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PHOTOGRAPHIC COMPOSITIONS AND PROCESSES

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18 Claims. (Cl. 96—29)

The present invention relates to photography and, more particularly, to photographic compositions and processes.

Photographic processing compositions capable of forming water-soluble, complex silver salts are known to be useful in many phases of silver halide photography. In particular, a photographic composition which includes a silver halide developer as well as a silver complexing agent is useful in processing a silver halide element by reducing its exposed silver halide to silver, by reacting with its unreduced silver halide to form a water-soluble, complex silver salt and by transferring the salt to a silver-receptive element where it forms a visible image.

The silver complexing agents of the prior art have various shortcomings with respect to transfer processes of this type. For example: certain complexing agents, e.g., ammonia, are too weak to be effective in the production of transfer images; others, e.g., sodium thiosulfate, leave on the transfer image a harmful sulfur residue; and, still others, e.g., sodium cyanide, are often impractical because of their dangerous toxicity.

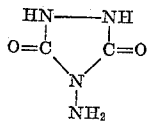
The object of the present invention is to provide compositions and processes employing a novel association of two silver complexing agents which, together, avoid these shortcomings.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the composition possessing the features, properties and relation of elements, and the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the appended claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The present invention is predicated upon the discovery that amino urazole,



and at least one nitrogenous base, together, are unusually adapted to react with silver halide to form water-soluble, complex silver salts. It has been found that these complexing agents, together, perform a more effective complexing function than does either independently.

A great variety of nitrogenous bases may be associated with the amino urazole. Preferred nitrogenous bases are soluble in aqueous alkali and are selected from the class consisting of ammonia, amines, hydroxylamine, aliphatic hydroxylamines, hydrazine and aliphatic hydrazines. Typical preferred nitrogenous bases are:

(1) Ammonia
(2) Sec. amylamine

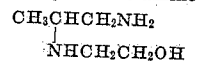
(3) Ethylamine
(4) n-Butylamine
(5) Allylamine
(6) Diethylamine
(7) Dipropylamine
(8) Trimethylamine
(9) Triethanol amine
(10) $NH_2CH_2CH_2NHCH_2CH_2NH_2$

Diethylene triamine

(11) $NH_2—(CH_2CH_2NH)_2CH_2CH_2NH_2$

Triethylene tetramine

(12)



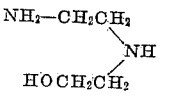
N-hydroxyethyl propylene diamine

(13) $NH_2—CH_2CH_2CH_2NH_2$

Trimethylene diamine

(14) Ethylene diamine

(15)



Aminoethyl ethanol amine

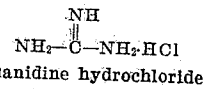
(16) $HOCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$

Hydroxyethyl diethylene triamine

(17) $NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$

Tetraethylene pentamine

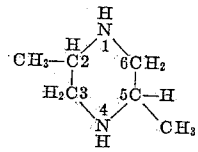
(18)



Guanidine hydrochloride

(19) Piperidine
(20) Pyrrolidine

(21)



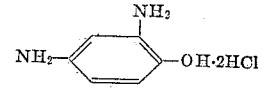
2,5-dimethyl piperazine

(22) $[—C_2H_4NH—]_n$

Polyethylene imine

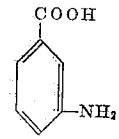
(23) p-Aminophenol

(24)



2,4-diaminophenol dihydrochloride

(25)



Meta-amino-benzoic acid

(26) Hydrazine
(27) Methyl hydrazine
(28) $CH_3NH—NHCH_3$

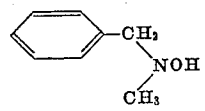
Symmetrical dimethyl hydrazine

(29) $(CH_3)_2N—NH_2$

Unsymmetrical dimethyl hydrazine

(30) Hydroxylamine hydrochloride
(31) N,N-diethyl hydroxylamine
(32) N-ethyl hydroxylamine

(33)



Methyl benzyl hydroxylamine

(34) H_2NOCH_3

O-methyl hydroxylamine

A transfer-reversal process embodying the present invention employs an aqueous alkaline solution of amino urazole, at least one nitrogenous base, and a suitable silver halide developer. Typically, the solution is spread in a uniformly thin layer between the superposed surfaces of a photoexposed gelatino silver halide element and a silver-receptive element, for example by advancing the elements between a pair of pressure-applying rollers. The elements are maintained in superposed relation for a predetermined period, preferably of the order of 40 to 120 seconds in duration, during which exposed silver halide is reduced to silver and unreduced silver halide forms a water-soluble, complex silver salt which diffuses through the layer of solution to the silver-receptive element where it is reduced to silver to form a visible print. At the end of this period, the silver halide element is stripped from the silver-receptive element. Materials useful in one such transfer process are described in United States Patent No. 2,543,181, issued in the name of Edwin H. Land on February 27, 1951. In one such process, both the amino urazole and the nitrogenous base are sulfur free.

Of the variety of silver halide developers to be used in a solution of the foregoing type, preferred are organic developers such as hydroquinone, chlorohydroquinone, bromohydroquinone, dichlorohydroquinone, toluhydroquinone, Metol (p-methyl aminophenol sulfate), Glycin (p-hydroxyphenyl-aminoacetic acid), p-aminophenol hydrochloride, pyrocatechin, pyrogallol and ascorbic acid. Such a nitrogenous base as p-aminophenol can perform at once both a developing function and a complexing function.

The various components of the solution may be varied within wide limits. However, where the processing period is short, for example, ranging from 40 to 120 seconds in duration, practical results are achieved where, in concentration by total weight of the solution, the amino urazole ranges from 1 to 25% and the concentration of the nitrogenous base ranges from .15 to 15%.

The alkalinity of the solution should be high, ranging from a pH of 11 to a hydroxyl ion concentration of 5 N. As examples of bases which are capable of imparting such an alkalinity to the solution, mention may be made of alkali-metal hydroxides such as sodium and potassium hydroxide and amines such as diethylamine and allylamine. Such a nitrogenous base as diethylamine can perform, at once, both this function and a complexing function.

A silver-receptive element of the above-described type preferably includes certain materials, the presence of which, during the transfer process, has a desirable effect on the amount and character of silver precipitated on the silver-receptive element. Materials of this type are specifically described in copending U. S. patent applications Serial No. 727,385, filed by Edwin H. Land on February 8, 1947 (now U. S. Patent No. 2,698,245), and Serial No. 449,995, filed by Edwin H. Land on August 16, 1954 (now U. S. Patent No. 2,698,237).

A composition employed in the foregoing manner preferably is relatively viscous, of the order of 100 to 200,000 centipoises at a temperature of 20° C., so as to be easily controlled when spread. If desired, the viscosity of the composition can be increased by including within it a suitable thickening agent, such, for example, as a water-soluble synthetic polymer, an insoluble, emulsifiable oil, a starch, or a gum. It is possible that such a nitrogenous base as polyethylene imine performs, at once, both a thickening function and a complexing function.

Stripping of the silver halide stratum from the silver-receptive stratum separates the layer of processing solution from the silver-receptive stratum or permits the layer of processing solution to remain in contact with the silver-receptive stratum in order to provide it with a protective coating. Techniques which enable such stripping to be accomplished, as desired, are taught in United States Patent No. 2,647,056, issued to Edwin H. Land on July 28, 1953. In general, the reaction product residue of the solution and the silver halide, which is present on the silver image, either as a trace remaining after the processing solution layer has been separated from the silver or which remains as a protective coating on the silver image, as indicated above, has little tendency to harm the image. However, any existing tendency of this residue to harm the image may be minimized by so formulating the solution that as many of its components as possible are volatile. Thus, in a preferred form, the processing solution comprises, in addition to amino urazole, which is not volatile, a volatile nitrogenous base, e. g., ammonia or a low molecular weight amine, as a complexing agent, and a volatile developer, e. g. hydroxylamine or a low molecular weight hydroxylamine. Here, the tendency of the processing solution residue to harm the image is minimized by volatilization of the nitrogenous base which otherwise might continue silver complex formation and by volatilization of the developer which otherwise might oxidize to a visible product.

A thin layer of the following formulation was maintained between the superposed surfaces of gelatino silver halide and silver-receptive elements of the above-described types for sixty seconds:

Water ---------- cc--	400
Sodium carboxymethyl cellulose (High viscosity) ---------- g--	14.4
Sodium hydroxide ---------- g--	30.2
Sodium sulfite ---------- g--	45.6
Amino urazole ---------- g--	36.0
Hydroquinone ---------- g--	4.3
Metol ---------- g--	0.05
Aminoethyl ethanol amine ---------- cc--	9.0

The excellent image which was formed in the silver-receptive stratum was of blue-black tone and high contrast, and had a maximum density of 1.8 and a minimum density of .04.

Excellent results also were obtained with formulations similar to the foregoing except that the aminoethyl ethanol amine was replaced by an equal quantity of triethylene tetramine, guanidine hydrochloride or allylamine; or 18 cc. of piperidine, pyrrolidine or N-hydroxyethyl propylene diamine; or the hydroquinone was replaced by 1.8 g. of amidol or Metol.

In preparing the foregoing compositions, the carboxymethyl cellulose and sodium hydroxide first were dissolved in water at room temperature. Next the sodium sulfite was dissolved in the solution. Thereafter, the amino urazole was added to the solution and the two phases were mixed until the amino urazole completely dissolved. Finally, the developer and the nitrogenous base were added to the solution with sufficient mixing only to insure their dissolution, care being taken to prevent oxidation and/or volatilization of the developer and/or volatilization of the nitrogenous base.

It is to be expressly understood that compositions embodying the present invention may be employed in photographic processes other than those involving transfer image formation. For example, an alkaline aqueous solution of amino urazole and a nitrogenous base is capable of being used as a fixer to dissolve the unreduced silver halide of a gelatino silver halide, preferably hardened, emulsion which has been photoexposed and developed.

Since certain changes may be made in the above com-

position and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic processing composition comprising, in alkaline aqueous solution, a plurality of agents including amino urazole and a nitrogenous base which, together, are capable of reacting with silver halide to form water-soluble, complex silver salts, one agent of said plurality being a silver halide developer.

2. A photographic processing composition comprising, in highly alkaline aqueous solution, a plurality of agents including amino urazole and a nitrogenous base which, together, are capable of reacting with silver halide to form water-soluble, complex silver salts, at least one component of said plurality being a silver halide developer.

3. A photographic processing composition comprising, in highly alkaline aqueous solution, a plurality of agents including amino urazole and a nitrogenous base which, together, are capable of reacting with silver halide to form water-soluble, complex silver salts, at least one agent of said plurality being a silver halide developer, the concentration of said amino urazole, by total weight of said solution, ranging from 1 to 25%, and the concentration of said nitrogenous base, by total weight of said solution, ranging from .15 to 15%.

4. A photographic processing composition comprising, in highly alkaline aqueous solution, a plurality of agents including amino urazole and a nitrogenous base which, together, are capable of reacting with silver halide to form water-soluble, complex silver salts, at least one agent of said plurality being a silver halide developer, the concentration of said amino urazole, by total weight of said solution, ranging from 1 to 25%, the concentration of said nitrogenous base, by total weight of said solution, ranging from .15 to 15%, and the alkalinity of said solution ranging from a pH of 11 to hydroxyl ion concentration of 5 N.

5. The photographic method of processing a photo-exposed silver halide element and an image-receptive element which are in superposed relation, said method comprising the steps of spreading, in a thin layer, between the adjacent surfaces of said elements, a viscous alkaline aqueous solution of a plurality of agents including amino urazole and a nitrogenous base which, together, are capable of reacting with silver halide to form water-soluble, complex silver salts, one agent of said plurality being a silver halide developer, maintaining said layer in contact with said adjacent surfaces for a predetermined period during which a silver image forms on said image-receptive element, and thereafter stripping said silver halide element from said image-receptive element.

6. The photographic method of claim 5 wherein said layer adheres to said silver halide element when said silver halide element is stripped from said image-receptive element.

7. The photographic method of claim 5 wherein said layer adheres to said image-receptive element when said silver halide element is stripped from said image-receptive element.

8. The photographic method of claim 5 wherein the concentration of said amino urazole ranges from 1 to 25% and the concentration of said nitrogenous base ranges from .15 to 15%.

9. The photographic method of claim 8 wherein the alkalinity of said solution ranges from a pH of 11 to a hydroxyl ion concentration 5 N.

10. The photographic method of processing a photo-exposed silver halide material and an image-receptive material which are in contiguous relation, said method comprising the steps of subjecting said materials to a viscous, alkaline, aqueous solution of a plurality of agents including amino urazole and a nitrogenous base which, together, are capable of reacting with silver halide to form water-soluble, complex silver salts, one agent of said plurality being a silver halide developer, reacting said silver halide developer with said silver halide material in order to preferentially reduce photoexposed silver halide, reacting said amino urazole and said nitrogenous base with unreduced silver halide to form a complex silver salt, and transferring said complex silver salt to said image-receptive material for the reduction thereof in order to form a silver image.

11. The photographic method of claim 10 wherein the concentration of said amino urazole ranges from 1 to 25% and the concentration of said nitrogenous base ranges from .15 to 15%.

12. The photographic method of claim 10 wherein the alkalinity of said solution ranges from a pH of 11 to a hydroxyl ion concentration of 5 N.

13. The photographic method of claim 10 wherein the concentration of said amino urazole ranges from 1 to 25%, the concentration of said nitrogenous base ranges from .15 to 15%, and the alkalinity of said solution ranges from a pH of 11 to a hydroxyl ion concentration of 5 N.

14. A photographic method of processing a silver halide material and a silver-receptive material which are in superposed relation, said method comprising the steps of subjecting said silver halide material and said silver-receptive material to an alkaline, aqueous solution of a plurality of agents including amino urazole and a nitrogenous base, one agent of said plurality being a silver halide developer, reacting said silver halide developer with photoexposed silver halide in order to reduce said photoexposed silver halide to silver, reacting said amino urazole and said nitrogenous base with unreduced silver halide in order to produce a complex silver salt, transferring said complex silver salt to said silver-receptive material for the formation of a silver print, and separating said silver halide material from said silver-receptive material.

15. The photographic method of claim 14 wherein the residue of said solution adheres to said silver halide material when said silver halide material is separated from said silver-receptive material.

16. The photographic method of claim 14 wherein the residue of said solution adheres to said silver-receptive material when said silver halide material is separated from said silver-receptive material.

17. The photographic method of claim 14 wherein the concentration of said amino urazole ranges from 1 to 25% and the concentration of said nitrogenous base ranges from .15 to 15%.

18. The photographic method of claim 14 wherein the alkalinity of said solution ranges from a pH of 11 to a hydroxyl ion concentration of 5 N.

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