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PHOTOGRAPHIC PROCESSES AND COMPOSITIONS

Walter D. Baldsiefen, Metuchen, N. J., assignor,
by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to photography. More particularly it relates to photographic processes for producing blue-black tones in silver images and to photographic elements and compositions therefor. In one of its important aspects, it relates to radiation sensitive silver halide layers which contain novel compounds which impart blue-black tones to developed silver halide images. It also relates to photographic developer solutions and treating solutions which are useful for producing blue-black tones in developed silver images.

An object of this invention was to find new and useful processes and agents for imparting blue-black tones to developed photographic images. A further object is to provide new photographic elements which can be processed in a simple manner to yield blue-black images. A further object is to modify fine grain silver halide emulsions so that they yield upon development blue-black images instead of neutral black or brown to sepia tones. A still further object is to modify fine-grain silver halide emulsions suitable for positive cinematographic prints which produce pleasing blue-black images without losing the fineness of grain during processing of photographic elements. Still another object is to provide simple and economical means for producing such blue-black images. Still other objects will be apparent from the herein described invention.

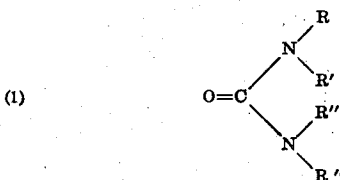
It has been found that photographs in blue-black tones can be made by utilizing organic compounds containing at least one methylol or lower alkoxymethyl radical attached to an amide nitrogen atom, or methylol nitromethanes in their production. The amide compounds include not only open chain amides but cyclic amides wherein no oxygen is present in the amide linkage.

The novel agents are brought into association with the silver salt layers at some stage of the manufacture or processing of photographic elements. To be more specific, the novel agents may be added to silver halide emulsions or photographic elements such as plates, films and photographic papers containing such emulsion layers prior to or subsequent to development of such materials or elements. The agents can be used in developing solutions or may be included in the support for the photographic layer, subbing layers, any sub- or intermediate layer, backing layer or protective layer such as an anti-abrasion layer or anti-static layer of such elements. In the case of photographic or printing papers, the agents may be included in the barytes, the size

for the paper, the paper pulp or in a coating on the paper support, included in the emulsions or protective layers therefor. In addition, it is possible to obtain satisfactory results by bathing films, plates or print papers in a solution of one of the novel agents prior to development or by adding the agents to the developing baths employed in processing.

According to one important aspect of the invention the agents are open chain methylol amides and lower alkoxymethyl amides wherein the methylol or alkoxymethyl radical or radicals are attached directly to an amide nitrogen atom.

A preferred class of open chain methylolamides includes the methylolureas wherein at least one methylol radical is attached to a nitrogen atom thereof. Symmetrical and unsymmetrical urea derivatives of this type are included. Preferred agents of this type have the general formula:



wherein at least one of the R's is a methylol radical ($-\text{CH}_2\text{OH}$) and the other R's are the same or different and may be hydrogen, hydrocarbon or methylol.

The degree of blue-black tone obtained with the novel agents of this invention varies with the halide ratio of the emulsion, the degree of hardness of the emulsion, the developer used and the particular agent chosen and other factors in a similar manner to known blue-black toning agents. The degree of tone also varies with the particular type of sensitizing dye used in the photographic emulsion processed. They are compatible with sensitizing dyes and other emulsion constituents as evidenced from the following description.

The concentration of the particular compound used will vary according to the manner in which it is applied to the photographic material; and as certain compounds are more potent than others, a certain amount of variation is to be expected when different compounds are employed in the same way. In general, molecular equivalents of different compounds will approximate the desired effect and the optimum concentration of one substance can be translated into the correct concentration of another without harmful effects. The following table gives the

approximate range of concentrations which will be found most suitable for the average blue-black agent in different applications:

Type of application		Range of concentration
		Per cent
1	In developers.....	0.05 to 0.75
2	In emulsions.....	0.01 to 0.5
3	In anti-abrasion layers.....	0.1 to 1.0
4	In subbing layers.....	0.25 to 3.0
5	In film base.....	0.5 to 3.5
6	In paper.....	0.2 to 3.0
7	In baths.....	0.05 to 1.0

In the practice of the invention, it has been determined that lesser quantities of the active ingredient are required in processes involving the addition of blue-black agents to the emulsion if the film is aged for some time at elevated temperatures and humidity. The period of aging can vary from several months to a few hours depending upon the temperature to which the emulsion is subjected. Temperatures from 65 to 140° F. can be employed with proportionally shorter times of aging as the temperature is raised to the maximum. In applications 2 to 6 (vide supra) it is almost impossible to dispense with the aging period and obtain satisfactory results.

The invention will be further illustrated but is not intended to be limited by the following examples:

Example I

Twenty milliliters of water in which is dissolved 0.1 gram of monomethylol urea were added to 1 liter of a fine grain photographic emulsion ready for pouring which contained 40 grams of a silver halide, comprising 95% silver bromide and 5% silver iodide, and 70 grams of gelatin. The emulsion was then coated on a cellulose nitrate base and dried, after which it was stored for a period of 60 days at 70° F. At the end of this time the emulsion was exposed under a negative film containing an image in the manner known to the art and then processed in an ordinary metol-hydroquinone, positive type developer and fixed. The image produced was found to have a distinctly blue-black color in comparison with a sample of the same emulsion used as a control which gave a neutral-black image under identical conditions.

Example II

One and five-tenths grams of trimethylol melamine were dissolved in 150 ml. of water and added to 1 liter of a fine-grain photographic emulsion comprising 45 grams of mixed silver halides representing 98% silver bromide and 2% silver iodide and 77 grams of gelatin. This emulsion was then coated on a suitable support and dried at a temperature of 110° F. for a period of 20 hours. At the end of this time the material was rehumidified at 80% humidity and exposed to an object field. After exposure, the element was processed in alkaline metol-hydroquinone developer and fixed in an acid-hardening fixing bath. A sharp blue-black image of high resolving power was obtained instead of the neutral-black-to-brownish image of a control to which no blue-black agent had been added.

Example III

One thousand milliliters of a fine grain gelatino-silver halide emulsion commonly used for lithographic practice and containing 60 grams of mixed silver halides per liter, comprising 97%

silver chloride plus 3% silver iodide and a small amount of 9 ethyl 3-3' dimethyl 2-5' benzoxo rhodanine merocyanine was modified by the addition of 0.8 grams of symmetrical dimethylol urea. The resulting mixture was then coated on a cellulose acetate film base and dried at a temperature of 100° F. for a period of 4 days. The film was then rehumidified at 70° F. in an atmosphere of 75% humidity and exposed. After exposure in a camera, the film was developed in a standard metol hydroquinone solution, washed and fixed. It was found that the image had a distinctly blue-black tone as compared to that produced by control strips of the same film to which no blue-black agent had been added.

Example IV

A photographic printing paper stock is coated with a chloro-bromide emulsion and bathed for a period of 5 minutes in a bath containing 2 grams of symmetrical dimethylol urea dissolved in 1 liter of water. It is dried for some time and then printed. The exposed print is then developed in a metol-hydroquinone developer and fixed. The image obtained is a definite blue-black color instead of the brownish-black obtained with an untreated control print.

Example V

A photographic film bearing a light sensitive gelatino-silver halide layer is overcoated with an anti-abrasion mixture containing 20 grams of gelatin and 6 grams of dimethylol formamide per liter. The coating is then dried at a temperature of about 130° F. for a short time. When exposed in the usual manner and developed and fixed with the common solutions employed in the art, a cool, blue-black tone is produced in the image.

Example VI

A photographic element bearing a light-sensitive silver halide emulsion layer on a suitable base is bathed for about an hour in a solution composed of 0.65 gram of symmetrical dimethylol urea in a mixture of methyl alcohol and water. The element is then dried at constant temperature and humidity and exposed in a known manner, developed and fixed. It is found that the image has a blue-black tone and that the tendency of the emulsion layer to soften during processing is somewhat reduced.

Example VII

A solution of 0.5 gram trimethylol nitromethane in 8 ml. of water was added to 1 liter of a photographic emulsion containing 40 grams of mixed silver chloro-bromide-iodide and 85 grams of gelatin. The emulsion was then coated on photographic paper base and dried after which it was subjected to a temperature of 130° F. for a period of 8 hours. At the end of this time the material was exposed, developed and fixed in the usual manner and it was found that an excellent blue-black image was obtained instead of the usual brown-black type.

Example VIII

A solution containing 0.75 gram of trimethylol nitromethane dissolved in 20 ml. of water was added to a liter of a gelatino-silver halide emulsion containing 50 grams of silver halide. The emulsion was then coated on a suitable base, dried and then held at 120° for 14 hours. At the end of this time the emulsion coating was exposed to light in the manner known to the art, developed

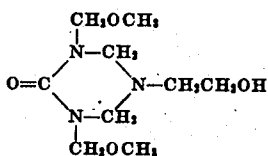
and fixed. A blue-black image color was strongly evident instead of the somewhat brownish tones obtained from a similar emulsion without the presence of the methylol compound.

Example IX

To 1 liter of the substratum solution used to anchor a silver halide emulsion to its support there is added 10 grams of trimethylol nitromethane. This solution is then coated on a suitable film base and a fine grain silver-halide emulsion superimposed upon it as described in previous examples. After an aging period of about 1 week at slightly elevated temperature, the film is exposed and processed in the customary manner. A blue-black image is formed in the emulsion.

Example X

One and five-tenths grams of tetrahydro-1,3-dimethoxymethyl-5-beta-hydroxyethyl-s-triazone-2 of the formula:



were added to 1 liter of a photographic emulsion containing approximately 50 grams of mixed silver halides representing 97% silver bromide and 3% silver iodide and containing 70 grams of gelatin. The emulsion was then coated on a suitable support and dried at a temperature of 120° C. for a period of 4 hours. The film was then rehumidified at 80% humidity and exposed. After development and fixation the film was washed and dried. When compared with a control of identical composition, but containing no triazone, which had been processed in the same way it was observed that the treated film had a distinctly blue-black tone.

Example XI

One and three-tenths grams of N,N'-bis(methoxymethyl) urea were dissolved in a small quantity of a suitable solvent and incorporated in 1000 ml. of a gelatino silver bromo-iodide emulsion suitable for radiographic film and containing 6% combined silver halides of which 2% were silver iodide. The emulsion was then coated on a suitable support, dried and aged for a period of 8 weeks at 75° F. X-ray exposures made using this film and processed in the usual manner produced images with a blue-black tone in comparison with film coated with the identical emulsion less the N,N'-bis(methoxymethyl) urea.

While the agents hereof may be used in various types of solutions and emulsions as previously stated they are preferably used in emulsion layers. In developing baths the effect produced varies somewhat with the pH and composition of the particular solution used.

In place of the specific blue-black toning agents mentioned in the above examples may be substituted one or more other compounds having the above described characteristics in like manner. Likewise, the compounds of the several examples can be interchanged in any desired manner. Suitable additional compounds which are methylol amides or lower alkoxyethyl amides wherein the alkoxy radicals contains 1 to 5 carbon atoms include N,N' dimethyl monomethylol urea, cyclic dimethylol diurea (Goldschmidt's compound), methylol formamide, dimethylol form-

amide, dimethyloladipamide, methylol acetamide, methylol phthalimide, N-methylol urethane, N-methylol-N-butyl urethane, dimethylolmelamine, N,N',N''-tris(methoxymethyl) melamine, N,N',N''-tris(ethoxymethyl) melamine, N,N'-bis(methoxymethyl) urea, tetrahydro 1,3-dimethoxymethyl-5-methyl-s-triazone-2, N,N'-bis(methoxymethyl)uron, N,N'-bis(methoxymethyl) oxamide, N,N'-bis(methoxymethyl) fumaramide, N,N'-bis(methoxymethyl) succinamide, N,N'-bis(methoxymethyl) sebacamide, N,N'-bis(methoxymethyl) adipamide, monomethylol and dimethylol nitromethane may also be used in like manner.

The novel agents of this invention as above stated may be utilized in the production of photographs in blue-black tones in many ways. They are compatible with the various components of developing agents which makes them of considerable value. They are particularly useful in providing fine grain emulsions for positive cinematographic pictures and yield excellent blue-black images on exposure and processing in the usual manners.

They are not limited as has been clearly demonstrated above to any one special type of silver halide emulsion. On the contrary they may be used with various reducible silver salts, e. g. silver chloride, silver bromide and silver iodide, or various mixtures of any of these with one or more of the others. They are useful with cinema, lithographic, radiographic and camera film, stripping films, printing papers and the like bearing such emulsions.

While the novel blue-black toning agents have been described as being useful with gelatino-silver halide emulsion layers, they may be used with silver halide layers having various colloid binding agents or gelatin substitutes such as cellulose derivatives, regenerated cellulose, synthetic resins, agar-agar, albumins, gums, etc.

The agents have considerable utility and may be used with or in photographic emulsions containing sensitizing dyes such as cyanine, carbocyanine, pseudocyanine, kryptocyanine, neocyanine, merocyanine, styryl, cyazine, rhodanine and other dyes including the salts and bases. They may also be used with photographic desensitizing agents, fog inhibiting compounds, emulsion stabilizers and hardeners etc. They may also be used with the usual types of surface active agents, spreading agents etc., such as the sodium higher alkyl sulfonates and sulfates, saponine, etc.

One of the most important advantages of the invention is that it produces images on positive motion-picture film and on positive print papers with a distinctly blue-black tone that is pleasing to the eye and creates the illusion of greater brilliancy of the print. Psychologically, blue is a "cold" color, connotive of purity of the image as distinct from one contaminated by brown staining. A further advantage is that the compounds employed to give these desirable effects are not so subject to decomposition as many of the compounds such as nitrobenzimidazole and benzothiazole which have been recommended for this purpose in the past. A still further advantage of the invention lies in the fact that the materials employed do not hinder the normal processing of the film or paper and do not tend to increase defects in the emulsion such as fog to any measurable extent. An additional and equally major advantage is that they harden the emulsion.

As many apparently widely different embodiments of this invention may be made without

departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited to the specific embodiments herein except as defined by the appended claims.

I claim:

1. The process which comprises developing a photographic element containing a reducible silver salt image in the presence of an organic amide having at least one radical taken from the group consisting of methylol and lower alkoxy-methyl radicals directly attached to an amide nitrogen atom.

2. The process which comprises developing a photographic element containing a reducible silver salt image in the presence of a methylolamide wherein the methylol radical is attached to an amide nitrogen atom.

3. The process which comprises developing a photographic element containing a reducible silver salt image in the presence of a methylolurea having at least one $-\text{CH}_2\text{OH}$ group attached to an amide nitrogen atom thereof.

4. A photographic element comprising a support, a light sensitive silver salt layer and a stratum containing a small amount of an organic amide having at least one radical taken from the group consisting of methylol and lower alkoxy-methyl radicals directly attached to an amide nitrogen atom.

5. A photographic element comprising a support, a light sensitive silver halide layer having intimately associated therewith at least one methylolamide having at least one $-\text{CH}_2\text{OH}$ radical directly attached to an amide nitrogen atom.

6. A photographic element comprising a support, a light sensitive silver halide layer having intimately associated therewith at least one methylolurea having at least one $-\text{CH}_2\text{OH}$ radical directly attached to an amide nitrogen atom thereof.

7. A photographic element comprising a support having a light sensitive silver halide emulsion layer thereon said layer containing a small amount of an organic amide having at least one methylol radical attached to an amide nitrogen atom.

8. A photographic element comprising a support having a light sensitive silver halide emulsion layer thereon said layer containing a small amount of an organic amide taken from the class consisting of methylolamides and lower alkyl ethers thereof wherein at least one $-\text{CH}_2\text{O}-$ radical is directly attached to an amide nitrogen atom.

9. A photographic element comprising a sup-

port having a light sensitive silver halide emulsion layer thereon, said layer containing one methylolurea having at least one $-\text{CH}_2\text{OH}-$ radical directly attached to an amide nitrogen atom thereof.

10. A photographic element comprising a support having a light sensitive silver halide emulsion layer thereon and a stratum in intimate contact therewith containing a small amount of an organic amide having at least one radical taken from the group consisting of methylol and lower alkoxy-methyl radicals directly attached to an amide nitrogen atom.

11. A light sensitive silver halide emulsion containing a small amount of an organic amide having at least one radical taken from the group consisting of methylol and lower alkoxy-methyl radicals directly attached to an amide nitrogen atom thereof.

12. A light sensitive silver halide emulsion containing a small amount of an organic amide having at least one radical taken from the group consisting of methylol and lower alkoxy-methyl radicals directly attached to an amide nitrogen atom thereof and a sensitizing dye.

13. A process of manufacturing light sensitive silver halide emulsion layers which yield developed photographic images in blue-black tones, the step which comprises adding to a constituent of the emulsion layer prior to complete development a small amount of an organic amide having at least one radical taken from the group consisting of methylol and lower alkoxy-methyl radicals directly attached to an amide nitrogen atom thereof.

14. An aged, light sensitive, silver halide, emulsion containing a small amount of an organic amide having at least one radical taken from the group consisting of methylol and lower alkoxy-methyl radicals directly attached to an amide nitrogen atom thereof.

15. A photographic element comprising a support having a light sensitive silver halide emulsion layer thereon, said layer containing a small amount of dimethylol urea.

16. A photographic element comprising a support having a light sensitive silver halide emulsion layer thereon, said layer containing a small amount of trimethylol melamine.

17. A photographic element comprising a support having a light sensitive silver halide emulsion layer thereon, said layer containing a small amount of N,N'-bis(methoxymethyl) urea.

WALTER D. BALDSEFFEN.