

United States Patent

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[54] **NOVEL PHOTOGRAPHIC COMPOSITIONS AND PROCESSES**
9 Claims, No Drawings
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96/61 M, 96/66 R
[51] Int. Cl. G03c 5/30,
G03c 5/54
[50] Field of Search. 96/66 R, 61
M, 29; 260/586

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ABSTRACT: Substituted reductic acid compounds and preferably, tetrasubstituted reductic acid compounds are used as developing agents for silver halide emulsions in photographic processes, particularly diffusion transfer processes.

NOVEL PHOTOGRAPHIC COMPOSITIONS AND PROCESSES

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

Diffusion transfer processes are well-known. In such processes, an exposed silver halide emulsion is treated with an aqueous alkaline processing composition whereby exposed silver halide is developed and an imagewise distribution of diffusible image-forming components is formed as a function of the point-to-point degree of development. This distribution of diffusible image-forming components is transferred by imbibition to an image-receiving stratum positioned in superposed relationship with the silver halide emulsion to form a transfer image thereon. In silver diffusion transfer processes wherein a silver image is formed, processing is effected in the presence of a silver halide solvent, such as sodium thiosulfate, which forms a diffusible complex with the unexposed and undeveloped silver halide.

Certain enediols have long been known to be capable of developing an exposed silver halide emulsion. Among such developing agents is ascorbic acid. This enediol has been employed in conventional photographic processing and also in diffusion transfer processes where it has been especially useful in developing the positive, i.e., in enhancing the formation of a silver image in the sheet comprising the image-receiving stratum. However, photographic utilization of ascorbic acid has been somewhat limited, especially in diffusion transfer procedures, because of its instability in alkaline media.

It has now been found that certain other enediols exhibit unexpected properties as developing agents in photographic processes and offer many unexpected advantages when compared with ascorbic acid. In particular, it has been discovered that reductic acid compounds, while possessing many of the desirable properties of ascorbic acid, are substantially more stable than ascorbic acid in the presence of alkali. Besides excellent alkali stability, such compounds are even more effective in developing the positive silver image and considerably more discriminating in their development of the negative image.

It is therefore a primary object of the present invention to provide silver halide developing agents which are highly useful in photographic developing processes and particularly in diffusion transfer processes.

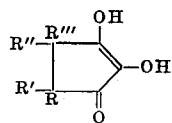
It is another object of the present invention to provide compositions and processes employing said silver halide developing agents in the development of exposed silver halide emulsions and in the formation of silver transfer images.

Further objects of this invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products and 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.

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

Specifically, the photographic developing agents comprehended by the present invention may be represented by the general formula:



wherein R, R', R'' and R''' each are selected from the group consisting of hydrogen, fluorine and the radical $-\text{CH}_2\text{R}''''$ wherein R'''' is hydrogen or a monovalent organic radical, at

least one of said R, R', R'' and R''' being $-\text{CH}_2\text{R}''''$. R'''' may be any monovalent organic radical, e.g., amino, cyano, halo, hydroxyl, carboxyl, sulfonyl, alkyl, cycloalkyl, aryl of the benzene or naphthalene series, or alkaryl. The alkyl and aryl substituents in turn may be substituted with hydroxyl, carboxyl, sulfonyl, halogen, amino and so forth. It will be understood that the R, that the R', R'' and R''' substituents chosen will be such that the compound is soluble in alkaline solution.

In a preferred embodiment each of R, R', R'' and R''' comprises the radical $-\text{CH}_2\text{R}''''$ wherein R'''' may be the same or different. When the reductic acid is substituted in this manner, it is exactly a two electron developer, i.e., one molecule of the tetrasubstituted reductic acid reduces exactly two molecules of silver halide to silver metal. Such developing agents allow the degree of development to be carefully controlled so that they may be used advantageously in photographic processes where such precision is desirable. The tetrasubstituted reductic acid compounds also possess greater alkali stability than those compounds with only one, two or three substituents. An especially useful compound of this type is tetramethyl reductic acid.

The compounds of the present invention may be synthesized, for example, according to the procedures disclosed by Francis and Wilson, *Journal of the Chemical Society*, page 2,238 (1913) and Hesse and Wehling, *Annalen* 679, page 100 (1964). Thus, for example, there can be readily produced such compounds as tetramethyl reductic acid by reacting phorone with bromine to give a tetrabromide, which eliminates hydrogen bromide with pyridine. The dibromo phorone is cyclized with loss of HBr by sulfuric acid, and a bromine atom on the cyclized material is displaced with hydroxide to give tetramethyl reductic acid.

As indicated above, the subject reductic acid compounds are useful as silver halide developing agents in both conventional or "tray" development and in diffusion transfer processes, both dye and silver. In such processes, these compounds may be used as the sole silver halide developing agent, and if desired may be employed in combination with another silver halide developing agent. Since these compounds do not give rise to oxidation products which tend to stain the transfer image, they are especially valuable for use in processes where it is inconvenient to wash the transfer print.

When the compounds are used in diffusion transfer procedures, the processing composition if it is to be applied to the emulsion by being spread thereon in a thin layer, may include a film-forming thickening agent such as a high molecular weight polymer, sodium carboxymethyl cellulose. For silver transfer purposes, the compositions have incorporated therein as a further ingredient a silver halide solvent, such as sodium thiosulfate. Where desirable, the composition may be further modified by the inclusion of other common components of developer compositions, such as restrainers, preservatives and so forth.

Rather than being dissolved in the aqueous alkaline processing composition prior to application thereof to an exposed silver halide emulsion, the reductic acid developing agent may be disposed prior to exposure in the photosensitive element comprising the silver halide emulsion. In this instance the processing composition containing the developing agent is formed by permeating the emulsion with aqueous alkali capable of solubilizing the agent. In diffusion transfer processes, the substituted reductic acid compound is usually contained in the processing composition.

The developing agents of the present invention are especially useful in photographic processes wherein it is desired to eliminate or minimize the need for washing or stabilizing operations subsequent to the formation of the positive print. Examples of such processes are disclosed in U.S. Pat. No. 2,647,056 to Edwin H. Land.

The following examples are given to further illustrate the present invention and are not intended to limit the scope thereof.

EXAMPLE 1

A gelatino silver iodobromide emulsion was exposed to a step tablet and processed by spreading a layer of processing composition approximately 0.0018 inches thick between the thus exposed emulsion and an image-receiving element. The image-receiving element comprised a silver-receptive stratum containing silver-precipitating nuclei dispersed in a matrix of colloidal silica coated on a water-impervious base. The processing composition employed was prepared by adding 0.6 g. tetramethyl reductic acid to 10 cc. of the following formulation:

Hydroxyethyl cellulose	366 g.
Sodium hydroxide	425 g.
Sodium sulfite	260 g.
Sodium thiosulfate	741 g.
Gum arabic	100 cc.
Water	8,289 g.

After an imbibition period of approximately 30 seconds, the emulsion element was stripped from the image-receiving element to reveal a negative image showing all 15 steps of the step tablet as well-defined blocks. The maximum and minimum transmission densities measured for the negative were 0.80 and 0.18, respectively. The positive image showed 12 well-defined steps indicating quite good discrimination in development.

To determine the stability of the tetramethyl reductic acid developing agent in alkaline processing composition, a second gelatino silver iodobromide emulsion was exposed to a step tablet and processed in the same manner as described above except that the processing composition containing the developing agent, rather than being used fresh, had been stored in a closed container for 16 hours at 90° C. The images obtained using the stored solution were substantially identical to those obtained using the freshly prepared composition. The negative showed 15 well-defined density steps and had maximum and minimum densities of 0.78 and 0.16, respectively, while the positive showed 12 steps.

In a further comparison, two silver halide emulsion elements were exposed and processed according to the same procedure outlined above except that the tetramethyl reductic acid was replaced by 0.6 g. of ascorbic acid and was added to 10 cc. of the above formulation as the only developing agent. One of the exposed elements was processed with the freshly prepared solution while the other was processed with solution that had been stored in a closed container for 16 hours at 90° C. The negative images obtained with the freshly prepared and stored solutions both showed only 10 not too clearly defined steps and had maximum and minimum densities of 0.18 and 0.05 and 0.22 and 0.04, respectively. Upon visual inspection of the positive silver image obtained with the freshly prepared solution, only two steps were discernible while no steps were visually discernible in the positive produced with the stored solution, i.e., there was substantially overall transfer of the silver.

EXAMPLE 2

The experiment of example 1 was repeated using the same procedure and materials for comparing images obtained with freshly prepared versus aged developer compositions containing tetramethyl reductic acid and ascorbic acid, respectively, except that the processing compositions additionally contained 15 g. potassium iodide and 10.8 g. of 6-nitrobenzimidazole nitrate and were stored for 16 hours at 90° C.

Both of the positive images obtained using tetramethyl reductic acid as the developing agent were of very good quality showing all 15 density steps using both the aged processing solution and the freshly prepared solution. Both the negative images likewise exhibited 15 clearly defined steps and gave maximum and minimum transmission density measurements

of 0.78 and 0.14 and 0.80 and 0.14, respectively. In comparison, the positive images obtained with the ascorbic acid compositions were inferior to those obtained with the tetramethyl reductic acid. With fresh solution, a positive silver image showing five steps was obtained while no steps were discernible in the positive produced with the aged ascorbic solution. Examination of the developed silver halide emulsion layers showed very low density. The densities measured for the negatives prepared with the fresh and aged solutions containing ascorbic acid as the only developing agent were 0.30 and 0.02 and 0.09 and 0.02, respectively.

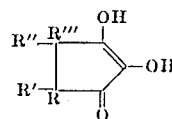
From the above results, it was readily apparent that tetramethyl reductic acid as compared to ascorbic acid is a better agent for developing silver transfer images. The transfer images formed with the tetramethyl reductic acid developer showed at least 12 density steps whereas transfer images produced with the ascorbic acid developer showed only a few steps. It was also apparent that tetramethyl reductic acid is a much more discriminating and effective agent for developing a latent image in a negative as evidenced by the higher maximum densities obtained and by the development of all 15 density steps as well defined steps. The effectiveness of tetramethyl reductic acid in developing a latent image is readily apparent from the significant amount of density obtained in the negative even after relatively brief imbibition times. Most important, the developing agents of the present invention are markedly more stable in alkaline media as demonstrated by the production of prints with aged solution that were comparable in quality to those processed with fresh solution. In comparison, the deterioration of the ascorbic acid-containing composition upon standing at high temperatures was evident from the reduction in density steps for the prints obtained with the aged solutions.

It will be apparent that the relative proportions of the ingredients including the developing agent set forth above may be varied to suit the requirements of the operator. Thus, it is within the scope of this invention to combine the aforementioned developing agent with other suitable alkalis, silver halide solvents, etc., other than those specifically mentioned. As mentioned previously, it is also contemplated to include in the processing composition common components such as preservatives, restrainers and so forth.

Since certain changes may be made in the above compositions, products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description should be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic developer composition comprising an aqueous alkaline solution containing a silver halide solvent and a silver halide developing agent selected from the group consisting of compounds within the formula



wherein R, R', R'' and R''' each are selected from the group consisting of hydrogen and the radical $-\text{CH}_2\text{R}''''$ wherein R'''' is hydrogen or a monovalent organic radical selected from the group consisting of amino, cyano, halo, hydroxyl, carboxyl, sulfonyl, alkyl, cycloalkyl, aryl of the benzene or naphthalene series and alkaryl of the benzene or naphthalene series, at least one of said R, R', R'' and R''' being $-\text{CH}_2\text{R}''''$.

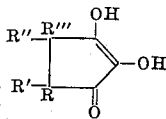
2. A composition as defined in claim 1 wherein said R, R', R'' and R''' each are the radical $-\text{CH}_2\text{R}''''$.

3. A composition as defined in claim 1 wherein said developing agent is tetramethyl reductic acid.

4. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion containing a latent image with an aqueous alkaline solution contain-

5

ing a silver halide developing agent selected from the group consisting of compounds within the formula



wherein R, R', R'' and R''' each are selected from the group consisting of hydrogen and the radical $-\text{CH}_2\text{R}''''$ wherein R'''' is hydrogen or a monovalent organic radical selected from the group consisting of amino, cyano, halo, hydroxyl, carboxyl, sulfonyl, alkyl, cycloalkyl, aryl of the benzene or naphthalene series and alkaryl of the benzene or naphthalene series, at least one of said R, R', R'' and R''' being $-\text{CH}_2\text{R}''''$.

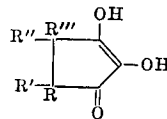
5. A method according to claim 4 wherein each of said R, R', R'' and R''' are the radical $-\text{CH}_2\text{R}''''$.

6. A process according to claim 4 wherein said developing agent is tetramethyl reductic acid.

7. 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 super-

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posed on said silver halide emulsion to form a silver transfer image on said image-receiving material, said developing agent being selected from the group consisting of compounds represented by the formula



wherein R, R', R'' and R''' each are selected from the group consisting of hydrogen and the radical $-\text{CH}_2\text{R}''''$ wherein R'''' is hydrogen or a monovalent organic radical selected from the group consisting of amino, cyano, halo, hydroxyl, carboxyl, sulfonyl, alkyl, cycloalkyl, aryl of the benzene or naphthalene series and alkaryl of the benzene or naphthalene series, at least one of said R, R', R'' and R''' being $-\text{CH}_2\text{R}''''$.

8. A process according to claim 7 wherein each of R, R', R'' and R''' is the radical $-\text{CH}_2\text{R}''''$.

9. A process according to claim 7 wherein said developing agent is tetramethyl reductic acid.

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