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ASCORBIC ACID IN PHOTOGRAPHIC
DEVELOPING SOLUTIONS

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This invention relates to anti-oxidants in photographic developing solutions.

In the production of relief images in gelatin, one of the most rapid methods involves the use of so-called tanning developers. These developers are usually of the catechol-sodium hydroxide, or pyrogallol-sodium hydroxide type, which depend, for their operation, upon the fact that the reaction product of the development hardens the gelatin in the immediate vicinity of the silver halide being reduced. Because of the instability of these developing agents at the pH at which they are used, they oxidize quite rapidly, being useful only for a relatively short time. It has been the practice in the past to use these solutions a very short time, usually only for one development, then to discard the solution. Since the formulas of this type must be kept as two stock solutions, a great deal of time is lost mixing and cooling a fresh bath for each sample.

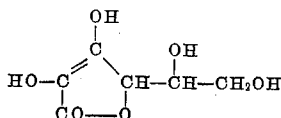
Sodium sulfite, which is the anti-oxidant commonly used in developing solutions, cannot be used in tanning developers since a quantity sufficient to prevent oxidation for any length of time would greatly reduce or completely destroy the hardening action of the developer (Neblette "Photography Principles and Practice," 4th edition, 1942, page 766). Tanning developers may tolerate a small amount of sulfite but, when an amount greater than about 2 grams per liter is used, the tanning action is so slight as to render the solution impracticable as a tanning developer.

It is, therefore, an object of the present invention to provide a tanning photographic developer which is stable to aerial oxidation. A further object is to provide a novel anti-oxidant for photographic developing solutions.

These objects are accomplished by incorporating in a silver halide developing solution, especially a solution of a tanning developer, one or more of the forms of ascorbic acid.

We have found that both the laevo ascorbic acid and the dextro-iso-ascorbic acid possess the property of reducing aerial oxidation of photographic developing solutions. With laevo ascorbic acid a concentration of 4 grams per liter of developing solution was found to be satisfactory. Concentrations as low as 0.1 gram per liter were tested and showed some action and amounts as great as 10 grams or more per liter were also found to be satisfactory. The ascorbic acids may also be used as their alkali metal salts, for example, as the sodium salts.

Ascorbic acid is believed to have the following structural formula:



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Iso ascorbic acid is an isomeric form of ascorbic acid and is believed to have the same structural formula.

In addition to its action in tanning developers, ascorbic acid also decreases the aerial oxidation of non-tanning developers. Developing solutions containing considerable sodium sulfite may be improved and their keeping time increased by the addition of ascorbic acid or isoascorbic acid to the developing solution. In such developing solutions containing sulfite, the addition to the solution of a small amount of ascorbic acid will provide better keeping properties than the addition of the same quantity of sodium sulfite.

Ascorbic acid and isoascorbic acid may also be used to prevent the aerial oxidation of Elon-hydroquinone developers such as the Kodak D-72 developer but they are not so effective in these developers as in developers containing dihydroxy benzenes such as pyrogallol, pyrocatechol, or hydroquinone, as the developing agent.

Our invention will be further illustrated by reference to the following specific examples:

EXAMPLE 1

A tanning photographic developer of the following composition was found to have greatly improved keeping properties over the same solution containing no ascorbic acid:

Sodium sulfate	grams	150
Pyrocatechol	do	8
Potassium bromide	do	1
Laevo ascorbic acid	do	4
Water to	cubic centimeters	900
Sodium hydroxide (10% solution)	cubic centimeters	100

EXAMPLE 2

The sodium salt of isoascorbic acid was added in various amounts to the following high-energy Elon-catechol developer which had a pH of 9.5.

Solution A

Pyrocatechol	grams	30
Monomethyl-p-aminophenol sulfate	grams	15
Sodium bisulfite	do	0.75
Sodium sulfate (anhydrous)	do	100
6-nitrobenzimidazole nitrate	do	0.05
Water to	cubic centimeters	800

Solution B

Sodium carbonate	grams	25
Sodium hydroxide	do	14
Water to	cubic centimeters	200

Combine A and B immediately before using.

When this developer was mixed and allowed to stand, it showed darkening in about 10 minutes.

The addition of increasing amounts of sodium

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salt of isoascorbic acid to portions of the solution improved the keeping of the developer as follows:

Grams per liter	Time for developer to darken
0.0	10 min.
0.5	15 min.
1.0	20 min.
2.0	40 min.
4.0	Over 1 hour.
10.0	2 hours.

EXAMPLE 3

The sodium salt of isoascorbic acid was found to improve the keeping of the following non-tanning developing solution:

Solution A

Water	-----cubic centimeters	750
Pyrocatechol	-----grams	100
Sodium sulfite (desiccated)	-----do	100
Water to	-----liters	1

Solution B

Cold water	-----cc	500
Sodium hydroxide	-----grams	60
Potassium bromide	-----do	100
Water to	-----liters	1

For use, A is mixed with B and 50 cc. of formaldehyde are added.

This developing solution was found to discolor and darken on mixing and standing for about one hour. When 10 grams of the sodium salt of isoascorbic acid were added to one liter of the developing solution, the time required for the solution to darken was increased to more than 20 hours.

We have found, therefore, that ascorbic acid and its isomers are powerful anti-oxidants in solutions of dihydroxy benzene developing agents such as catechol, and that they are active even in the presence of considerable sulfite. They do not destroy the tanning action of tanning developers containing little or no sulfite and in such developers are very effective in improving the keeping properties of the developing solution. They may be used in aminophenol developing solutions but appear to be less effective in such solutions than in solutions of phenolic developers such as catechol.

The examples and modifications included herein are illustrative only and it will be understood that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A tanning photographic developer substantially free of sulfite, containing an alkaline solution of a dihydroxy benzene developing agent and an aerial-oxidation-inhibiting amount of ascorbic acid.

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2. A tanning photographic developer free of sulfite, containing an alkaline solution of a dihydroxy benzene developing agent and from about 0.1 gram to at least 10 grams per liter of ascorbic acid.

3. A tanning photographic developer free of sulfite, containing an alkaline solution of pyrocatechol as a developing agent and from about 0.1 gram to at least 10 grams per liter of ascorbic acid.

4. A tanning photographic developer free of sulfite, containing an alkaline solution of pyrocatechol as a developing agent and about 4 grams per liter of ascorbic acid.

5. A tanning photographic developer free of sulfite, containing an alkaline solution of pyrocatechol as a developing agent and about 4 grams per liter of isoascorbic acid.

6. A photographic developing solution possessing stability to aerial oxidation, comprising an alkaline solution of an ortho-dihydroxy benzene photographic developing agent and an aerial-oxidation-inhibiting amount of ascorbic acid.

7. A photographic developing solution possessing stability to aerial oxidation, comprising an aqueous sodium hydroxide solution of an ortho-dihydroxy benzene photographic developing agent and an aerial-oxidation-inhibiting amount of ascorbic acid.

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