

1

2,939,788

NOVEL PHOTOGRAPHIC DEVELOPERS

Elkan R. Blout, Belmont, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed Feb. 26, 1959, Ser. No. 795,602

23 Claims. (Cl. 96-29)

This invention relates to photography and, more particularly, to compositions and processes useful in the development of photosensitive silver halide elements.

This application is a continuation-in-part of my copending application, Serial No. 580,988, filed April 27, 1956, now abandoned.

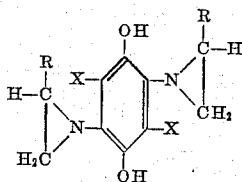
It is one object of the present invention to provide novel developer compositions and processes employing such novel developer compositions for the development of silver halide emulsions.

A further object of this invention is to provide novel developer compositions useful in diffusion-transfer processes, and particularly in high-speed, diffusion-transfer processes wherein the silver halide emulsion has been underexposed.

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

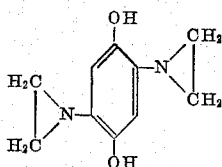
I have now discovered a novel class of silver halide developing agents which are highly useful in photographic developing processes, and especially diffusion-transfer processes. This class of silver halide developing agents may be described as ethylenimino-substituted hydroquinones, i.e., aromatic compounds substituted by hydroxyl groups in the 1 and 4 positions and by at least one ethylenimine group in a position ortho to one of said hydroxyl groups.

A preferred group of ethylenimino-substituted hydroquinones may be represented by the formula:



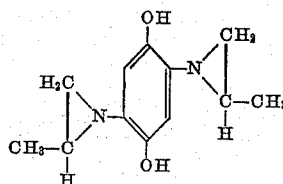
wherein R may be hydrogen or alkyl, preferably methyl, and each X may be hydrogen, halogen or alkyl, preferably methyl.

A preferred silver halide developing agent within this group is 2,5-bis-ethylenimino-hydroquinone, of the structure:

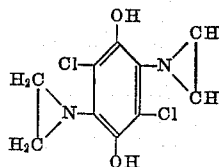


As examples of other developers within the scope of this invention, mention may be made of the following:

2



2,5-bis-methylethylenimino-hydroquinone



2,5-bis-ethylenimino-3,6-dichloro-hydroquinone

A number of ethylenimino-hydroquinones have been described in the literature; see, for example, *Experientia*, vol. XI/5, May 15, 1955, pp. 184-186; U.S. Patent No. 2,770,617, issued on November 13, 1956, to Adrian Marxer; U.S. Patent No. 2,833,760, issued on May 6, 1958, to Adrian Marxer; Belgian Patent 561,910, published on February 15, 1958; and German patent application F17603 IVb/12 p, published November 8, 1956.

The novel developing agents of this invention are useful in conventional black-and-white development.

As previously mentioned, the novel silver halide developers of this invention are also useful in diffusion-transfer processes, both dye and silver, and are especially useful in such photographic processes wherein it is desired to eliminate or minimize the need for washing or stabilizing operations in liquid baths subsequent to the formation of the silver print. Examples of such processes are disclosed in U.S. Patent No. 2,647,056 to Edwin H. Land.

In diffusion-transfer processes of this type, as is well known in the art, an exposed silver halide emulsion is treated with a liquid processing composition while in superposed relationship with an image-receiving material. The liquid processing composition develops exposed silver halide to silver and reacts with unexposed silver halide to form a complex silver salt which is transferred to the image-receiving material and there reduced to silver to form a positive print. The processing composition includes a silver halide solvent, such as sodium thiosulfate, and may also contain a film-forming material for increasing the viscosity of the composition. As used herein, the term "silver halide solvent" refers to reagents which will form a soluble complex with silver halide, as is well known in the art of forming silver images by transfer.

In particular, the novel developing agents of this invention are highly useful in so-called "high-speed" diffusion-transfer processes wherein high quality silver transfer prints are obtained from a silver halide emulsion which has been substantially underexposed in relation to its A.S.A. speed rating. Such an exposure provides a latent image having a density gradient confined to the low exposure or toe region of the negative material's characteristic curve. Processes of this type are disclosed and claimed in the copending application of Edwin H. Land, Meroe M. Morse and Milton Green, Serial No. 564,492, filed February 9, 1956. In such high-speed processes, processing of the underexposed silver halide emulsion is effected in the presence of a silver-receptive material distributed in a stratum superposed on said emulsion. The expression "equivalent overall speed," as set forth herein and in said copending application, indicates generally the correct exposure rating to which an A.S.A. exposure meter must be set in order that it give correct exposure data.

for producing positive pictures of satisfactory high quality by the silver-transfer process.

The following example is intended to illustrate the use of the novel developers of this invention in diffusion-transfer processes, and especially high-speed processes of the type just mentioned, and is intended to be illustrative only.

Example 1

A silver iodobromide emulsion sold by Eastman Kodak under the trade name "Royal Pan" was exposed and processed with a composition comprising:

Sodium carboxymethyl cellulose-----g--	13.35
Sodium hydroxide-----g--	10.64
Chlorobenzotriazole -----g--	5.0
Sodium sulfite-----g--	17.10
Sodium thiosulfate-----g--	3.60
2,5-bis-ethylenimino-hydroquinone -----g--	9.0
Water -----cc--	265.50

The image-receiving element comprised a silver-receptive stratum containing silver precipitating nuclei dispersed in a matrix of colloidal silica coated on a water-impermeable base according to the practice described in U.S. Patent No. 2,823,122, issued February 11, 1958. The silver halide emulsion was exposed to a subject through a stop which gave rise to an equivalent overall speed of 1320 reciprocal mcs. The exposed emulsion and the image-receiving element were then advanced, in superposed relationship, between a pair of pressure-applying rollers to spread the processing solution between them in a thin layer approximately 0.003 of an inch thick. After an imbibition period of approximately sixty seconds, the emulsion, together with the layer of solution, was stripped from the image-receiving element to uncover the positive print, which had a maximum density of 1.5, a minimum density of 0.06, and a range of 70.

The concentration of the developing agent may be varied over a wide range. Good results have been obtained, for example, using quantities ranging from 4.5 to 12.0 g. in the process described in Example 1; higher or lower quantities may also be used.

The developing ability of the novel developing agents of this invention was unobvious, since it has been found that 2,5-bis-dimethylamino-hydroquinone is a substantially nondiscriminatory developer.

It has also been found that 2,5-bis-ethylenimino-hydroquinone is a superior developing agent as compared, for example, with hydroquinone. Thus, the equivalent overall speed obtained by repeating Example 1 using 11.4 g. of hydroquinone was 100 reciprocal mcs.

In practice, ethylenimino-hydroquinones preferably are not kept in the presence of aqueous alkali for prolonged periods prior to use. Thus, if tray development is contemplated, it is preferred that the developing solution be prepared just prior to use. In diffusion-transfer processes, undesired contact of the ethylenimino-hydroquinone with aqueous alkali may be avoided, for example, by incorporating the developing agent in the negative or positive in accordance with well-known practices. Thus, 2,5-bis-ethylenimino-hydroquinone may be ground up and dispersed in the silver halide emulsion or in another layer in the negative.

It will be apparent that the relative proportions of the novel developing agents of the developer composition set forth above may be varied to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the above developer composition by the substitution of preservatives, alkalies, silver halide solvents, antifoggants, etc., other than those specifically mentioned. Where desirable, it is also contemplated to include in the developer composition common components such as restrainers, accelerators, etc.

As noted above, the developing agents of this invention are also useful in dye transfer processes. In

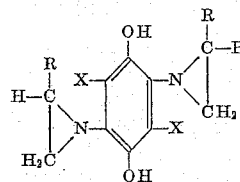
particular, they are useful as accelerating developers in processes employing dye developers, i.e., silver halide developing agents which are also dyes. Processes employing dye developers are disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 748,421, filed July 19, 1958, as a continuation-in-part of Serial No. 415,073, filed March 9, 1954 (now abandoned). A suitable composition for use in such a process, employing a negative containing the dye developer, comprises:

	Percent
Sodium carboxymethyl cellulose-----	4.5
Sodium hydroxide-----	3.0
Potassium bromide-----	0.2
2,5-bis-ethylenimino-hydroquinone -----	0.4

Since certain changes may be made in the above compositions and processes 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. As a new developer composition, an aqueous solution comprising an alkaline material, a silver halide solvent, and a silver halide developing agent selected from the group consisting of compounds within the formula:



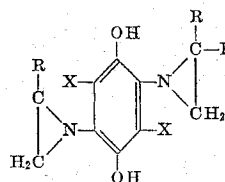
wherein each R is selected from the group consisting of hydrogen and alkyl groups, and each X is selected from the group consisting of hydrogen, halogen and alkyl groups.

2. A new developer composition as defined in claim 1, including a viscosity-increasing, film-forming material.

3. A new developer composition as defined in claim 2, wherein said viscosity-increasing, film-forming material is carboxymethyl cellulose.

4. As a new developer composition, an aqueous solution comprising an alkaline material, a silver halide solvent, and 2,5-bis-ethylenimino-hydroquinone.

5. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion containing a latent image with an aqueous solution comprising an alkaline material and a silver halide developing agent selected from the group consisting of compounds represented by the formula:



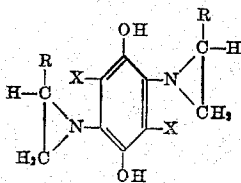
wherein each R is selected from the group consisting of hydrogen and alkyl radicals, and each X is selected from the group consisting of hydrogen, halogen and alkyl radicals, for a sufficient time to develop the latent image to a silver image.

6. A method of developing a silver halide emulsion as defined in claim 5, wherein said silver halide developing agent is disposed, prior to exposure, in the photosensitive element containing said silver halide emulsion.

7. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion containing a latent image with an aqueous solution comprising an alkaline material and 2,5-bis-ethylenimino-hydroquinone for a sufficient time to develop the latent image to a silver image.

5

8. A photographic process comprising the steps of developing a silver halide emulsion with an aqueous alkaline solution comprising a silver halide developing agent and a silver halide solvent in the presence of an image-receiving material superposed on said silver halide emulsion, said developing agent being selected from the group consisting of compounds represented by the formula:



wherein each R is selected from the group consisting of hydrogen and alkyl groups and each X is selected from the group consisting of hydrogen, halogen and alkyl groups, to form a positive silver print on said image-receiving material.

9. A process as defined in claim 8, wherein said developing agent is 2,5-bis-ethylenimino-hydroquinone.

10. A process as defined in claim 8, including the steps of underexposing said silver halide emulsion with respect to its A.S.A. rated speed to produce therein a faint latent image, developing said emulsion in the presence of a silver-receptive material distributed in a stratum superposed on said emulsion, and forming a positive silver print of full pictorial density in the presence of said silver-receptive material.

11. A process as defined in claim 8, wherein said developing agent is 2,5-bis-ethylenimino-hydroquinone.

12. A process as defined in claim 8, wherein said silver halide developing agent is disposed, prior to exposure, in a photosensitive element containing said emulsion and the solution containing said developing agent is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said developing agent.

13. A process as defined in claim 8, wherein said silver halide developing agent is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

14. As a new developer composition, an aqueous composition comprising sodium hydroxide, 2,5-bis-ethylenimino-hydroquinone, carboxymethyl cellulose and sodium thiosulfate.

15. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion containing a latent image with an aqueous solution comprising sodium hydroxide, 2,5-bis-ethylenimino-hydroquinone and carboxymethyl cellulose for a sufficient time to develop the latent image to a silver image.

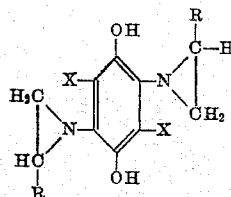
16. A photographic process comprising the steps of developing a silver halide emulsion with an aqueous alkaline solution comprising 2,5-bis-ethylenimino-hydroquinone, sodium thiosulfate, sodium hydroxide and carboxymethyl cellulose in the presence of an image-receiving material superposed on said silver halide emulsion to form a positive silver print on said image-receiving material.

17. A process as defined in claim 16, including the steps of underexposing said silver halide emulsion with respect to its A.S.A. rated speed to produce therein a faint latent image, developing said emulsion in the presence of a silver-receptive material distributed in a stratum superposed on said emulsion and forming a positive silver print of full pictorial density in the presence of said silver-receptive material.

18. A photographic process comprising the steps of developing a silver halide emulsion with an aqueous

6

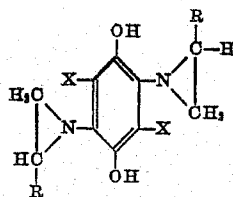
alkaline solution comprising a silver halide developing agent selected from the group consisting of compounds represented by the formula:



wherein each R is selected from the group consisting of hydrogen and alkyl groups and each X is selected from the group consisting of hydrogen, halogen and alkyl groups, transferring image-providing components from unexposed areas of said silver halide emulsion to a superposed image-receiving layer to form a positive transfer image.

19. A photographic process as defined in claim 18, wherein said silver halide developing agent is 2,5-bis-ethylenimino-hydroquinone.

20. A photographic product comprising a plurality of layers, a silver halide emulsion located in one of said layers and a silver halide developing agent located in one of said layers, said silver halide developing agent being selected from the group consisting of compounds represented by the formula:



wherein each R is selected from the group consisting of hydrogen and alkyl groups and each X is selected from the group consisting of hydrogen, halogen and alkyl groups.

21. A photographic product as defined in claim 20, wherein said silver halide developing agent is 2,5-bis-ethylenimino-hydroquinone.

22. As a new developer composition, an aqueous solution comprising an alkaline material, a silver halide solvent, and an ethylenimino-hydroquinone, said ethylenimino-hydroquinone being an aromatic compound substituted in the 1 and 4 positions by hydroxyl groups and being further substituted by at least one ethylenimine group in a position ortho to one of said hydroxyl groups.

23. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion containing a latent image with an aqueous solution comprising an alkaline material and an ethylenimino-hydroquinone, said ethylenimino-hydroquinone being an aromatic compound substituted in the 1 and 4 positions by hydroxyl groups and being further substituted by at least one ethylenimine group in a position ortho to one of said hydroxyl groups, for a sufficient time to develop the latent image to silver.

References Cited in the file of this patent

UNITED STATES PATENTS

2,533,990	Blake	Dec. 12, 1950
2,544,910	Yule	Mar. 13, 1951
2,606,900	Parker et al.	Aug. 12, 1952
2,619,484	Wenner	Nov. 25, 1952
2,759,825	Land	Aug. 21, 1956
2,779,617	Marxer	Nov. 13, 1956