United States Patent Office

3,337,342
Patented Aug. 22, 1967

3,337,342
PHOTOGRAPHIC DEVELOPING AGENTS

Milton Green, Newton Center, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed May 26, 1965, Ser. No. 459,112
14 Claims. (Cl. 96—29)

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

A primary object of this invention is to provide novel silver halide developing agents, and products, compositions and processes employing said novel silver halide developing agents, for the development of exposed silver halide emulsions.

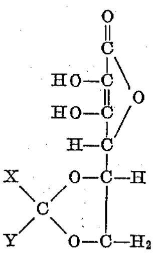
A further object of this invention is to provide novel silver halide developing agents particularly useful in diffusion transfer processes.

Further objects of this invention will be obvious from from the description of this invention given hereinafter.

The invention accordingly comprises 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.

Ascorbic acid has long been known to be capable of developing an exposed silver halide emulsion. Photographic utilization of ascorbic acid has been limited, however, because of its acknowledged "weak" action as a silver halide developing agent.

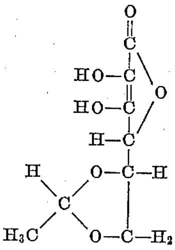
It has now been discovered that certain ketal derivatives of ascorbic acid exhibit unexpexcted properties as silver halide developing agents and offer many unexpected advantages when compared with ascorbic acid or isoascorbic acid. These ascorbic acid ketals may be represented by the formula:



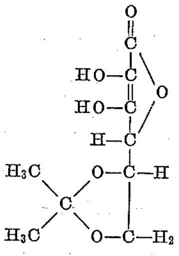
wherein X and Y each are lower alkyl or hydrogen, provided that at least one of X and Y is lower alkyl, i.e., an alkyl group of from 1 to 5 carbons. In the preferred embodiments, the lower alkyl group is a methyl group.

The ascorbic acid ketals with which this invention is concerned are known compounds; see, for example, Berichte, vol. 69B, p. 879 (1936) [Chemical Abstracts, vol. 30, p. 4466]; J. Biol. Chem., vol. 187, p. 453 (1950) [Chemical Abstracts, vol. 48, p. 4292]; Nature, vol. 130, p. 847 (1932).

Particularly useful and preferred ascorbic acid ketals are:

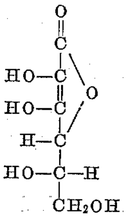


5,6-ethylidene ascorbic acid

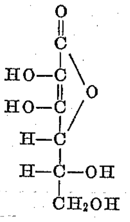


5,6-isopropylidene ascorbic acid

It will be understood that the ketals of isoascorbic acid also are within the scope of this invention, and the term "ascorbic acid ketals" when used herein in a generic sense is intended to include the ketals of ascorbic acid:



and of isoascorbic acid:



As indicated above, the ascorbic acid ketals are useful as silver halide developing agents in both conventional or "tray" development and diffusion transfer processes. The ascorbic acid ketals may be used as the sole silver halide developing agent, although they are most effective when employed in combination with another silver halide developing agent. The developer composition may include the usual components, it being generally found that an ascorbic acid ketal frequently may simply be used to replace ascorbic acid or isoascorbic acid in known developer formulations.

Diffusion transfer processes are well known and the details thereof need not be given here. It is sufficient to note that in such processes an exposed silver halide emulsion is treated with an aqueous alkaline processing composition, 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 imagewise distribution of diffusible image-forming components is transferred, by diffusion, to an image-receiving stratum positioned in superposed relationship with the silver halide emulsion, thereby forming a transfer image in or on said image-receiving stratum. Where the transfer image is to be a silver image, processing is effected in the presence of a silver halide solvent, such as sodium thiosulfate, which forms a diffusible complex with undeveloped silver halide. As used herein, the term "silver halide solvent" refers to reagents which will form a soluble, diffusible complex with silver halide, as is well known in the art of forming silver images by transfer. In a particularly useful embodiment of the diffusion transfer process, the processing composition includes a film-forming, viscosity-increasing material, and a thin layer of the processing composition is spread between the exposed silver halide emulsion and the image-receiving stratum as they are brought into superposed relationship; see, for example, U.S. Patents Nos. 2,543,181 and 2,647,056 issued to Edwin H. Land. The image-receiving stratum preferably includes a silver precipitating agent, as is also well known in the art. In certain embodiments, the processing composition may include a silver precipitating agent, and a solidified layer of said processing composition may be employed as the image-receiving stratum, as described in U.S. Patent No. 2,662,822, also issued to Edwin H. Land.

The following example of the synthesis of an ascorbic acid ketal is given for purposes of illustration only.

Example 1

A mixture of 10 g. L-ascorbic acid, 75 cc. of 2,2-dimethoxy-propane, 50 cc. of dioxane and 0.5 cc. of trifluoroacetic acid was heated with distillation on a steam bath for 7 hours. The solution was then evaporated under vacuum at 60° C., giving 11 g. (90% yield) of 5,6-isopropylidene-L-ascorbic acid as an off-white powder. The product was recrystallized from a minimum amount of a 50:50 mixture of acetone and 2 B ethanol to give a white solid, melting at 206–209° C. (dec.) and soluble in water and dioxane.

The following examples of the use of the ascorbic acid ketals as silver halide developing agents are intended to be illustrative only.

Example 2

The efficiency with which an exposed silver halide emulsion was developed by the ascorbic acid ketals was tested as follows: four silver halide negatives were exposed to a step tablet and processed by spreading a layer of processing composition 0.0026" thick between the exposed negative and an image-receiving element. A processing composition base was prepared comprising:

Water	cc..	165
Sodium carboxymethyl cellulose	g..	7.5
Sodium hydroxide	g..	4.6
Sodium sulfite	g..	5.9
Potassium thiosulfate	g..	2.5
Diethylamine	cc..	9
Aqueous solution of sodium sulfide (156 mg. Na_2S/cc.)	cc..	0.18
Aqueous solution of lead acetate and cadmium acetate (100 cc. H_2O; 2.9 g. lead acetate; 2.1 g. cadmium acetate)	cc..	6.4

The processing compositions were prepared by adding 0.6 g. of each developing agent recited below to different 10 cc. portions of the above processing composition base. After an imbibition period of 60 seconds, the negatives were separated and the transmission $D_{max.}$ and $D_{min.}$ of the negatives (the negatives were fixed during imbibition and were not subjected to further fixing after imbibition) were measured and found to be:

	$D_{max.}$	$D_{min.}$
Ascorbic acid	0.68	0.25
Isoascorbic acid	0.87	0.23
5,6-isopropylidene-ascorbic acid	1.60	0.33
5,6-ethylidene-ascorbic acid	1.21	0.28

It will be noted that the ascorbic acid ketals developed much more silver than either ascorbic acid or isoascorbic acid, i.e., they gave greater density in the exposed areas, on a molar basis, since they were employed in the same weight concentrations but the molecular weights of 5,6-ethylidene ascorbic acid and 5,6-isopropylidene ascorbic acid are 202 and 216, respectively, as compared with 176 for ascorbic acid and isoascorbic acid.

Example 3

A silver halide negative was exposed to a step tablet and processed by spreading a layer of processing composition approximately 0.0026" thick between the exposed negative and an image-receiving element of the type used in type 42 Polaroid Land film. The processing composition comprised 10 cc. of the base described in Example 2 to which 0.6 g. of ascorbic acid and 0.02 g. of 2,4-diamino-ortho-cresol were added. This procedure was repeated, retaining the 0.02 g. of 2,4-diamino-ortho-cresol and replacing the ascorbic acid first with 0.6 g. of isoascorbic acid and then with 0.6 g. of 5,6-isopropylidene ascorbic acid. After an imbibition period of 60 seconds, the transmission densities, slopes and speeds of the negatives were measured as follows:

	$D_{max.}$	$D_{min.}$	4/0.5 Speed	3/4-1/4 Slope
Ascorbic acid	1.74	0.43	80	0.85
Isoascorbic acid	1.73	0.43	80	0.95
5,6-isopropylidene ascorbic acid	1.57	0.35	46	0.61

It will thus be seen that use of the 5,6-isopropylidene ascorbic acid gave a negative of lower contrast or slope. This lower contrast is very desirable in reusable negatives formed in diffusion transfer processes.

Example 4

The procedure described in Example 3 was repeated, the processing composition being prepared by adding 0.6 g. of isoascorbic acid and 0.02 g. of 2,6-dimethoxy-4-aminophenol to a first 10 cc. portion of the processing composition base described in Example 2, and adding 0.3 g. of isoascorbic acid, 0.3 g. of 5,6-isopropylidene isoascorbic acid and 0.02 g. of 2,6-dimethoxy-4-aminophenol to a second 10 cc. portion of said processing composition base. After an imbibition period of 60 seconds, the negative and positive were separated, and the following results were noted on the negative images:

	$D_{max.}$	$D_{min.}$	4/0.5 Speed	3/4-1/4 Slope
Isoascorbic acid	1.72	0.41	64	0.90
Isoascorbic acid plus 5,6-isopropylidene ascorbic acid	1.69	0.42	64	0.80

It will be noted that the densities and speeds of the two negative images were essentially identical, but that the contrast of the negative developed with 5,6-isopropylidene ascorbic acid was significantly lower than that of the negative developed with isoascorbic acid. Examination of the positive transfer images showed the following:

	$D_{max.}$	$D_{min.}$
Isoascorgic acid	1.4	0.06
Isoascorbic acid plus 5, 6-isopropylidene ascorbic acid	1.46	0.08

It will thus be seen that the ascorbic acid ketals may be used in combination with ascorbic acid or isoascorbic acid to obtain a more desirable balance of sensitometric results, while maintaining maximum and minimum densities without substantial change.

Example 5

An exposed negative and an image-receiving element of the type employed in type 42 Polaroid Land film were processed by spreading therebetween a layer of processing solution 0.0022" thick as they were brought into superposed relationship. The processing solution comprised:

Water	cc	8.76
Sodium carboxymethyl cellulose	g	0.33
Sodium hydroxide	g	1.32
Uracil	g	0.99
Ammonium hydroxide	cc	0.138
Ascorbic acid	g	0.6

After an imbibition period of 60 seconds, the superposed elements were separated and the image-receiving element contained a dense positive transfer image of low speed and high minimum density. When this test was repeated replacing the ascorbic acid with the same amount by weight of isoascorbic acid, the positive transfer image had a lower minimum density and a film speed about four times faster; in addition, examination of the negative showed greater silver development. Replacement of the isoascorbic acid with 0.6 g. of 5,6-isopropylidene ascorbic acid gave much faster development. Use of a mixture of 0.3 g. of ascorbic or isoascorbic acid in combination with 0.3 g. of 5,6-isopropylidene ascorbic acid gave transfer images of very good density and low highlight density, and equivalent A.S.A. film speeds or exposure indices of approximately 400.

Example 6

A processing composition comprising:

Diethylamine	cc	1.0
Isoascorbic acid	g	0.4
5,6-isopropylidene ascorbic acid	g	0.4
Sodium carboxymethyl cellulose	g	0.4
Potassium thiosulfate	g	0.02

was spread in a layer 0.0015" thick between an exposed negative and a silver receptive layer. After an imbibition period of 60 seconds, the silver receptive layer was found to have a good quality positive silver transfer image.

While the ascorbic acid ketals have been employed in the processing solutions in the examples set forth above, it will be understood that they may be initially located in a layer of the photosensitive element or of the image-receiving element. It it also contemplated that the ascorbic acid ketals may be employed in color diffusion transfer processes.

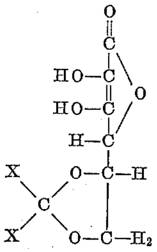
One skilled in the art may readily vary the relative proportions of the ascorbic acid ketals and the other components of the developer compositions to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the above developer compositions by the addition or substitution of alkalis, silver halide solvents, preservatives, antifoggants, etc., other than those specifically mentioned. Furthermore, one may omit the viscosity-increasing component where a non-viscous developer solution is desired.

The ascorbic acid ketals are particularly useful in the photographic processes disclosed in the copending application of Meroe M. Morse, Ser. No. 438,044, filed Mar. 8, 1965. Thus, the ascorbic acid ketals are particularly useful in combination with a high-energy aminophenol silver halide developing agent, wherein one or both positions ortho to the hydroxyl group is substituted by a lower alkyl or a lower alkoxy group. The ascorbic acid ketals are also useful in silver transfer processes of the type disclosed in the copending application of Edwin H. Land et al., Ser. No. 437,739, filed Mar. 8, 1965.

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 shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic developer composition comprising water, an alkaline material, a silver halide solvent, and a silver halide developing agent selected from the group consisting of compounds within the formula:



wherein one of X and Y is a lower alkyl group and the other is selected from the group consisting of hydrogen and lower alkyl groups.

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

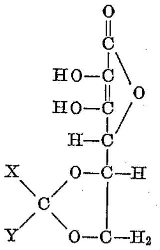
3. A photographic developer composition as defined in claim 2, wherein said viscosity-increasing, film-forming material is carboxymethyl cellulose.

4. A photographic developer composition as defined in claim 2, wherein said viscosity-increasing, film-forming material is hydroxyethyl cellulose.

5. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is 5,6-ethylidene ascorbic acid.

6. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is 5,6-isopropylidene ascorbic acid.

7. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion 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:

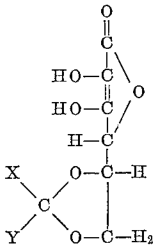


wherein one of X and Y is a lower alkyl group and the other is selected from the group consisting of hydrogen and lower alkyl groups.

8. A method of developing a silver halide emulsion as defined in claim 7, wherein said silver halide developing agent is disposed, prior to exposure, in the photosensitive element containing said silver halide emulsion.

9. 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:



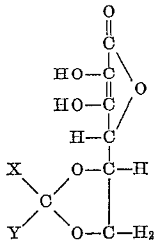
wherein one of X and Y is a lower alkyl group and the other is selected from the group consisting of hydrogen and lower alkyl groups, to form a positive silver print on said image-receiving material.

10. A process as defined in claim **9**, wherein said developing agent is 5,6-ethylidene ascorbic acid.

11. A process as defined in claim **9**, wherein said developing agent is 5,6-isopropylidene ascorbic acid.

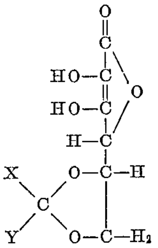
12. A process as defined in claim **8**, wherein said solution includes a silver precipitating agent.

13. A photographic process comprising the steps of developing a silver halide emulsion with an aqueous alkaline solution comprising a silver halide developing agent selected from the group consisting of compounds represented by the formula:



wherein one of X and Y is a lower alkyl group and the other is selected from the group consisting of hydrogen and lower 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.

14. A photographic product comprising a support, a silver halide emulsion in a layer on said support, and a silver halide developing agent in a layer on the same side of said support as said silver halide emulsion, said silver halide developing agent being selected from the group consisting of compounds represented by the formula:



wherein one of X and Y is a lower alkyl group and the other is selected from the group consisting of hydrogen and lower alkyl groups.

No references cited.

NORMAN G. TORCHIN, *Primary Examiner.*

R. E. MARTIN, *Assistant Examiner.*

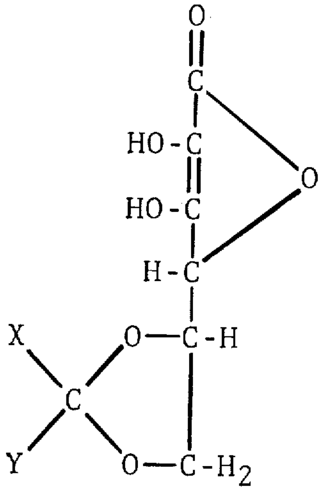
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,337,342 August 22, 1967

Milton Green

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 18 to 28, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 27th day of August 1968.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents