Patented Jan. 4, 1949

2,458,376

UNITED STATES PATENT OFFICE

2,458,376

PHOTOGRAPHIC DEVELOPER ANTIOXIDANTS

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No Drawing. Application March 14, 1946, Serial No. 654,527

7 Claims. (Cl. 95—88)

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This invention relates to a composition and mehod for retarding oxidation of developer solutions.

Photographic developing compositions contain chemical reducers which are capable of reducing the exposed silver bromide in the photographic emulsions to small grains of metallic silver. Examples of such reducing or developing agents which are commonly used are pyrogallic acid, hydroquinone, monomethyl p-aminophenol sulfate and glycin. These developing agents can not develop at all when used by themselves. In order to be effective they must be employed in alkaline solution, and their energy depends upon the amount of alkali present. Since developers are reducing agents and have a great affinity for oxygen, developing solutions containing only the developing agent and the alkali would be rapidly spoiled from oxidation by the air. In order to preserve the developer, there is added to the developing solution, in addition to the reducing agent and alkali, some sodium sulfite or sodium bisulfite, which protects the developer from the oxygen of the air.

A developing solution designed for maximum contrast with process materials must produce density readily in the photographic negative. A high alkali concentration is necessary for such rapid development. But, the more strongly alkaline the developer, the more rapid the rate of oxidation, and therefore an increased amount of sodium bisulfite preservative is required. There are occasions when it is desirable to maintain an extremely high concentration of alkali in the developer with pH over 12, and yet at the same time keep the sulfite ion concentration low to allow high contrast development. This is the case, for example, when using tanning developers, and high contrast process developers. To accomplish this it has already been proposed to add to developers carbonyl-bisulfite addition products of the acetone-bisulfite and formaldehyde-bisulfite types.

It is, therefore, an object of the gresent invention to provide a photographic developing solution having a high alkalinity, low sulfite ion concentration, and high resistance to oxidation. A further object is to provide an improved developer antioxidant of the carbonyl-bisulfite addition product type.

I have found that highly improved oxidation resisting developing solutions may be obtained by the addition to such solutions of cyclohexanone-bisulfite and substituted cyclohexanone-bisulfite addition products.

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The bisulfite addition compounds are believed to undergo partial hydrolysis in the developing solutions, yielding a supply of sulfite ions which, when destroyed by oxidation, is replaced as the result of further hydrolysis of the original complex in accordance with the normal equilibrium reactions. This reaction may be represented as follows:

$$\text{Carbonyl—NaHSO}_3 \rightleftarrows \text{Carbonyl compound} + \text{Na}^+ + \text{H}^+ + \text{SO}_3^-$$

The carbonyl-bisulfite addition compounds may be used in crystalline form or as mixtures of the carbonyl compound and an alkali metal sulfite or other sulfite. When using the mixture it is desirable to employ an excess of the carbonyl compound to shift the equilibrium to the left and further decrease the sulfite ion concentration. Since the concentration of the sulfite ion is controlling, sulfites other than sodium bisulfite may be used in forming the addition compounds, for example, sodium sulfite, potassium sulfite, and other alkali metal sulfites. Metabisulfites, bisulfites, and other soluble sulfites may also be employed.

In determining the effectiveness of my new developer antioxidants I have compared them with other carbonyl-bisulfite addition products added to highly alkaline hydroquinone developing solutions. The developing solution in each case was exposed to air and the time taken to darken to a given level determined with the aid of a colorimeter. The concenrations of the carbonyl-bisulfite addition compounds added were found equivalent in allowing similar high contrast development.

Example I.—Oxidation test.—To a developer containing 5 grams of hydroquinone, 25 grams of sodium hydroxide and 1000 cc. of water, the following concentrations of carbonyl-bisulfite addition compounds were added:

Compound	Concentration	Time to darken
	Grams per liter	
Sodium sulfite	2	50 minutes.
Acetaldehyde sodium bisulfite	4	95 minutes.
Acetone sodium bisulfite	5	95 minutes.
Methyl ethyl ketone sodium bisulfite	8	75 minutes.
Ethyl acetoacetate sodium bisulfite	8	80 minutes.
Cyclohexanone sodium bisulfite	20	Over 4 hours.
Methyl Cyclohexanone sodium bisulfite	20	Over 4 hours.

Example II.—The following developer was found to give as much contrast as a developer

containing only 1 gram of sodium sulfite per liter, yet to oxidize as slowly as one containing 5 grams of sulfite per liter:

Hydroquinone	grams	5.0
Sodium hydroxide	do	25.0
Methyl benzotriazole	do	0.2
Cyclohexanone—sodium bisulfite	do	20.0
Water to	cc	1000

The developers prepared according to my invention give exceptionally high contrast. Gamma values of from 6 to 10 have been achieved, the H. and D. curve having a very short toe. High contrast of this order can be obtained only when the sulfite ion concentration is kept to a minimum as in the case of developers containing the cyclohexanone-bisulfite antioxidants.

I claim:

1. A composition of matter adapted to form a developing solution having a low sulfite ion concentration and a high resistance to oxidation when dissolved in water in the presence of a strong inorganic base, comprising a photographic silver halide developing agent and a member selected from the class consisting of cyclohexanone-bisulfite, methyl cyclohexanone-bisulfites, mixtures of cyclohexanone and a soluble sulfite, and mixtures of cyclohexanone and a soluble bisulfite.

2. A composition of matter adapted to form a developing solution having a low sulfite ion concentration and a high resistance to oxidation when dissolved in water in the presence of a strong inorganic base, comprising a photographic silver halide developing agent and a compound of cyclohexanone with sodium bisulfite.

3. A composition of matter adapted to form a developing solution having a low sulfite ion concentration and a high resistance to oxidation when dissolved in water in the presence of a strong inorganic base, comprising a photographic silver halide developing agent and a compound of p-methyl cyclohexanone with a soluble bisulfite.

4. A composition of matter adapted to form a developing solution having a low sulfite ion concentration and a high resistance to oxidation when dissolved in water in the presence of a strong inorganic base, comprising hydroquinone and a cyclohexanone-sodium bisulfite addition product.

5. A photographic developer comprising hydroquinone, sodium hydroxide and cyclohexanone-sodium bisulfite.

6. A composition of matter adapted to form a developing solution having a low sulfite ion concentration and a high resistance to oxidation when dissolved in water in the presence of a base comprising a silver halide developing agent, cyclohexanone, and a soluble sulfite.

7. A photographic developer comprising hydroquinone, sodium hydroxide, and p-methyl cyclohexanone-sodium bisulfite.

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