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STABILIZED PHOTOGRAPHIC DEVELOPERS FOR COLOR PHOTOGRAPHY

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1 Claim. (Cl. 96—66)

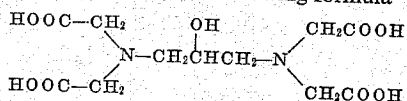
This invention relates to developers for color photography which have been stabilized by the addition of 1,3-diamino-2-propanol tetracetic acid thereto.

It has been previously proposed in developers in color photography to employ in conjunction with the usual color developing agent and the alkali metal sulfite, an hydroxylamine salt and an ethylenediamine salt. However, it has been found that in some manner, as yet not completely understood, the alkali metal sulfite, hydroxylamine salt and ethylenediamine salt interact in solution, the result being that the effective concentrations of the alkali metal sulfite and hydroxylamine salt become progressively lower upon storage even where the solution is carefully stoppered and free of contact with air. Thus, there is a variable and unpredictable change in the sensitometric properties of such solutions upon storage, such as is customary in commercial processing of color materials. The aforementioned developing solutions are concerned primarily with the treatment of color materials having a coupling component present in the differentially sensitized layers for coupling with the oxidation products of the color developer.

It is, accordingly, an object of my invention to provide photographic developing solutions for color photography which can be stored for extended periods of time without substantial loss of the effective concentration of the active ingredients. Another object is to provide photographic developing solutions for treatment of differentially sensitized color materials containing coupling compounds in the sensitized emulsion layers. Still another object is to provide a method for making such solutions. Other objects will become apparent from a consideration of the following description and examples.

My invention provides a means of stabilizing photographic developing solutions of the type under consideration by the addition of 1,3-diamino-2-propanol tetracetic acid to the developing solutions. It has been shown in the art that this tetracetic acid derivative can be used in photographic developing solutions (U. S. Patent 2,656,273), although it was quite unexpected that this compound, which had been shown to be useful as a sequestering agent, could also be used to stabilize an otherwise unstable developing solution containing an alkali metal sulfite, an hydroxylamine salt and an ethylenediamine salt.

By 1,3-diamino-2-propanol tetracetic acid, I mean the compound represented by the following formula



The tetracetic acid derivative employed in my invention is employed in combination with a phenylenediamine color developer which upon oxidation couples with the conventional coupling components employed in incorporated coupler photography. Such phenylenediamine developing agents include the hydrochloride or sulfate

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of N,N-diethyl-p-phenylenediamine, N-methyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine, etc.

5 The amount of 1,3-diamino-2-propanol tetracetic acid added to the developing composition will vary somewhat, depending upon the particular developing agent employed and amounts of other ingredients present. In general, the concentration of the tetracetic acid can vary from 10 about 0.2 g. to about 2.0 g. per liter.

The advantages of my invention can be illustrated as follows: An aqueous solution, designated solution A, was prepared having the following composition:

15	Sodium metaborate octahydrate	G.
	Sodium sulfite	40.1
	Color developer ¹	2.0
	Hydroxylamine sulfate	4.0
	Ethylenediamine sulfate	4.7
20	Water to make one liter	6.5

¹ 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl] - m - toluidine sesquisulfate monohydrate.

A second solution, designated solution B was prepared 25 identical with solution A except that it contained 1.0 g. per liter of 1,3-diamino-2-propanol tetracetic acid. These two solutions were then stored for two weeks at 75° F., both in closed, tightly-stoppered bottles and in open containers. By chemical analysis, the loss of concentration 30 of sodium sulfite and hydroxylamine sulfate was determined.

35		Loss in concentration (2 weeks' storage)			
		Closed Container		Open Container	
		Sodium Sulfite	Hydroxylamine Sulfate	Sodium Sulfite	Hydroxylamine Sulfate
40		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>
		79	52	89	62
Solution A		12	22	20	26
Solution B					

45 It is evident from the above table that the tetracetic acid derivative of my invention has a marked effect on the stability of the stored developing solutions. While the above table shows a concentration of 1.0 g. per liter of the stabilizing agent, I have found that a concentration of from about 0.5 to 1.0 g. per liter gives quite outstanding results.

50 The following example will illustrate the manner of using the photographic developing solutions of my invention.

Example

55 A multilayer reversal color material of the type described in Yutzy and Van Campen U. S. application Serial No. 524,362, filed July 26, 1955, or a reversal color material of the type described in Meeussen and Bellay U. S. Patent 2,673,800, was exposed in the usual manner to an appropriate subject. The exposed color film was then
60 developed in a black-and-white developer for six minutes, the developer having the following composition:

		G.
65	Sodium hexametaphosphate	2.0
	N-methyl-p-aminophenolsulfate	0.90
	Hydroquinone	2.35
	Sodium sulfite (anhydrous)	8.0
	Sodium metaborate octahydrate	25.5
	Potassium bromide	0.55
70	Sodium chloride	0.20
	5-methylbenzotriazole	0.02
	Water to make one liter.	

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The developed material was then treated in a stop bath for four minutes, the stop bath having the following composition:

	G.
Sodium diacetate.....	22.0
Sodium bisulfite.....	27.0
Water to make one liter.	

The color material was then washed for eight minutes and subdued room lights turned on after the washing had begun. The material was then re-exposed for ten seconds on each side at a distance of one foot from a No. 1 Photoflood. The re-exposed material was then color developed for four minutes in a developer of the type having the composition shown above and then treated in a second stop bath for three minutes, this particular bath having the following composition:

	G.
Sodium bisulfite.....	12.4
Sodium diacetate.....	14.8
Sodium acetate.....	6.5
Boric acid.....	7.5
Potassium aluminum sulfate.....	30.0
Water to make one liter.	

The material was then washed for three and one-half minutes and next treated in a bleach bath for eight minutes, the bleach bath having the following composition:

	G.
Potassium ferricyanide.....	70.0
Potassium bromide.....	40.0
Water to make one liter.	

The material was then washed for six minutes and treated in a fixing bath having the following composition:

Sodium sulfite (anhydrous).....g--	6.8
Potassium aluminum sulfate.....g--	13.4

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Glacial acetic acid.....ml--	10.0
Sodium thiosulfate (anhydrous).....g--	160.0
Zinc sulfate heptahydrate.....g--	5.0
Water to make one liter.	

The material was then washed for seven minutes and dried for ten minutes.

It is to be understood that the tetracetic acid stabilizing compound employed in my invention exists in the alkaline developing solutions in its ionized form. While an alkali metal salt undoubtedly is first formed from the acid, this exists in ionic form in the developing solution. In like manner, the ethylenediamine salt and the hydroxylamine salt exist in ionic form in the developing solution. In addition to the sulfate salts illustrated in the above examples, other salts, such as the hydrochloride, phosphate, etc., can be used, provided such salts are soluble in water. Other alkali metal sulfites, such as potassium sulfite, etc., can be employed in place of the sodium sulfite illustrated in the example. The alkaline agent in the developer can be an alkali metal carbonate, such as sodium carbonate, potassium carbonate, etc., or an alkali metal hydroxide, such as sodium hydroxide, etc., in place of the metaborate salt illustrated above.

What I claim as my invention and desire secured by Letters Patent of the United States is:

A photographic developing composition comprising an alkaline solution of 1,3-diamino-2-propanol tetracetic acid, sodium sulfite, hydroxylamine sulfate, ethylenediamine sulfate, and 4-amino-N-ethyl-N-[β -methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate.

References Cited in the file of this patent

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	2,656,273	Henn et al.	Oct. 20, 1953