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		UNITED STATES PATENTS	
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[54] COLOR-DEVELOPING COMPOSITION
CONTAINING AN ANTIOXIDANT
19 Claims, No Drawings
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G03c 5/30
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55

ABSTRACT: Color-developing compositions comprising a primary aromatic amine color-developing agent and as an antioxidant certain linear compounds that are capable of existing in equilibrium with an enol form of said compound and that are not capable of intramolecular cyclization are advantageously used for color development because substantially less color-developing agent is lost from aerial oxidation than is lost from color developer compositions containing prior art antioxidants without the undesirable reduction in pH produced in prior art developer compositions by prolonged exposure to air.

COLOR-DEVELOPING COMPOSITION CONTAINING AN ANTIOXIDANT

This invention relates to photography, compositions for making photographic developer solutions and methods for stabilizing photographic developer solutions against aerial oxidation.

The aqueous alkaline developer solutions used to develop the latent image in image-exposed silver halide emulsions are usually held in photographic processing machine tanks that are open to the air and are aerated by exposure to the air and by the passage of photographic film or paper through the solutions. Unprotected solutions must be replaced often and require a high rate of replenishment with fresh developer solution to replace developing agent and other oxidizable chemicals that are destroyed by aerial oxidation. Overcoming the effects of aerial oxidation by replacing aerially oxidized developer solutions is not only expensive from the standpoint of labor, time and chemical costs but also creates additional water pollution problems where these solutions are disposed. The aerial oxidation of developer solutions is particularly serious in color developer solutions for a number of reasons including (1) the more exacting sensitometric requirements, (2) the more expensive chemicals including developing agent, dye-forming couplers when used in the developer solution and other addenda, (3) the developing agents used are usually more subject to oxidation, (4) the higher pH levels usually used in color developer solutions, etc.

Various compounds have been used as color developer additives in an effort to minimize aerial oxidation of the developing agent. For example, British Pat. No. 886,269 cites the use of 2-methylcyclammonium salts for this purpose. The patent adds that some of the examples couple with oxidized color developer to form dyes which must be removed from the emulsion. In addition, the compounds cited as examples are not readily available. U.S. Pat. No. 2,728,669 cites the use of Dextrose and p-hydroxyphenylglycine as antioxidants adding, however, that they decrease the development potential of the developer solution. In U.S. Pat. No. 2,401,713 the use of ascorbic acid is advocated. However, a later patent (U.S. Pat. NO. 2,923,627) points out that ascorbic acid is stable for only 2 to 3 hours and another patent (British Pat. No. 782,304) adds that ascorbic acid is so unstable that its presence must be controlled by a specific addition of ascorbic acid solution as the compound decomposes. Oxytetric acids are mentioned in British Pat. No. 782,304 as being cheap antioxidants, but in U.S. Pat. No. 2,923,627 their effectiveness is found to be limited to 4 hours. Hydroxylamine and N,N-substituted hydroxylamines are also recommended in a number of patents. Hydroxylamine, however, also decreases development potential (U.S. Pat. No. 2,656,272) and also decomposes readily even as the crystalline material (German Pat. No. 976,605). Substituted hydroxylamines are relatively more expensive and still have disadvantages which will be pointed out below.

Although a large number of compounds with a great range of structures have been proposed as antioxidants for developer solutions, at present, only hydroxylamine is known to be in common use as an antioxidant in color developers. Substituted hydroxylamines and ascorbic acid have very limited use in photographic applications.

Hydroxylamine and hydroxylamine derivatives have the following disadvantages that have not been mentioned herein previously.

1. Hydroxylamine acts as a silver halide solvent (in a manner similar to that of ammonia and other amines) thereby causing physical development. It also causes severe fog in certain emulsions as well as mismatched contrasts. Developer solutions containing hydroxylamine also experience a buildup of ammonia because of the instability of hydroxylamine solutions. The ammonia is a silver halide solvent which also causes fog. Even at "safe" levels of hydroxylamine, it is possible to build up an undesirable ammonia concentration.

2. Developer solutions undergo a slight drop in pH on standing by absorption of carbon dioxide from the air. When hydroxylamine or its derivatives are added to the developer, this pH drop is enhanced, especially when the solution is not at the maximum buffering pH of its constituents.

3. Hydroxylamine is toxic and can cause serious reactions in humans upon repeated contact.

From the above discussion it is obvious that better antioxidants for developer compositions are desired.

It is therefore an object of our invention to provide a novel class of antioxidants that are valuable for protecting developer compositions against aerial oxidation for more extended periods of time than the prior art antioxidants without the disadvantages posed by the prior art antioxidants.

Another object of our invention is to provide novel improved color-developing solutions.

Another object of our invention is to provide a novel color-developing solution which is substantially more stable to aerial oxidation as a result of incorporating one of our antioxidizing agents.

Another object of our invention is to provide novel color developer solutions which are more stable to pH change upon prolonged exposure to air than are solutions containing the usual prior art antioxidants.

Another object of our invention is to provide novel color-developing solutions containing our antioxidizing agents which are characterized by producing better photographic speeds and densities than the corresponding color-developing solutions containing either no antioxidants or antioxidants of the prior art.

Still another object of our invention is to provide a novel means for protecting color developer solutions against aerial oxidation for a longer period of time than is possible with prior art means and to do this with a minimum of sensitometric changes which are characteristic of prior art means.

These and still other objects of our invention will become obvious from a consideration of the following specification and claims.

These and other objects of our invention are obtained by making and using our color developer compositions comprising a primary aromatic amine color-developing agent and as an antioxidant for said color developing agent a linear compound having the formula:



wherein R represents hydrogen, the carboxy group, alkyl having from one to two carbon atoms (e.g., methyl, ethyl) and hydroxyalkyl having from one to two carbon atoms (e.g., hydroxymethyl, 2-hydroxyethyl and 1-hydroxyethyl) and R' represents hydrogen, the carboxy group, the hydroxymethyl group and the formyl group, such that when R represents carboxy, R' is not hydroxymethyl and such that when R' is carboxy or formyl, R is not hydroxyalkyl, and such that said compound is capable of existing in equilibrium with an enol form of said compound and is not capable of intramolecular cyclization.

Our compositions usually contain sufficient color-developing agent and sufficient antioxidizing compound to produce a solution having a concentration of from about 0.5 gram per liter to about 14 grams per liter of said developing agent and from about 0.1 gram per liter to about 20 grams per liter of said antioxidant. Our preferred compositions contain enough antioxidant to give a concentration when dissolved in water of from about 0.5 gram per liter to about 15 grams per liter and an especially useful range of concentrations is from about 1 gram per liter to about 5 grams per liter of our antioxidizing agent.

We have found that use of our antioxidizing agents of formula I in color developer compositions gives more protection to the color-developing agent against aerial oxidation than

does hydroxylamine without the disadvantages posed by hydroxylamine. For example, the pH of our color developer solutions does not drop as does pH in prior art color-developing solutions containing hydroxylamine upon prolonged exposure to air. Our antioxidizing agents can be used at substantially higher concentrations than is possible with hydroxylamine with no adverse effects from the developed dye image. Our antioxidizing agents cause very little fog when contained in either a fresh solution or in a solution that has been exposed for prolonged periods of time to the air. Unlike hydroxylamine or its decomposition products, our antioxidizing agents are not silver halide solvents. Our antioxidizing agents of formula I are nontoxic.

The following typical antioxidizing agents of our invention are included in those of formula I.

Antioxidizing Agent	Name
1	Dihydroxyacetone (i.e., 1,3-Dihydroxypropanone)
2	Glycolaldehyde (i.e., α -Hydroxyacetaldehyde)
3	Glycerlaldehyde (i.e., 2,3-Dihydroxypropion-aldehyde)
4	Dihydroxymaleic acid

These compounds illustrate compounds of the formula:



in which the values of R and R₁ are as follows:

Compound	R	R'
1-----	-CH ₂ OH	-H
2-----	-H	-H
3-----	-H	-CH ₂ OH
4-----	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OH} \end{array}$

Our antioxidizing agents are used advantageously in color developer compositions containing any of the well-known primary aromatic amine silver halide developing agents, such as the P-Phenylenediamines including the alkyl phenylenediamines and alkyl toluene diamines. These developing agents are usually used in the salt form such as the hydrochloride or sulfate which are more stable than the amine. The aminophenols and their substitution products may also be used as color-developing agents when the amine group is unsubstituted. The N-alkyl sulfonamido alkyl-p-phenylenediamine agents of U.S. Pat. No. 2,193,015 are also very useful. All of the developing agents have an unsubstituted amino group which enables the oxidation product of the developer to couple with the color-forming products that form a dye image. Included among the color developers are, such typical illustrative examples as the following:

1. N-(4-Amino-3-methylphenyl)morpholine
2. 4-Amino-N-ethyl-N-carbamoylmethylaniline
3. 4-Amino-3-chloro-N,N-diethylaniline
4. 4-Amino-3-methyl-N-ethyl-N-carbamoylmethylaniline
5. N-(4-Aminophenyl)piperidine
6. 4-Amino-N-ethyl-N-(β -methoxyethyl)aniline
7. 4-Amino-N-ethyl-N-(β -acetamidoethyl)aniline
8. 4-Amino-N-ethyl-N-(N-methyl- β -methylsulfonamidoethyl)aniline
9. 4-Amino-N-ethyl-N-(β -ethoxyethyl)aniline
10. N-(4-Amino-3-methylphenyl)piperidine
11. 4-Amino-2-methoxy-5-methyl-N,N-diethylaniline
12. 4-Amino-N,N-dimethylaniline
13. 4-Amino-N-ethyl-N-tetrahydrofurfurylaniline

14. 4-Amino-N-methyl-N-ethylaniline
15. 4-Amino-N-methyl-N-(n-butyl)aniline
16. 4-Amino-N-methyl-N-(n-propyl)aniline
17. 4-Amino-3-methyl-N-ethyl-N-(N-methyl- β -methylsulfonamidoethyl)aniline
18. 4-Amino-N,N-diethylaniline
19. 4-Amino-3-methylsulfonamidomethyl-N,N-diethylaniline
20. 4-Amino-N-ethyl-N-(β -methylsulfonamidoethyl)aniline
21. 4-Amino-3-hydroxymethyl-N,N-diethylaniline
22. 4-Amino-N-ethyl-N-(n-propyl)aniline
23. 4-Amino-3-(β -acetamidoethyl)-N,N-diethylaniline
24. 4-Amino-3-(β -hydroxyethyl)-N,N-diethylaniline
25. 4-Amino-3-(β -aminoethyl)-N,N-diethylaniline
26. 4-Amino-N-ethyl-N-(β -hydroxyethyl)aniline
27. 4-Amino-N,N-di(n-propyl)aniline
28. 4-Amino-3-methyl-N-methyl-N-(β -methylsulfonamidoethyl)aniline
29. 4-Amino-3-ethyl-N,N-diethylaniline
30. 4-Amino-3-(N-methyl- β -methylsulfonamidoethyl)-N,N-diethylaniline
31. 1-(4-Aminophenyl)pyrrolidine
32. 4-Amino-3-methyl-N-ethyl-N-tetrahydrofurfurylaniline
33. 4-Amino-3-(β -methylsulfonamidoethyl)N,N-diethylaniline
34. 4-Amino-3-acetamido-N,N-diethylaniline
35. 4-Amino-3-methyl-N-ethyl-N-(β -methylsulfonamidoethyl)aniline
36. 4-Amino-3-methyl-N,N-diethylaniline
37. 6-Amino-1-(β -methylsulfonamidoethyl)-1,2,3,4-tetrahydroquinoline
38. 4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline
39. 6-Amino-1-ethyl-1,2,3,4-tetrahydroquinoline
40. 4-Amino-3-ethoxy-N-ethyl-N-(N-methyl- β -methylsulfonamidoethyl)aniline
41. 4-Amino-3-ethoxy-N-ethyl-N-(β -methylsulfonamidoethyl)aniline
42. 4-Amino-3-methoxy-N,N-diethylaniline
43. 4-Amino-3-ethoxy-N,N-diethylaniline
44. 4-Amino-3-dimethylamino-N,N-diethylaniline
45. 4-Amino-3-ethylamino-N,N-diethylaniline

In addition to the color-developing agent and our antioxidant of formula I our color-developing compositions comprise any addenda commonly found in color developer solutions, such as, water, an alkali such as, alkali metal carbonates, alkali metal borates, etc., alkali metal sulfites, alkali metal sulfates, alkali metal bromides, alkali metal iodides, silver halide solvents, antifoggants, diffusible dye-forming couplers, diffusible competing couplers, thickening agents, e.g., carboxymethyl cellulose, carboxy lower alkyl substituted cellulose, etc.

The following examples are included for a further understanding of our invention.

Example 1

Three 1,100 ml. solutions of a color developer of the following composition are labeled A, B and C.

Benzyl alcohol	5.0 ml.
Sodium hexametaphosphate	2.5 g.
Sodium sulfite	1.85 g.
Sodium bromide	1.40 g.
Potassium iodide	0.5 mg.
Sodium hydroxide	12.5 g.
Sodium tetraborate · 10H ₂ O	44.9 g.
4-Amino-3-methyl-N-ethyl-N-(β -methanesulfonamidoethyl)aniline sesquisulfate hydrate	6.1 g.
Water to	1 l.
pH 10.60	
70 Solution A is used as a control. Two grams of hydroxylamine sulfate are added to solution B, and 2 grams of dihydroxy acetone are added to solution C. The pH's of solutions B and C are adjusted to the pH of solution A, i.e., 10.60. The solutions A, B and C are allowed to stand in uncovered containers.	
75 The volume of each solution is maintained at 1,100 ml. by	

water replenishment to compensate for evaporation. After 5 and 10 days, respectively, the changes of their pH and the concentration of color-developing agent (i.e., 4-amino-3-methyl-N-ethyl-N- β -(methanesulfonamido)ethylaniline sesquisulfate

nidealkali metal bromide bleach solution and a conventional alkali metal thiosulfate solution is used as a fix in the process. The threshold speed and maximum density of the red, green and blue images in the strips are determined and the speed and

TABLE 3

Strip	Days	Threshold speed change			Maximum density change		
		Red	Green	Blue	Red	Green	Blue
1b	5	-0.30	-0.13	-0.18	-0.28	-0.06	-0.04
1c	10	-0.64	-0.40	-0.13	-0.64	-0.17	-0.22
2b	5	-0.30	-0.12	-0.15	-0.30	-0.06	-0.20
2c	10	-0.48	-0.12	-0.23	-0.45	-0.14	-0.37
3b	5	-0.22	-0.09	-0.10	-0.16	-0.05	-0.04
3c	10	-0.28	-0.15	-0.20	-0.23	-0.06	-0.10

hydrate are determined from 100 ml. samples of A, B and C and recorded in table 1. The remainder of the processing solutions is used for processing as shown in example 2.

TABLE 1

	Change in pH	Change in Developing Agent Concentration
Solution A (after 5 days)	-0.09	-1.95
(after 10 days)	-0.20	-3.1
Solution B (after 5 days)	-0.29	-0.7
(after 10 days)	-0.49	-0.8
Solution C (after 5 days)	-0.10	+0.2
(after 10 days)	-0.20	-1.0

The results in table 1 show that the hydroxylamine in solution B caused a substantially greater loss in pH than did dihydroxy acetone in solution C. Solution C showed essentially the same loss in pH as did the control solution A. Aerial oxidation of developing agent in solutions B and C is substantially reduced by the hydroxylamine and the dihydroxy acetone, respectively, compared to the unprotected control solution A. Dihydroxy acetone gives more antioxidant protection to the developing agent in solution C than the hydroxylamine in solution B over the 5-day period and about the same protection over the 10-day period.

Example 2

Nine strips of a conventional multicolor, multilayer color film such as is described in the example of Hanson U.S. Pat. No. 2,449,966 containing incorporated color-forming couplers are labeled 1a, 1b, 1c, 2a, 2b, 2c, 3a, 3b and 3c, respectively. These strips are identically exposed to a neutral scale test object and developed (14 minutes at 75° F.) by treating the strips as indicated in table 2 in the developer solutions A, B and C described in example 1.

TABLE 2

Strip No.	Developer Solution	Condition
1a	A	fresh
1b	A	after 5 days
1c	A	after 10 days
2a	B	fresh
2b	B	after 5 days
2c	B	after 10 days
3a	C	fresh
3b	C	after 5 days
3c	C	after 10 days

The processing of the color developed films is then completed with the following process steps:

Acid stop bath	6'15"
Formalin Hardener	4'41"
First water wash	3'7"
Bleach	6'15"
Second water wash	3'7"
Fix	3'
Third water wash	6'15"
Drying	

A conventional acetic acid-sodium acetate solution is used as the acid stop bath, a conventional formalin hardener solution is used for hardening, a conventional alkali metal ferricya-

maximum density losses caused by use of the 5- and 10-day-old solutions are listed in table 3.

The results show that solution C protected by our antioxidant dihydroxy acetone gave better speeds in processed film than did solutions B and A after 5 days' and after 10 days' storage of the solutions. The improvement in film speed from use of our developer solution C is particularly noticeable in the red speed which is maintained closer to the green and blue speeds than in the films processed with either developer solution A or B. The data show that the D max losses for red, green and blue are substantially lower for strips 3b and 3c processed through our color developer C containing dihydroxy acetone than in strips 2b, 2c or control strips 1b and 1c. The improvement produced by our developer solution is most pronounced in the maximum density of the cyan dye image. The greatly improved stability of our color developer solution to the effects of aerial oxidation as demonstrated by improved sensitometric results provides a valuable technical advance.

Example 3

Seven 1-liter solutions are made identically as solutions 1 through 7, respectively, having the composition:

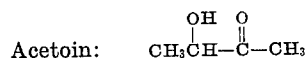
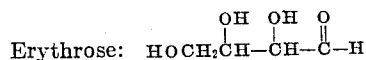
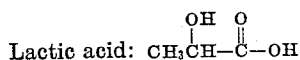
Benzyl alcohol	12.0 ml.
Diaminopropanol tetraacetic acid	3.0 g.
Sodium sulfite	2.0 g.
Sodium bromide	0.4 g.
Sodium chloride	0.7 g.
Sodium metaborate 8H ₂ O	45.0 g.
4-Amino-3-methyl-N-ethyl-N- β -(methanesulfonamido)ethylaniline sesquisulfate hydrate (developing agent)	5.0 g.
Water to	1 l.

Solution No. 1 having a pH of 10.60 is used as a control. Two grams per liter of the compounds indicated in table 4 are added to the other solutions, and their pH's adjusted to 10.60. Five hundred-ml. portions of these solutions are stored for 10 days in 1-liter open beakers. At the end of this time the volume of solution is brought up to 500 ml. with water and analytical determinations are made of pH and concentration of the developing agent remaining in the solutions. An average of two developing agent concentration analyses is used in computing the percent loss in developing agent concentration based on the analyzed concentration in a fresh mixed control solution.

TABLE 4

Developing Solution No.	Compound Added 2 g./l.	After 10 Days Exposure to Air Loss in	
		Developing Agent Concentration Based on Fresh Mixed Control	Loss in pH
1	none	60%	0.37
2	Dihydroxy acetone	4%	0.39
3	Glycolaldehyde	8%	0.42
4	Hydroxylamine	18%	0.72
5	Lactic Acid	59%	0.31
6	Erythrose	47%	0.32
7	Acetoin	42%	0.39

Lactic acid, erythrose and acetoin are compounds that are outside our invention but have structures that are similar to compounds of our invention. The structures are as follows:



The results show that very closely related compounds, lactic acid, erythrose and acetoin give very little if any antioxidant protection to the developing agent when subjected to 10 days' aerial oxidation. It is not obvious from these data that the compounds of our invention, such as, dihydroxy acetone, glyoxaldehyde, etc., give excellent protection to the developing agent against oxidation. Not only is hydroxylamine a relatively poor antioxidant compared to our compounds, such as, dihydroxy acetone and glyoxaldehyde, but the pH loss suffered in the hydroxylamine solution is about 1.7 to 1.8 times the pH loss in our solutions.

Example 4

Examples 1 and 2 are repeated using glycolaldehyde, glyceraldehyde and dihydroxymaleic acid in place of dihydroxyacetone. The results obtained show that color developer solutions containing these compounds can be subjected to aeration and will undergo substantially less loss in pH and loss in developing agent concentration than the developer solution containing hydroxylamine. Aeration of our developer solutions causes less of a shift in the sensitometric results of film processed in them than aeration of the developer solution containing hydroxylamine.

Example 5

Examples 1 and 2 are repeated using developing agents from 1 through 45, producing results similar to those demonstrated in examples 1 and 2.

Our antioxidants of formula I are advantageously used in developer solutions at concentrations in the range from about 0.1 g./l. to about 20 g./l., with the preferred concentration range from about 0.5 g./l. to about 15 g./l.

Example 6

Three 1-liter solutions are made and identified as A, B and C. Solution A has the composition of solution A in example 1. Solution B has the composition of solution A and has in addition 5 g./l. of hydroxylamine sulfate. Solution C has the composition of solution A and has in addition 5 g./l. of dihydroxyacetone. Three strips labeled 1, 2 and 3 of a conventional multicolor, multilayer color film such as is described in the example of Hanson U.S. Pat. No. 2,449,966 containing color-forming couplers are given identical exposures. The exposed strips 1, 2 and 3 are developed 14 minutes at 75° F. in freshly prepared developer solutions A, B and C, respectively, and then the processing of the developed strips is completed with the acid stop, formalin hardener, wash, bleach, wash, fix, wash and drying steps described in example 2. Sensitometric curves relating developed cyan dye image densities with the corresponding image exposure steps are made for the processed strips. A comparison of the sensitometric curves for strips 1 and 2 shows that 5 g./l. hydroxylamine causes in strip 2 an increase of 0.12 in fog (minimum density) over the fog in control strip 1. Also the hydroxylamine produces an appreciable loss in contrast. A comparison of the sensitometric curves for

strips 1 and 3 shows that 5 g./l. of dihydroxyacetone produces only a 0.06 increase in fog and substantially no change in contrast over the control. In color photography, it is important that the cyan, magenta and yellow image reproductions have essentially the same contrast. A loss in cyan dye image contrast such as is produced by the addition of 5 g./l. of hydroxylamine can produce a contrast mismatch between the images in the various layers which is very undesirable and even unacceptable. As mentioned above, the addition of 5 g./l. of dihydroxyacetone produces no shift in cyan dye contrast and demonstrates valuable technical advance.

Example 7

- 15 Four 1-liter solutions are made identically having the composition of control solution A in example 1. One liter of this identified in the immediate example as solution No. 1 is used as the control. Two grams per liter of dihydroxy acetone are added to another liter of the solution identified as solution No.
- 20 2. Two grams per liter of dihydroxy maleic acid are added to another liter of the solution identified as solution No. 3. Two grams of hydroxylamine sulfate are added to the fourth liter of the solution which is identified as solution No. 4. The pH's of solutions 2, 3 and 4 are each adjusted to the pH of control solution No. 1. The solutions are allowed to stand in uncovered containers for 7 days. Water is added to each container to bring the volume of each solution up to its initial 1 liter. The change in pH and in developing agent concentrations caused by the 7-day storage are recorded in table 5.

Table 5

Solution No.	Antioxidant	Change in pH	Change in Developing Agent Conc.
1	control	none	2.5 g./l.
2	Dihydroxy acetone	-0.05	-0.5 g./l.
3	Dihydroxy maleic acid	-0.19	-0.2 g./l.
4	Hydroxylamine sulfate	-0.26	-0.40

Results similar to those obtained in examples 1, 3 and 7 are obtained when these examples are repeated using developer solutions having the following composition as the control solution and adding to this one of the compounds of formula I of our invention.

50	Benzyl alcohol	0-15 ml.
	Sodium hexametaphosphate	2-3 g.
	Sodium sulfite	1-2 g.
	Sodium bromide	0.2-2 g.
	Sodium chloride	0-10 g.
	Potassium iodide	0-10 mg.
	Sodium hydroxide	0-20 g.
55	Sodium tetraborate · 10H ₂ O	20-50 g.
	4-Amino-3-methyl-N-ethyl-n-β-(methanesulfonamido)ethyl aniline sesquisulfate hydrate	2-8 g.
	Water to	1 l.

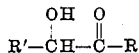
- 60 The valuable antioxidant properties of our compounds shown in the above examples are also demonstrated when these compounds are used in cyan color developer solutions containing diffusible cyan dye-forming couplers, in yellow color developer solutions containing diffusible yellow dye-forming couplers and in magenta color developer solutions containing diffusible magenta dye-forming couplers that are used in processing multilayer, multicolor films that do not contain incorporated couplers. In these solutions our antioxidants not only prevent loss in color-developing agent by aerial oxidation but also prevent loss of the color-forming coupler which would otherwise be used up by coupling reaction with the aerially oxidized color-developing agent.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will

be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In a color-developing composition containing a primary aromatic amine color-developing agent and an antioxidant, the improvement comprising the antioxidant having the formula:



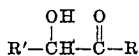
wherein R represents a member selected from the class consisting of hydrogen, the carboxy group, alkyl having one or two carbon atoms and hydroxyalkyl having one or two carbon atoms; and R' represents a member selected from the class consisting of hydrogen, the hydroxymethyl group and the formyl group, such that when R represents carboxy, R' is not hydroxymethyl and such that when R' is formyl, R is not hydroxyalkyl and such that said compound is capable of existing in equilibrium with an enol form of said compound and is not capable of intramolecular cyclization, enough of said antioxidant being added to said composition to give an antioxidant concentration in the range of from about 0.1 g./l. to about 20 g./l. when dissolved in water.

2. A composition of claim 1 in which the antioxidant is dihydroxyacetone.

3. A composition of claim 1 in which the antioxidant is glycolaldehyde.

4. A composition of claim 1 in which the antioxidant is glyceraldehyde.

5. In a color-developing composition containing a primary aromatic amine color-developing agent, an alkali metal tetraborate, an alkali metal sulfite, and an antioxidant, the improvement comprising the antioxidant having the formula:



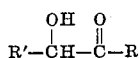
wherein R represents a member selected from the class consisting of hydrogen, the carboxy group, alkyl having one or two carbon atoms and hydroxyalkyl having one or two carbon atoms; and R' represents a member selected from the class consisting of hydrogen, the hydroxymethyl group and the formyl group, such that when R represents carboxy, R' is not hydroxymethyl and such that when R' is formyl, R is not hydroxyalkyl, and such that said compound is capable of existing in equilibrium with an enol form of said compound and is not capable of intramolecular cyclization, enough of said antioxidant being added to give an antioxidant concentration in the range of from about 0.5 g./l. to about 15 g./l. when dissolved in water.

6. The composition of claim 5 containing a sufficient amount of said antioxidant to produce, when dissolved in water, a solution having a concentration of from about 0.5 g./l. to about 15 g./l. of said antioxidant.

A composition of claim 5 in which the antioxidant is dihydroxyacetone.

8. In a color-developing composition containing a primary aromatic amine color-developing agent and an antioxidant, the improvement comprising the antioxidant selected from the class consisting of dihydroxyacetone, glycolaldehyde and glyceraldehyde, a sufficient amount of said antioxidant being added to give a concentration in the range of from about 0.1 g./l. to about 20 g./l. when dissolved in water.

9. In an aqueous alkaline color developer solution comprising a primary aromatic amine color-developing agent, an alkali, and alkali metal sulfite, and an antioxidant, the improvement comprising the antioxidant having the formula:



wherein R represents a member selected from the class consisting of hydrogen, the carboxy group, alkyl having one or two carbon atoms and hydroxyalkyl having one or two carbon atoms; and R' represents a member selected from the class consisting of hydrogen, the hydroxymethyl group and the for-

myl group, such that when R represents carboxy, R' is not hydroxymethyl and such that when R' is formyl, R is not hydroxyalkyl, and such that said compound is capable of existing in equilibrium with an enol form of said compound and is not capable of intramolecular cyclization, enough of said antioxidant being added to give an antioxidant concentration in the range of from about 0.1 g./l. to about 20 g./l.

10. An aqueous alkaline color developer solution of claim 9 containing an alkali metal tetraborate.

11. An aqueous alkaline color developer solution of claim 9 containing a dye-forming diffusible coupler.

12. In an aqueous alkaline color developer solution containing 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sesquisulfate hydrate, an alkali, an alkali metal sulfite and an antioxidant, the improvement comprising the antioxidant being selected from the class consisting of dihydroxyacetone, glycolaldehyde and glyceraldehyde, said antioxidant having a concentration in the range of from about 0.1 g./l. to about 20 g./l.

13. In an aqueous alkaline color developer solution containing 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sesquisulfate hydrate, an alkali, an alkali metal sulfite and an antioxidant the improvement comprising dihydroxyacetone as the antioxidant being in the range from about 0.1 g./l. to about 20 g./l.

14. In an aqueous alkaline color developer solution containing 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sesquisulfate hydrate, an alkali, an alkali metal sulfite and an antioxidant, the improvement comprising glycolaldehyde as the antioxidant being in the range of from about 0.1 g./l. to about 20 g./l.

15. In an aqueous alkaline color developer solution containing 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sesquisulfate hydrate, an alkali, an alkali metal sulfite and an antioxidant, the improvement comprising glyceraldehyde as the antioxidant being in the range of from about 0.1 g./l. to about 20 g./l.

16. An aqueous alkaline color developer solution of pH 10.6 containing

1. benzyl alcohol	12 ml./l.
2. sodium sulfite	2 g./l.
3. sodium metaborate · 8H ₂ O	45 g./l.
4. 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethyl-aniline sesquisulfate hydrate	5 g./l. and
5. dihydroxyacetone	2 g./l.

17. An aqueous alkaline color developer solution of pH 10.6 containing

1. benzyl alcohol	12 ml./l.
2. sodium sulfite	2 g./l.
3. sodium metaborate · 8H ₂ O	45 g./l.
4. 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethyl-aniline sesquisulfate hydrate	5 g./l. and
5. glycolaldehyde	2 g./l.

18. An aqueous alkaline color developer solution of pH 10.6 containing

1. benzyl alcohol	12 ml./l.
2. sodium sulfite	2 g./l.
3. sodium metaborate · 8H ₂ O	45 g./l.
4. 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethyl-aniline sesquisulfate hydrate	5 g./l. and
5. glyceraldehyde	2 g./l.

19. An aqueous alkaline color developer solution of pH 10.6 containing

1. benzyl alcohol	5.0 ml./l.
2. sodium sulfite	1.85 g./l.
3. sodium tetraborate · 10H ₂ O	44.9 g./l.
4. 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethyl-aniline sesquisulfate hydrate	6.0 g./l. and
5. dihydroxyacetone	5.0 g./l.

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