 218 et seq. of Thorne Baker's "Photographic Emulsion Technique," 2nd ed., published in 1948 by the American Photographic Publishing Co., Boston.

The method of testing the colloidal surface coatings containing the water soluble, amorphous, resinous urea-formaldehyde condensation products consists of coating two film or paper supports with the same warm tone emulsion. One of the sheets is then coated in total darkness with an aqueous solution of the colloidal carrier containing the condensation product. The other sheet is surface coated with a solution of the colloidal carrier without the condensation product. Both materials are allowed to dry, exposed under a suitable pattern or in a sensitometer, developed, shortstopped, fixed, washed and dried. They are then subjected to an atmosphere containing the aforementioned gases, for instance, oxides of nitrogen, oxides of sulfur, or hydrogen sulfide which have a tendency to cause warm tone silver images to fade. The fading or changing in color of the silver images in the two materials is observed after several days or weeks.

The following examples will serve to illustrate ways in which the invention is practiced but are not to be construed as limiting the invention.

Example I

One gram of sodium acetate and 2 grams of 28% aqueous ammonia are dissolved in 200 grams of a 37% by weight aqueous formaldehyde solution. Seventy five grams of urea are added and the resultant mixture heated under reflux and with mechanical stirring to 90° C. The mixture is kept at this temperature for 1 hour and then cooled. Its pH is adjusted to 7.3 by the addition of an aqueous solution of sodium carbonate. The solution is then further diluted by the addition of 200 milliliters of water. Its stability in this diluted form is infinite.

Seventy square feet of a warm tone projection paper commercially available under the trade name of "Ansco Indiatone Kashmir White" was divided into two equal sections. One of them was overcoated in total darkness with 200 milliliters of a surface coating obtained by dissolving 8 grams of the above described formaldehyde urea condensation product in a liter of a 1.2% by weight aqueous gelatin solution. The other section was surface coated with a plain 1.2% aqueous gelatin solution. Both samples were allowed to dry, exposed under a negative, and subsequently developed for 2 minutes at 68° F. (20° C.) in a warm tone developer of the following composition:

	Grams
4-methylaminophenol sulfate (Metol)	0.8
Hydroquinone	3.3
Sodium carbonate (monohydrate)	12.0
Sodium sulfite (anhydrous)	12.0
Potassium bromide	1.4

Water to make 1 liter.

The developed papers were shortstopped in a bath of the following composition:

Acetic acid (28%) ml	45

Water to make 1 liter.

The shortstopped material was fixed in a fixer solution having the following composition:

	Grams
Sodium thiosulfate	240.0
Sodium sulfite	15.0
Acetic acid (28%)	75.0
Borax	14.5
Potassium alum	15.0

Water to make 1 liter.

The fixed papers were thoroughly washed 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 products of an unvented burner utilizing natural gas. After several days, the print provided with the protective surface coating containing the resinous urea-formaldehyde condensation product showed no fading or change in the silver image and retained its beautiful brown warm tone, whereas the print which had been coated with a plain gelatin surface coating showed considerable fading.

Example II

Sixty grams of N-(β-hydroxethyl)urea, 66 grams of 37% aqueous formaldehyde solution and 4 grams of glacial acetic acid were mixed together and heated with stirring to 130° C. The mixture was kept at this temperature until most of the water had been evaporated, cooled to room temperature, diluted with 140 milliliters of water and neutralized to a pH of 7.3 by the addition of dilute aqueous sodium hydroxide solution. Six milliliters of the resinous urea-formaldehyde condensation product were dispersed in a liter of a 1.2% by weight aqueous gelatin solution. The resultant dispersion was coated over a warm tone contact printing paper commercially available under the name of "Ansco Cykon Paper." A control sample of the same paper was surface coated with a plain 1.2% gelatin solution which contained no urea-formaldehyde condensation product.

Both samples were allowed to dry, exposed through the same negative and subsequently developed for 1½ minutes at 68° F. (20° C.) in a developer having the following composition:

	Grams
4-methylaminophenol sulfate (Metol)	.8
Hydroquinone	3.3
Sodium sulfite (anhydrous)	12.0
Sodium carbonate (monohydrate)	12.0
Potassium bromide	2.8
Water to make 1 liter.	

The developed papers were shortstopped, fixed, washed and dried. At this point, both prints appeared identical and were characterized by a pleasant, warm brown-black image tone. The prints were then stored in an atmosphere containing hydrogen sulfide. After one week, the type material which had been coated with only a plain gelatin surface layer was badly faded and discolored while the sample protected by the surface coating containing the urea-formaldehyde condensation product showed no indication of fading and had retained its original pleasant, warm brown-black image tone.

Example III

Example I was repeated with the exception that the 4 grams of the formaldehyde-urea condensation product thereof were replaced by 3 grams of a commercially available solution of a urea-formaldehyde condensation product sold under the name of "Hercules Resin 138" by Hercules Powder Co. This material had a pH of 7.3, a solid content in water of 42%, a viscosity (Gardner-Holdt scale) of from D to E, a nitrogen content of 27% on a dry basis when determined by the Kjeldahl method of nitrogen analysis and a degree of polymerization on the order of 12 to 14.

The finished warm tone prints were exposed for several days to an atmosphere containing oxides of nitrogen. The print provided with the surface coating containing the resinous urea-formaldehyde addition product showed no fading or change of color whereas the print which had been overcoated with the plain gelatin layer showed appreciable fading and change of color in the silver image.

Example IV

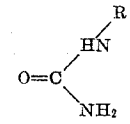
Five grams of guanidine nitrate is dissolved in 250 milliliters of formaldehyde solution (37% by weight). The pH of the resulting solution is adjusted to 5.3 by the addition of a 2 N sodium hydroxide solution. Sixty grams of urea are added, the mixture is heated to boiling and reflux for 2 hours with mechanical stirring, then cooled to room temperature, and diluted with 250 milliliters of water. The pH of the resultant solution is adjusted to 7.1 by the addition of 3 N sodium hydroxide solution.

A warm tone paper prepared in accordance with the procedure given on pages 119 and 218 et seq. of Thorne Baker's book "Photographic Emulsion Technique" is divided into two equal sections. One is overcoated with a 1.5% aqueous gelatin solution containing 10 milliliters of the above formaldehyde-urea condensation product per liter of gelatin solution. The other section is overcoated with a plain 1.5% gelatin solution in water and used as a comparison sample. Both samples are dried, exposed, developed, fixed, washed and dried according to the photographic processing procedure of Example I and then exposed for a period of several weeks to an atmosphere containing the combustion products of a burner using natural gas. The sample provided with the surface coating containing the formaldehyde-urea condensation product, showed no signs of fading or discoloration, whereas the comparison sample which had been surface coated only with a plain gelatin surface layer showed appreciable discoloration and fading.

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

I claim:

1. A photographic element comprising a support and a light-sensitive silver halide emulsion capable of being developed into a silver image having a warm image tone, said emulsion provided with a colloidal surface coating comprising a colloidal carrier having dispersed therein, an antifading amount of a water soluble, amorphous resinous addition product of formaldehyde and a urea having a median degree of polymerization ranging from about 8 to 30, said urea being selected from the class consisting of those having the following formula:

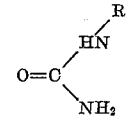


wherein R represents a member selected from the class consisting of hydrogen, lower alkyl and lower hydroxyalkyl, said antifading amount of resinous addition product being on the order of from 33 to 333 milligrams per gram of colloidal carrier, from 3 to 35 milligrams per square foot of overcoated surface, and from 6 to 90 milligrams per gram of silver nitrate used in the preparation of said silver halide emulsion.

2. A photographic element according to claim 1 wherein the addition product is a water soluble, amorphous, resinous condensation product of urea and formaldehyde.

3. A photographic element according to claim 1 wherein the addition product is a resinous, amorphous, water soluble condensation product of N-(β-hydroxyethyl)urea and formaldehyde.

4. A photographic element comprising a support and a light-sensitive silver halide emulsion capable of being developed into a silver image having a warm image tone, said emulsion provided with a colloidal surface coating comprising a colloidal carrier having dispersed therein, an antifading amount of a water soluble, amorphous, resinous addition product of formaldehyde and a urea having a median degree of polymerization ranging from about 8 to 30, said urea being selected from the class consisting of those having the following formula:



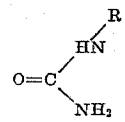
wherein R represents a member selected from the class consisting of hydrogen, lower alkyl and lower hydroxyalkyl, said antifading amount of resinous addition product being on the order of from 0.4 gram to 5 grams per liter of a 1.2 to 1.5 percent aqueous solution of the colloidal carrier used in the preparation of said surface coating, from 3 to 35 milligrams per square foot of overcoated surface, and from 6 to 90 milligrams per gram of silver nitrate used in the preparation of said silver halide emulsion.

5. A photographic element according to claim 4 wherein the addition product is a water soluble, amorphous, resinous condensation product of urea and formaldehyde.

6. A photographic element according to claim 4 wherein the addition product is a resinous, amorphous, water soluble condensation product of N-(β-hydroxyethyl)urea and formaldehyde.

7. In the process of forming silver images having a warm tone, involving coating onto a support a light-sensitive silver halide emulsion capable of being developed to a warm image tone, exposing said emulsion, developing the same in a black and white developer to a silver image having a warm image tone, short-stopping, fixing, washing and drying the developed material, the improvement which comprises overcoating the emulsion prior to exposure with a colloidal surface coating comprising an aqueous solution of a colloidal carrier having dispersed therein, a water soluble, amorphous, resinous

addition product of formaldehyde and a urea selected from the class consisting of those having the following formula:



wherein R represents a member selected from the class consisting of hydrogen, lower alkyl and lower hydroxyalkyl, said addition product having a median degree of polymerization ranging from about 8 to 30, and said condensation product being present in a concentration ranging from 0.4 to 5 grams per liter of a 1.2 to 1.5 percent aqueous solution of the colloidal carrier used in the preparation of said surface coating, and from 6 to 90 milligrams per gram of silver nitrate used in the preparation of said silver halide emulsion to form a surface layer which contains from 3 to 35 milligrams of said resinous addition product per square foot of overcoated surface.

8. A process according to claim 7 wherein said addition product is a water soluble, amorphous, resinous condensation product of urea and formaldehyde.

9. A process according to claim 7 wherein the addition product is a resinous, amorphous, water soluble condensation product of N-(β-hydroxyethyl)urea and formaldehyde.

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