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OXIDATION-STABLE DEVELOPER COMPOSITIONS

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This invention relates to photographic developers, and more particularly to photographic developers possessing improved stability to aerial oxidation.

The most common developers used in photography are alkaline solutions of organic reducing agents capable of reducing exposed silver halide emulsion grains to metallic silver in proportion to their exposure to light. These organic developing agents are primarily di-hydroxy, diamino, or amino-hydroxy substitution products of benzene such as glycin or hydroquinone, the sulphate of paramethyl aminophenol, 1,2,3-tri hydroxy benzene, etc. It is common practice to accelerate the slow reducing action of these developing agents to a range of practical activity by using them in an alkaline medium which in turn makes them subject to rapid aerial oxidation. Furthermore, it is common practice to use these alkaline developers in the presence of sodium sulfite which is capable of retarding the rate of aerial oxidation. Developing agents, once oxidized, lose their ability of reducing the silver salts to metallic silver, i.e., of developing an image.

Occasionally, developers are exhausted by processing a large quantity of film or paper continually within a short period of time. In this instance the rate of aerial oxidation may not be significant. However, and more often in practice, developers are used only periodically over a relatively long period of time. In this instance, and particularly in the case when airtight storage of used developers between processing periods is not feasible, aerial oxidation destroys the developer long before its processing capacity has been utilized.

In the fields of professional and technical photography it is not desirable to adjust (i.e. increase) exposures in order to obtain consistent and reproducible film or print densities, thus compensating for the gradual, or in some instances sudden, decline of developing power of a given developer formula due to oxidation.

I have discovered that the addition of an alkali metal arsenite to a sulfite containing developer will substantially increase the oxidation-stable characteristics of such a developer.

Improvement of the oxidation-resistance of sulfite containing developers is therefore an objective of the present invention, which provides a means of extending the useful life of developers.

By means of the addition of an alkali metal arsenite, the useful life of sulfite containing developers has been greatly extended. The results have been startlingly good, and could not possibly have been predicted beforehand. In fact the prior art suggests that arsenites would be ineffective. For example, Crabtree and Schwingel, in the Journal of the Society of Motion Picture Engineers for April 1940, state at page 389 that when a portion of the sodium sulfite in a developer was replaced by equivalent quantities of sodium arsenite and sodium hypophosphite, no improvement was noted. The probable explanation for the results of Crabtree et al. is that they substituted arsenite for sulfite. In the present invention, arsenite is added to the sulfite, and the amount of sulfite is not changed. The particular amount of sulfite in each developer is critical for that particular developer. When

Crabtree altered the sulfite concentration, he also admittedly altered the respective sensitometric characteristics of the developer, and the arsenite could not undo the damage. In the present invention, the amount of sulfite is not altered. Alkali metal arsenite is added to the developer, and not used as a substitute for sulfite in the formula.

To determine the effectiveness of arsenite addition as a means of improved resistance to aerial oxidation of sulfite containing developers, I have used the following test procedure.

Essentially, I have exposed identical developer compositions, with and without the addition of an arsenite salt to aerial oxidation in partially filled jars. At the start of this shelf aging period, and after certain intervals, I have developed film in these partially filled jars under carefully controlled conditions and compared the resulting densities of both the unprotected and protected developer compositions. Specifically, I have employed wide mouthed clear glass jars with 1000 ml. capacity which were charged with 100 ml., or 50 ml. of developer solutions.

At the start of the shelf aging test period, the arsenite salt was added to the coded jar, leaving the unprotected identical developer composition in the control jar. A sheet film of the appropriate developer-film emulsion combination was exposed behind a step wedge under standardized conditions, and developed in the jar containing the aged developer using reproducible mechanical agitation. The small volume of developer solution was chosen to leave a substantial column of air in the jar to react with the developer and so hasten its breakdown due to aerial oxidation. To minimize fluid loss due to evaporation, the mouth of each jar was covered during the shelf-aging periods. Periodically, however, each jar was uncovered for a fixed period to replace atmospheric oxygen consumed in the jars during the storage periods. At given intervals film was processed in the jars and evaluated by recording the resulting maximum density as measured by an Ansco Sweet Color Densitometer, Mod. 12.

The developers used in the following examples are representative of the commonly used types of developers. In the case of the developers known as ID–35, D–19, D–72, D–85, 61–D, 1–D and A.B.C. pyro-soda, the compositions used in the examples were made up according to the directions published in the literature for the developers known by those names.

In general the optimum amount of arsenite to be added varies with the composition of a developer. Concentrations as low as 0.05% have produced improvement in some cases, and so have concentrations as high as 30%. In general, however, the optimum concentration of the alkali metal arsenite in the developer solution is in the range of from about 1% to about 10%.

Sulfite containing developers are usually alkaline. When the developer is alkaline, the alkakli metal arsenite can be formed in situ by the addition of arsenic trioxide.

The following examples are given solely for purposes of illustration and are not to be considered as limiting the invention to these embodiments. Many modifications will be apparent to those skilled in the art without departing from the spirit or scope of the invention.

EXAMPLE I

Object: To determine the stabilizing or protective action of $NaAsO_2$ in a high contrast type developer suitable for photo-mechanical work and reversal processing of high contrast emulsions.

Formula ML–4

Part A:

Water	ml	375.0
Sodium sulfite, anhydrous	grams	15.0
Hydroquinone	do	22.5
Acid sulfuric C.P	do	2.0
1-phenyl 3-pyrazolidone	do	0.2

Water to make 500 ml.

Part B:

Water	ml	375.0
Sodium sulfite, anhydrous	grams	45.0
Sodium carbonate, monohydrated	do	17.5
Potassium carbonate	do	45.0
Potassium bromide	do	4.15
Benzotriazole in 10 ml. ethyl alcohol	do	0.2

Water to make 500 ml.

For use take equal parts of Part A and Part B. The pH of the working solution is 10.3. As is apparent Part A contains essentially the developing agents, and Part B contains essentially the alkali accelerators. The arsenite salt was added to Part B at the start of the aging test. Kodalith Ortho Type 2 sheet film was processed in accordance with the previously described method; the following table records the maximum densities obtained using at all times an exposure of 4 seconds and a developing time of 135 seconds. The temperature of the developers was adjusted at all times to 69° F.±1° F.

Developer formula	Addition of $NaAsO_2$/100 ml. of developer, g.	Maximum density at start of shelf aging	Maximum density after shelf aging	
			520 hrs.	828 hrs.
ML–4	0.00	4.68	1.72	No image
ML–4	3.80	[1] 3.98	3.64	3.01

[1] Initial depression of density due to addition of $NaAsO_2$.

These data illustrate the pronounced retarding action $NaAsO_2$ on the deterioration of the developer, i.e., a substantial extension of the useful life of the developer subjected to aerial oxidation. The following table illustrates how the optimum concentration of $NaAsO_2$ in the ML–4 developer was arrived at.

Developer formula	Addition of $NaAsO_2$/100 ml. of developer, g.	Molarity	Maximum density at start of shelf aging
(1) ML–4	0.13	0.01	4.61
(2) ML–4	0.65	0.05	4.37
(3) ML–4	3.25	0.25	4.07
(4) ML–4	6.50	0.50	3.98
(5) ML–4	13.00	1.00	3.80

MAXIMUM DENSITY AFTER SHELF AGING, HOURS

	166	170	454	478	502	526	598	794	862	934
(1)	4.49	4.48	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
(2)	4.37	4.25	3.28	2.57	0.48	(1)	(1)	(1)	(1)	(1)
(3)	4.01	3.90	3.66	3.57	3.58	3.54	3.75	2.76	2.28	1.99
(4)	3.79	3.92	3.45	3.17	3.28	3.06	2.20	0.49	0.23	(1)
(5)	3.43	3.53	0.73	0.39	(1)	(1)	(1)	(1)	(1)	(1)

[1] No image (zero density).

EXAMPLE II

Object: To determine the stabilizing action of $NaAsO_2$ in a developer designed for photo-mechanical work (process photography).

Formula ID–35

Stock solution A:

Water (125° F.)	ml	750.0
Hydroquinone	grams	37.5
Sodium sulfite, desiccated	do	94.0
Potassium bromide	do	9.0

Water to make 1000 ml.

Stock solution B:

Sodium carbonate, monohydrated	grams	217

Water to make 1000.0 ml.

For use, take equal parts of A and B.
The pH of the working solution is 11.0.

Kodalith Ortho Type 2 sheet film was exposed behind a step wedge for 2½ seconds and developed for 5 minutes at 69° F., using constant mechanical agitation.

The following table records the maximum densities obtained after an aeration period of 95½ hours.

Developer formula	Addition of $NaAsO_2$/100 ml. developer, g.	Maximum density at start of shelf aging	Maximum density after 95½ hours shelf aging
ID–35	0.00	4.71	[1] No image
ID–35	1.00	4.79	1.99

[1] Zero film density.

EXAMPLE III

Object: To determine the stabilizing action of $NaAsO_2$ in a normal to high contrast type developer which is identified as a long-life, non-staining tray developer, causing very little chemical fog. This developer was originally designed as an X-ray developer but is also recommended for the development of aerial films, and for films and plates when it is desirable to obtain high contrast with a short developing time.

Formula D–19

Water	ml	500
Elon (monomethyl para aminophenol sulfate)	grams	2.2
Sodium sulfite, desiccated	do	96.0
Hydroquinone	do	8.8
Sodium carbonate, monohydrated	do	56.0
Potassium bromide	do	5.0

Water to make 1000.0 ml.
The pH of the working solution is 11.0.

Developer formula	Addition of $NaAsO_2$/100 ml. developer, g.	Maximum density at start of shelf aging	Maximum Density after shelf aging	
			168 hrs.	192 hrs.
D–19	0.00	4.73	0.09	[1] No image
D–19	1.0	4.58	3.30	2.45

[1] Zero film density.

Kodalith Ortho Type 2 sheet film was exposed behind a step wedge for 4 seconds and developed for 2¼ minutes with constant mechanical agitation. Developer temperature was adjusted to 69° F.±1° F.

EXAMPLE IV

Object: To determine the stabilizing action of $NaAsO_2$ in a Universal type developer.

Formula D–72

Water	ml	500
Elon (monomethyl para aminophenol sulfate)	grams	3.1
Sodium sulfite, desiccated	do	45.0
Hydroquinone	do	12.0
Sodium carbonate, monohydrated	do	80.0
Potassium bromide	do	1.9

Water to make 1000.0 ml.

The developer was used undiluted. Kodalith Ortho Type 2 sheet film was exposed behind a step wedge for 4 seconds and developed for 5 minutes with constant mechanical agitation.

The pH of the solution (D–72) undiluted is 11.0 and in the customary 1:2 dilution the pH is 10.9.

Developer formula	Addition of $NaAsO_2$/100 ml. developer, g.	Maximum density at start of shelf aging	Maximum density after shelf aging	
			312 hrs.	364 hrs.
D-72	0.00	5.60	2.84	1.88
D-72	3.25	5.45	3.69	3.39

EXAMPLE V

Object: To determine the stabilizing action of $NaAsO_2$ in a litho-developer for lithofilm, plates, paper and stripping film producing line or half-tone negatives of extreme contrast. This developer has the property of cutting off development very sharply in the low densities, thus yielding very high gamma values in excess of gamma 7.0. In practice, its use is limited to 3–4 hours tray life. Kodalith Ortho Type 2 sheet film was exposed behind a step wedge for 5 seconds. Developing time was 135 seconds at 69° F.±1° F. under constant mechanical agitation.

Formula D–85

Water	ml	500
Sodium sulfite, desiccated	grams	30
Paraformaldehyde	do	7.5
Sodium bisulfite	do	2.2
Boric acid, crystals	do	7.5
Hydroquinone	do	22.5
Potassium bromide	do	1.6

Water to make 1000 ml.
The solution has a pH of 10.5.

Developer formula	Addition of $NaAsO_2$/100 ml. developer, g.	Maximum density at start of shelf aging	Maximum density after shelf aging		
			3 hrs.	5½ hrs.	7 hrs.
D-85	0.00	3.84	3.40	0.20	[1] No image
D-85	8.0	3.82	3.81	3.00	2.82

[1] Zero film density.

The volume of test solution was 100 ml.

EXAMPLE VI

Object: To determine the oxidation retarding, i.e., stabilizing effect of $NaAsO_2$ in an Amidol (diaminophenol di-hydro-chloride) developer. Such developers are preferentially used as paper developers due to their ability of producing an excellent silver deposit of a blue-black color and quite satisfactory tonal value. However, due to the extremely high reduction potential of the Amidol (30–40 vs. 1 of hydroquinone, for example) the developer is considered not too stable in comparison with a Metol-hydroquinone developer (such as D–72) in spite of the fact that there is no carbonate or other alkali present.

The paper used was Varigam, a multiple contrast paper, having projection speed characteristics. Filter selection and exposure were determined by the requirement of obtaining an optimum gradation, i.e., best possible reproduction of the step wedge. Development, carried out in trays, was for 4 minutes at 70° F. and with constant manual agitation. 150 ml. of developer solutions were aged in 1 quart capacity jars.

Formula 61–D

Water	ml	750
Sodium sulfite, desiccated	grams	15.4
Amidol	do	3.8
Potassium bromide	do	2.5

Water to make 1000.0 ml.
The pH of this solution is 7.0.

This Amidol developer formula shows very rapid deterioration of developing powers in a pronounced alkaline or acid medium. The sodium arsenite addition shifted the solution pH to the alkaline side; the $NaAsO_2$ protected solution was therefore buffered with citric acid to maintain the pH of 7.4 (i.e. essentially a neutral solution).

Developer formula	Addition of $NaAsO_2$/100 ml. developer, g.	Maximum density at start of shelf aging	Maximum density after shelf aging	
			25½ hrs.	45 hrs.
61–D	0.00	[1] 2.05	[1] 1.83	[1] 0.64
61–D	4.00	[1] 2.15	[1] 1.95	[1] 1.78

[1] Measured with the reflection head of the densitometer.

EXAMPLE VII

Object: To determine the stabilizing effect of $NaAsO_2$ in a representative one-bath developer-fixer (monobath).

Such solutions, when used for fixing and developing accomplish both the developing and fixing in a single operation. It is not necessary to remove the film or paper promptly after developing and fixing, because over-development cannot take place.

The processing kinetics are achieved by adjusting the concentration of the developing and fixing components in the single solution in such a manner that the reaction rate of the developing process proceeds at such a rate that it is practically finished by the time fixing action gains momentum. The necessarily high velocity of the developing process is obtained by a high concentration of alkaline acceleration which, in turn, make such formulas especially prone to aerial oxidation. The balance between developer activity and fixing rate must be adjusted to fit specific emulsion characteristics.

Scientific and patent literature make reference to various methods of combined developer-fixers. U.S. Patent 2,138,486 granted to Ernest Fournes and myself describes oxidation-stable fixer-developers which may be used over a relatively long period of time with reasonably good results.

The solutions of that patent contain an organic developing agent, a fixing agent, a caustic alkali and a reducing carbohydrate, the invention consisting in the use, along with the caustic alkali, of the reducing carbohydrate which renders the solutions stable.

The solutions of said Patent 2,138,486 while satisfactory for many purposes, have, in use, certain disadvantages. For example, when freshly prepared they give a degree of development different from that of a solution which has been used over a period of time, i.e., in which some of the active ingredients have been consumed. In addition, the obvious disadvantages of working with caustic alkalies are present, as well as the fact that with certain emulsions such formulas produce relatively coarse grain, causing lack of resolution or fine image detail.

The use of an alkali metal arsenite in conjunction with alkaline salts, such as sodium carbonate, trisodium phosphate, borax, etc. enlarges the range over which the formulation of fixer-developers can be carried out, i.e., low to high gamma characteristics, etc. These solutions containing an arsenite as will be illustrated by the following table give an almost uniform degree of development during their entire life, hitherto not possible in single solution developer-fixers.

Formula 74EM (monobath)

Water	ml	700
10% benzotriazole in ethyl alcohol	ml	10.0
Elon	grams	6.0
Hydroquinone	do	14.0
Sodium sulfite, desiccated	do	35.0
Sodium thiosulphate ($Na_2S_2O_3.5H_2O$)	do	40.0
Potassium bromide	do	6.0
Sodium phosphate, tribasic ($Na_3PO_4.12H_2O$)	grams	45.0

Water to make 1000 ml.
The pH of solution is 11.0.

Test procedure:

Film—Anklor-F (Anken Film and Chemical Corp.), a medium to high contrast chloride emulsion which permits contact exposures and handling under subdued room illumination.

Illuminant—Hanovia quartz lamp using a high-pressure quartz burner (200 watt).

Exposure—30 seconds at 13 inch lamp distance. 100 ml. developer-fixer solutions were aerated in one quart capacity jars.

Processing time—5 minutes under constant manual agitation.

Solution temperature 70° F.±1° F.

Shelf aging periods	Maximum density				Formula
	0 hrs.	47 hrs.	69 hrs.	138.5 hrs.	
Control	2.55	2.40	2.30	[1] 1.12	74EM unprotected.
1% $NaAsO_2$	2.45	2.20	2.04	1.78	74EM protected.
4% $NaAsO_2$	[2] 2.53	[2] 2.60	[2] 2.58	[2] 2.47	Do.
8% $NaAsO_2$	3.02	2.75	2.70	1.62	Do.

[1] Brownish film stain (emulsion gelatin, due to oxidation products of developing agent).
[2] Consistent reproducible developing characteristics.

EXAMPLE VIII

Object: To determine the stabilizing effect of potassium arsenite ($KAsO_2$) in a representative pyrogallol developer. The formula chosen for evaluation is a standard A.B.C. pyrosoda developer for which the following characteristics are recorded. Working solutions for sheet films should be used only once since the developing agent (pyrogallol) oxidizes rapidly and repeated use of the developer produces negatives with progressively darker pyro stain. Negatives of consistent quality are produced only when fresh developer is used for each batch.

Test procedure:

Film—a medium panchromatic continuous tone emulsion (Panatomic–X).

Exposure—2½ seconds behind a #3 step wedge which has 21 steps on a $\sqrt{2}$ transmittance scale. (This is equivalent to log E.0.3 increments.) A 32 candle power, 6 volt lamp was used at a fixed distance from the print frame. To limit deterioration of the lamp filament, a rheostat was used to reduce the applied line voltage. In addition, a current regulator was used to prevent current fluctuations and finally, an electronic timer regulated the exposure duration.

Development—5 minutes at 69° F.±1° F. with constant mechanical agitation which was achieved by the transfer of the aging vessel, and after the insertion of the exposed Panatomic–X film into a suitably designed laboratory ball-mill.

Formula 1–D

Stock solution A:

Water	ml	900
Sodium bisulfite	grams	9.8
Pyrogallol (pyrogallic acid)	do	60.0
Potassium bromide	do	1.1

Water to make 1000 ml.

Stock solution B:

Water	ml	900
Sodium sulfite, desiccated	grams	105.0

Water to make 1000 ml.

Stock solution C:

Water	ml	900
Sodium carbonate, monohydrated	grams	88.0

Water to make 1000 ml.

For use take:

1 part stock solution A
1 part stock solution B
1 part stock solution C
7 parts water

The pH of the working solution is 9.4.

	Shelf aging periods			Formula
	0 hours	2.0 hours	19.0 hours	
Control:				
Max. density	2.13	2.30	0.92	1–D unprotected.
Base density [1] plus dev. fog	0.12	0.17	0.20	1–D unprotected.
9% $KAsO_2$:				
Max. density	2.02	1.78	1.44	1–D protected.
Base density [1] plus dev. fog	0.08	0.08	0.08	1–D protected.

[1] Base densities are high due to stain caused by oxidation.

The test series recorded in the table demonstrates that the addition of potassium arsenite to the pyro developer has eliminated the pyro stain.

EXAMPLE IX

Several test series were also conducted using prepared commercial developers known to be particularly affected by aerial oxidation.

To evaluate the effect on prolonging the useful life of a representative litho developer by the simple addition of an alkaline oxidation-stable arsenite salt the following test was conducted.

Vivolith is a high energy, high contrast, lithographic type developer. It is known as an "infectious developer." It contains bisulfite and formaldehyde. Vivolith is the trademark of Photochem Company, Inc.

Developer formula	Addition of $NaAsO_2$/100 ml. developer, g.	Maximum density at start of shelf aging	Maximum density after 19 hours shelf aging
Vivolith	None	3.49	0.19
Do	10	3.45	2.85

EXAMPLE X

Object: To determine the effect of $NaAsO_2$ in a high contrast type developer (for photo-mechanical work) subjected to both aeration and exhaustion conditions. The formula used was ML–4. The film was Kodalith Ortho Type 2, 4″ x 5″ sheet film which was exposed behind a Kodak #3 step wedge for 4 seconds. The film was developed for 2¼ minutes; the developer temperature was adjusted to 69° F.

The solution volumes of both the unprotected control and the $NaAsO_2$-protected developer were 100 ml. each at the start of the test. A total of 50 4″ x 5″ sheet films were processed over a period of 12 days (289 hours) at which time the respective solution levels were down to 55 ml. At the beginning of the test single sheet films were developed at 30 minute intervals (films #1–#7), subsequently films were developed at 15 minute intervals (films #18–#42); finally, singles were processed to detect the first changes in developer characteristics.

Sequence of 4″ x 5″ sheet films developed	Time periods elapsed for shelf aging film processing, hrs.	Unprotected Formula ML–4		Protected Formula ML–4, 3.25 grams $NaAsO_2$/100 ml.	
		Max. density	Base	Max. density	Base
1st	Start	4.91	0.10	4.09	0.09
17th	25½	4.91	0.09	4.39	0.09
31st	97½	4.86	0.09	4.54	0.09
34th	100	4.64	0.09	4.48	0.09
42nd	104½	4.38	0.09	4.40	0.09
43rd	119	4.13	0.09	4.20	0.09
44th	193¾	2.50	0.08	3.91	0.08
45th	289	[1] [2] Zero	0.07	[1] 3.51	0.07
46th	363	[1] [2] Zero	-------	2.44	0.07
47th	432	[1] [2] Zero	-------	2.27	0.06
48th	482	[1] [2] Zero	-------	1.28	0.05

[1] Volume of respective developers 55 ml.
[2] No image.

In the course of research on oxidation-stable developers it has been found that concentrations as low as 0.05 percent sodium arsenite showed marked retardation of the developer breakdown due to atmospheric oxygen. Concentrations as high as 32.0 percent sodium arsenite in certain formulas gave a high degree of protection. Practical considerations, solubility, sediment formation after use, etc. made it desirable, however, to establish for each particular developer formula an optimum concentration of the alkali metal arsenite.

Sodium sulfite, a compound present in practically all types of developer formulas, shows marked stability against atmospheric oxygen in the presence of $NaAsO_2$. In order to determine the stabilizing action of $NaAsO_2$ on Na_2SO_3 solutions a test series was carried out using oxygenation as a means of aging.

A 5 percent Na_2SO_3 solution after ¼ hour oxygenation retained 26.8 percent of the original amount of Na_2SO_3.

By comparison, a 5 percent Na_2SO_3 solution to which were added 3.3 grams $NaAsO_2$/100 ml. retained after one hour 98.7% original Na_2SO_3 and after 19 hours of oxygenation 27.5 percent of the original amount of Na_2SO_3.

The susceptibility of a developer to oxidation is dependent upon the initial alkalinity of the solution, other components of the formula remaining constant, i.e., it depends upon the pH and not upon the particular alkali employed. It is apparent that for a given developer the rate of oxidation increases with increasing alkalinity.

It is known that in straight hydroquinone developers this rate is in relation to the square of the hydroxyl ion concentration.

It is also known that developers with a relatively high concentration of Na_2SO_3 (50–100 grams/1000 ml.) are generally more stable to oxidation than developers containing less sodium sulfite.

Even though it has not been possible to arrive at a general rule expressing the effectiveness of sodium arsenite in retarding oxidation in all developers it has been shown, however, that the addition of an alkaline metal arsenite applied to a wide range of developer types has substantially increased in all instances the stability of these developers.

What is claimed is:

1. A photographic developer having increased stability against aerial oxidation which comprises an aqueous solution of organic developing agent, alkali metal sulfite, and a concentration of from about 1% to about 10% of alkali metal aresenite; said developer containing the alkali metal arsenite in a concentration of from about 8% to about 10% when formaldehyde is also present therein.

2. A high contrast, photographic developer suitable for photo-mechanical work and reversal processing of high contrast emulsions and having increased stability against aerial oxidation consisting essentially of an aqueous solution of hydroquinone, 1-phenyl-3-pyrazolidone, alkali metal carbonate, sodium sulfite, potassium bromide, benzotriazole, sulfuric acid, and a concentration of from about 1% to about 10% alkali metal arsenite.

3. A photographic developer for process photography having increased stability against aerial oxidation consisting essentially of an aqueous solution of hydroquinone, sodium sulfite, sodium carbonate, potassium bromide, and a concentration of from about 1% to about 10% alkali metal arsenite.

4. An X-ray photographic developer having increased stability against aerial oxidation consisting essentially of an aqueous solution of monomethyl para aminophenol sulfate, hydroquinone, sodium carbonate, potassium bromide, a concentration of more than 5% sodium sulfite, and a concentration of from about 1% to about 10% alkali metal arsenite.

5. A photographic developer of the universal type having increased stability against aerial oxidation consisting essentially of an aqueous solution of monomethyl para aminophenol sulfate, hydroquinone, sodium carbonate, potassium bromide, a concentration of less than 5% sodium sulfite, and a concentration of from about 1% to about 10% alkali metal arsenite.

6. A photographic litho-developer having increased stability against aerial oxidation which comprises an aqueous solution of sodium sulfite, para-formaldehyde, sodium bisulfite, boric acid, hydroquinone, potassium bromide, and a concentration of from about 8% to about 10% alkali metal arsenite.

7. A photographic paper developer having increased stability against aerial oxidation consisting essentially of an aqueous solution of diaminophenol di-hydro-chloride, sodium sulfite, potassium bromide, a concentration of from about 1% to about 10% alkali metal arsenite, and a buffer to maintain the pH near 7.0.

8. A one-bath photographic developer-fixer having increased stability against aerial oxidation consisting essentially of an aqueous solution of benzotriazole; potassium bromide; hydroquinone; sodium sulfite; sodium thiosulfate; a compound selected from the group consisting of monomethyl para aminophenol sulfate and 1-phenyl-3-pyrazolidone; a compound selected from the group consisting of alkali metal phosphate, alkali metal carbonate and alkali metal hydroxide; and a concentration of from about 1% to about 10% alkali metal arsenite.

9. A photographic developer of the pyrosoda type having increased stability against aerial oxidation consisting essentially of an aqueous solution of sodium bisulfite, pyrogallol, potassium bromide, sodium sulfite, sodium carbonate, and a concentration of from about 1% to about 10% alkali metal arsenite.

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