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PRODUCTION OF BLUE-BLACK TONED SILVER IMAGES

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No Drawing. Application March 6, 1943, Serial No. 478,281

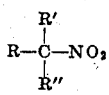
14 Claims. (Cl. 95—6)

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.

This application has been divided out of my copending application Serial No. 397,967, filed June 13, 1941, and is a continuation-in-part of such application.

It has been found that photographs having blue-black tones can be made by utilizing in their production methylol-nitromethanes. Such compounds have at least one methylol radical and a nitro radical attached to the methane carbon atom and may be represented by the general formula



wherein at least one of the R's is a methylol (—CH_2OH) radical and the remaining R's are either a methylol radical or an alkyl radical, e. g., 1 to 2 carbon atoms or a hydrogen atom.

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 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 antistatic layer of such eelments. 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.

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 complatible 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

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 II

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 4 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 III

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 IV

Twenty milliliters of water in which is dissolved 0.1 gram of 2-nitropropanediol-1,3 is added to 1 liter of a fine grain photographic emulsion ready for pouring which contains 40 grams of a silver halide, comprising 95% silver bromide and 5% silver iodide, and 70 grams of gelatin. The emulsion is then coated on a cellulose nitrate base and dried, after which it is stored for a period of 30 days at 70° F. At the end of this time the emulsion is 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 is 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 V

One gram of 2-nitro-2-methyl propanediol-1,3 is 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 is then coated on a suitable support and dried. After exposure, the element is processed in alkaline metol-hydroquinone developer and fixed in an acid-hardening fixing bath. A sharp blue-black image of high resolving power is obtained instead of the neutral-black-to-brownish image of a control to which no blue-black agent has been added.

In place of the specific blue-black toning agent specified in the above examples can be substituted one or more other methylolnitromethanes having the structural characteristics set forth above. Similarly the compounds of the several examples can be interchanged in any desired manner. Suitable additional compounds include monomethylolnitromethane, and 2-nitro-2-ethyl propanediol-1,3. The agents when used in making silver halide emulsions are added in amounts ranging from 0.2 to 10% of the weight of silver nitrate used. A preferred range being from 1.2 to 2.5%.

The methylolnitromethanes hereof moreover may be admixed with one or more of the methylolamides or lower alkoxy methylamides described in aforesaid application Serial No. 397,967. Suitable compounds which are described therein include monomethylol urea, dimethylol urea, N,N'-bis(methoxymethyl)urea, trimethylol melamine, dimethylol formamide, tetrahydro-1,3-dimethoxymethyl - 5(beta - hydroxyethyl) - s - triazone-2, N,N'bis(dimethyl monomethylol)urea, cyclic dimethylol diurea (Goldschmidt's compound), methylol formamide, dimethylol formamide, 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, etc.

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, 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.

The tone of the developed silver image on proper supports is often altered irreparably upon passing such elements through heated drying machines. It has been found that the present agents overcome this disadvantage and inhibit the change in tone of the silver image upon heated drying. The resulting developed elements therefore constitute improved articles of manufacture.

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 a methylol nitromethane.

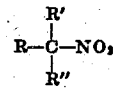
2. In a process of manufacturing light sensitive silver halide emulsion layers which yield developed photographic images in blue-black tones, the step which comprises adding to a constituent of the emulsion layer prior to complete development a small amount of a methylol nitromethane.

3. A light sensitive silver halide emulsion containing a small amount of a methylol nitromethane.

4. An aged light sensitive silver halide emulsion containing a small amount of a methylol nitromethane.

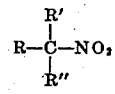
5. The process which comprises developing a photographic element containing a reducible silver halide image in the presence of a methylol nitromethane.

6. The process which comprises developing a photographic element containing a reducible silver salt image in the presence of a methylol nitromethane of the general formula



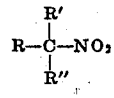
wherein at least one of the R's is a methylol radical and the remaining R's are members of the group consisting of hydrogen, methyl and ethyl radicals.

7. A photographic element comprising a support, a light sensitive silver salt layer and a stratum containing a small amount of a methylol nitromethane of the general formula



wherein at least one of the R's is a methylol radical and the remaining R's are members of the group consisting of hydrogen, methyl and ethyl radicals.

8. A photographic element comprising a support, a light sensitive silver halide layer having intimately associated therewith at least one methylol nitromethane of the general formula



wherein at least one of the R's is a methylol radical and the remaining R's are members of the group consisting of hydrogen, methyl and ethyl radicals.

9. In a photographic element having a support, a light-sensitive silver halide layer having intimately associated therewith trimethylol nitromethane.

10. In a photographic element having a support, a light-sensitive silver halide layer having intimately associated therewith 2-nitro-2-methyl-propanediol-1,3.

11. In a photographic element having a support, a light-sensitive silver halide layer having intimately associated therewith 2-nitropropanediol-1,3.

12. A light-sensitive halide emulsion containing a small amount of trimethylol nitromethane.

13. A light-sensitive silver halide emulsion containing a small amount of 2-nitro-2-methyl-propanediol-1,3.

14. A light-sensitive silver halide emulsion containing a small amount of 2-nitropropanediol-1,3.

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CERTIFICATE OF CORRECTION.

Patent No. 2,364,017. November 28, 1944.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 8, for "eelments" read --elements--; line 27-28, for "complatible" read --compatible--; page 3, second column, line 57, claim 12, before the word "halide" insert --silver--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 27th day of February, A. D. 1945.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.