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[54] **PRESERVATIVES FOR PHOTOGRAPHIC DEVELOPERS**

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[58] **Field of Search** 96/66.4, 50; 260/473

[56] **References Cited**

UNITED STATES PATENTS

3,515,556	6/1970	Russell et al.	96/66 R
3,644,481	2/1972	Howard et al.	260/473 F
3,716,574	2/1973	Howard et al.	260/473 F
3,754,937	8/1973	Howard et al.	260/473 F
3,810,941	5/1974	Buchholz et al.	260/559

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[57] **ABSTRACT**

The storage life of silver halide developer solutions is extended by the addition to the solutions of salts, esters and amides of plicatic acid.

14 Claims, No Drawings

PRESERVATIVES FOR PHOTOGRAPHIC DEVELOPERS

This invention relates to aqueous solutions for developing silver halide photographic materials, said solutions having extended storage life, and to a process for extending the storage life of said solutions.

Photographic developer solutions oxidize during storage so that they are commonly discarded prior to their exhaustion through the processing of film. This problem is of particular significance to those who process limited amounts of films at spaced or infrequent intervals where both the cost and inconvenience involved is preparing fresh solutions are important considerations.

Previous attempts to extend film developer aging life have consisted primarily in the physical displacement of the air over the solution in the storage container. A commercially available aerosol preparation is an illustration of one such attempt. Such displacement methods do not prevent developer aging by oxygen already in solution. Some antioxidants have also been used, but as antifoggants rather than film developer preservatives.

It is a primary object of this invention to provide a preservative for photographic developer solutions which effectively extends the storage life of such solutions.

It is an additional object of this invention to provide a relatively simple and inexpensive process for extending the storage life of photographic developer solutions which has no significant effect on the quality of the film developed with the solutions.

It has been found that salts, esters and amides of plicatic acid act as preservatives when added to solutions for developing silver halide photographic material. The plicatic acid compounds produce no loss in film speed when added to such solutions and have no significant effect on the fog level of the developed film.

Plicatic acid is a polyphenolic compound obtained from aqueous extracts of western red cedar wood. Processes for its separation and recovery are described in U.S. Pat. No. 3,716,574, assigned to the present assignee. The salts and esters of plicatic acid are disclosed in U.S. Pat. Nos. 3,754,937 and 3,644,481, both assigned to the present assignee. The amides of plicatic acid are disclosed in copending U.S. application Ser. No. 316,056, filed 12-18-72, now U.S. Pat. No. 3,810,941 also assigned to the present assignee. Examples of plicatic acid esters and salts which are useful in the invention are sodium and potassium plicatate and lower alkly plicatates such as methyl, ethyl, n-propyl, iso-propyl and 2-butyl plicatate. Examples of useful amides are ethyl and n-propyl plicatamide. Plicatic acid itself has been found to be too highly acidic to be useful — it tends to neutralize and thus impair the effectiveness of the normally alkaline developer solution.

While many of the foregoing salts, esters and amides have relatively limited water solubility, such limited solubility is adequate in the practice of this invention as long as the compounds are soluble in the relatively small proportions required. The amount of plicatic acid derivative used may, at the lower end, be any amount which is effective to extend the life of the developer. As little as 0.01% (0.1 grams/liter) has been found to be effective to extend the storage life of the solutions. The maximum amount of plicatic acid derivative is that which is soluble in the developer solution, normally about 0.5% (5 grams/liter). A preferred amount of the preservative is from 0.02 to 0.3% (.2 to 3 grams/liter). (Percentages of preservative, as used herein, are weight by volume, 100% being 1000 grams/liter). It is preferable that the normally somewhat acidic plicatic acid derivative be neutralized or made slightly alkaline prior to addition to the alkaline developer solution. This may conveniently be done, for example, by adding sodium carbonate or other mild alkali to a water solution of the plicatic acid derivative to raise its pH to 7 or above, preferably about 7.5. Neutralization avoids alteration of the alkalinity of the developer and hence prevents degradation of the quality of the developed film. Developers (such as Eastman Kodak D-76) are commercially available as premixed powders which the user dissolves in water to obtain the final developer solution. It is possible to obtain at least some of the plicatic acid derivatives in either neutral or slightly alkaline crystalline form which can be incorporated directly into such preparations.

Photographic developer solutions with which the preservatives of the invention are useful are well known in the art. They are chemical solutions widely used in developing exposed silver halide photographic materials and are described in detail, for example, in Photo-Lab-Index, Henry M. Lester, published by Morgan and Morgan, Dobbs Ferry, N.Y., 1973 (published annually with quarterly supplements). A typical composition consists of aqueous solutions of a reducer which is the developing agent, an accelerator (an alkali), a stabilizer to inhibit aerial oxidation and a retardant to limit development of unexposed silver grain. Commonly used developing agents are hydroquinone, p-aminophenol or p-methylaminophenol sulfate. Useful accelerators are alkalis such as borax or sodium carbonate. A commonly used stabilizer is sodium sulfite. Potassium bromide is a frequencly used retardant. It should be understood that the foregoing compositions are merely illustrative.

In developing photographic paper, rather than photographic negatives, highly dilute comparatively alkaline solutions are normally used in shallow trays. In such developing, a stock solution, the concentration of which varies, is diluted with water at a 1/1 or greater dilution ratios of water to developer. The high surface/-volume ratio of such solutions increases the oxidation problem to such an extent that stabilization of the working solutions is impractical. The preservatives of the invention therefor achieve best results and are accordingly preferably used in photographic negative processing or with photographic stock solutions prior to their dilution for photographic paper processing.

The following example illustrates the practice of the invention.

EXAMPLE

N-propyl plicatate was added to a commercially available developer solution (Eastmann Kodak D-76) of the following composition:

	Grams
P-methylaminophenol sulfate	2
sodium sulfite	100
hydroquinone	5
borax	2
water (to make 1 liter of solution)	

The n-propyl plicatate was added as a 0.2% (wt./volume) stock solution in place of a portion of the water used to make up the 1 liter solution of developer. The stock solution was made by dissolving 8 grams of n-propyl plicate in four liters of water maintained at 90°C. The stock solution was cooled and adjusted to a pH of 7.5 using a saturated solution of sodium carbonated.

Kodak Panatomic-X sheet film was exposed at ASA ratings of 64 and 80 using a Kodak gray scale as the subject. The film was then developed in the foregoing solution in accordance with the manufacturer's recommendations.

Comparative tests were run of a series of solutions prepared as above, both with and without the preservatives of the invention. In addition, solutions were also prepared, and tested where possible, containing six commercially available antioxidants. To test storage life, the solutions were aerated by admitting filtered air through the bottom of the processing tanks for the developers. Air flow was regulated using capillaries calibrated to give equal flow in the lines to the tank distribution tubes. Aeration was carried out at ambient room temperatures. The color and height of the developers in the tank were checked daily, the latter being maintained at 9.0 inches above the gas distribution tubes by the addition of distilled water to insure a constant hydrostatic pressure.

Negative film optical densities were measured with a photometer (blue sensitive probe) and a transmission light source with a diffusion filter. Every step in the gray scale image, a portion of a neutral density gray card image and an unexposed portion of each film was measured. A sheet of unexposed and undeveloped film was also cleared and measured to obtain a value for the base film density. This figure was then subtracted from the density of the unexposed portion of each film to obtain their fog densities. The combined base and fog densities were then substracted from all gray scale densities to obtain the values produced by the photographic emulsion alone.

The following six commercially available antioxidants were also investigated for their comparative value in extending the life of photographic developer solutions. The last three of the antioxidants were found unsuitable because of insufficient solubility.

1. Thiodipropionic acid.
2. Catechol.
3. Santoquin (Monsanto NEO2-008) — made up as 45% (wt./vol.) antioxidant in propylene glycol and dissolved directly in developer. An oil residue remained on the surface of the solution.
4. Butylated hydroxy toluene (BHT) — solubility in water (0.0575 gm./l.) was too low for comparative tests.
5. Butylated hydroxy anisole (BHA) — dissolved but greasy residue remained in developer. Not used because deposits formed on negatives after immersion in developer.
6. Nordihydroquiaretic acid — dissolved but formed turbid solution after neutralization which precipitated on standing.

The optical density of a series of film negatives developed and tested in accordance with the procedures set forth above was determined. Table I shows the aeration time required for optical density of films developed from each of the developer solutions to reach 70% of the initial optical density. It also shows the percentage of such aeration time relative to the control as a measure of the increase in useful life obtained by the addition of the antioxidant. In Table I, aeration times have been prorated from different test runs so that the results are directly comparable. Where antioxidant was added, the amount was 0.10%.

Table I

Antioxidant	Aeration, Hours*	Percent of Control
1. None (control)	218	100
2. N-propyl plicatate	362	166
3. N-propyl plicatamide	511	234
4. Potassium plicatate	516	237
5. Methyl plicatate	236	108
6. Thiodipropionic acid	577	265
7. Catechol	274	126
8. Santoquin	403	185

*Number of hours of aeration to reduce the maximum negative density to 70% of its initial value.

The results show that all of the plicatic acid derivatives extended the aging life of the developer. It also shows that, at the 0.10% level, the other commercial antioxidants also extended developer life. However, as will be shown below, thiodipropionic acid is not as effective as potassium plicatate when the porportion of additive is increased to 0.20%. Moreover, both Catechol and Santoquin have shortcomings, not shared with the plicatic acid compounds. Catechol is a developer itself and thus part of the result may reflect this property, rather than increased developer life. Moreover, Catechol will affect the kinetics of the developer solution because of its developer activity, whereas the plicatic compounds will not. Santoquin left an oily residue on the surface of the solutions making it objectionable for practical use.

Fog, or negative density produced by factors other than image exposure, is also an important factor in evaluating developers. High fog levels are undesirable because they reduce negative contrast and increase printing exposure time. A second series of tests was run to include this factor in the evaluation of the developer solutions. Calculations were made of the ratio of the maximum density to fog density both initially and at aeration time intervals. Higher negative to fog density ratios were indicative of better solution performance. Three groups of tests were performed and they are separately grouped in the following table. The tests of Groups 1 and 2 containing 0.1% additive were aerated at a rate of 2.5 liters per minute. The tests of Group 3 were aerated at 3.5 liters per minute in an attempt to reduce the time required to inactivate the solutions. Where no results are listed, no measurement was possible because there was no measurable image. Thiodiproprionic acid was compared on both an equimolar and equal percentage basis with potassium plicitate in the Group III results.

TABLE II

Antioxidant	Amount (%)		Negative Density to Fog Ratios				
Group 1		Aeration, Hours	0	121	235	340	436
1. None	—		16.57	14.27	6.85	—	—
2. N-propyl plicatate	0.10		16.57	14.06	13.73	9.41	12.25

TABLE II-continued

Antioxidant	Amount (%)	Negative Density to Fog Ratios					
Group 2		Aeration, Hours	0	304	393	441	535
1. N-propyl plicatate	0.10		10.59	5.23	1.04	—	—
2. N-propyl plicatamide	0.10		8.70	5.47	4.33	0.49	—
3. Potassium plicatate	0.10		11.31	5.60	6.30	1.00	—
4. Thiodipropionic acid	0.10		9.32	6.29	7.67	9.08	8.03
Group 3		Aeration, Hours	0	120	257	346	
1. None	—		13.69	13.03	10.51	—	
2. Potassium Plicatate	0.20		17.14	16.52	11.20	15.52	
3. Thiodipropionic acid	0.05		13.20	13.25	9.10	—	
4. Thiodipropionic acid	0.20		15.07	11.02	8.04	—	

The results of Table II indicate that at the 0.10% level, thiodipropionic acid performed better than the other compounds on the aerated solution. However, at the 0.20% level, potassium plicatate yielded consistently higher ratios than the solutions containing thiodipropionic acid at both the same concentration (0.20%) and the equimolar concentration (0.05%). Fresh solutions containing potassium plicatate also produced higher ratios than the unaerated solutions containing thiodipropionic acid. Potassium plicatate should, therefore, be capable of producing the most effective prolongation of useful developer life of any of the compounds tested at practical concentration levels.

The invention thus offers a relatively simple and economical method of increasing the working life of developer solutions. The invention is particularly significant where batches of films are processed at intervals and stored for prolonged periods between batches. It is accordingly applicable, not only to amateur photographic practice, but also to experimental laboratories, photographic studios and other processors using manual batch development as opposed to continuous machine processing.

We claim:

1. An aqueous solution for developing photographic material comprising a silver halide developing agent and as a preservative therefor a compound selected from the group consisting of salts, esters and amides of plicatic acid in an amount effective to extend the storage life of said solution, said amount being at least 0.01% on a weight/volume basis.

2. The solution of claim **1** in which the plicatic acid compound is neutralized to a pH of at least 7 prior to its addition to the solution.

3. The solution of claim **2** in which the plicatic acid compound is a salt.

4. The solution of claim **3** in which the salt is potassium plicatate.

5. The solution of claim **2** in which the plicatic acid compound is an ester.

6. The solution of claim **5** in which the ester is n-propyl plicatate.

7. The solution of claim **2** in which the plicatic acid compound is an amide.

8. The solution of claim **7** in which the amide is n-propyl plicatamide.

9. The solution of claim **2** in which the amount of plicatic acid compound is from 0.1 to 5 grams per liter.

10. A process for extending the storage life of aqueous solutions for developing photographic materials comprising

adding to said solution containing a silver halide developing agent a preservative compound selected from the group consisting of salts, esters and amides of plicatic acid in an amount effective to extend the storage life of said solution, said amount being at least 0.01% on a weight/volume basis.

11. The process of claim **10** in which the preservative compound is added as an aqueous solution of said plicatic acid compound neutralized to a pH of at least 7.

12. The process of claim **11** in which the preservative is potassium plicatate.

13. The process of claim **11** in which the aqueous solution is a stock solution.

14. The process of claim **11** in which the photographic material is photographic negative.

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