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3,462,269

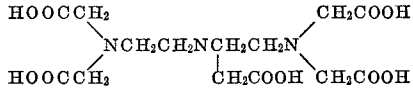
STABILIZED COLOR DEVELOPING SOLUTION CONTAINING DIETHYLENETRIAMINE PENTAACETIC ACID

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Int. Cl. G03c 5/30, 7/30
U.S. Cl. 96—55 1 Claim

ABSTRACT OF THE DISCLOSURE

In a photographic developing composition comprising an alkaline solution of a phenylenediamine color developer, alkali metal sulfite and a hydroxylamine salt, the improvement which comprises from 0.1 to 3 grams per liter of diethylenetriamine pentaacetic acid having the formula



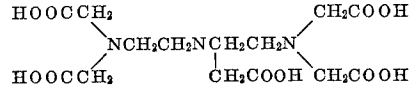
This invention relates to a novel and improved alkaline photographic developer composition. In one aspect this invention relates to a color photographic developer solution containing hydroxylamine salt and a sequestering agent.

The addition of sequestering agents and water softeners to photographic processing baths to offset the variability of local water supplies has been a common practice in the photographic industry. Unfortunately, the addition of certain sequestering agents tends to reduce the stability of developer solutions, particularly those containing oxidizable ingredients. Thus, for example, the addition of ethylenediamine tetraacetic acid and certain derivatives thereof produces a surprisingly large loss in the hydroxylamine salt concentration upon storage, adversely affecting photographic results. In U.S. 2,875,049 the use of ethylenediamine salts in conjunction with the usual color developing agents, i.e., alkali metal sulfite and hydroxylamine salts, is stated to result in an effective concentration loss of the alkali metal sulfite and the hydroxylamine salt. Quite unexpectedly patentee found that 1,3-diamino-2-propanol tetraacetic acid tends to stabilize photographic developer solutions of the abovementioned type in addition to its function as a sequestering agent. The mechanism of such stabilization is not fully known. However, other suitable sequestering agents with the ability to efficiently stabilize such developing solutions have been needed.

Accordingly, one of the objects of this invention is to provide a novel developing solution for color photography which includes an efficient sequestering agent and which can be stored for extended periods of time without substantial concentration loss of the active ingredients.

Another object is to provide photographic developing solutions for treating differentially sensitized color materials containing coupling compounds in the sensitized emulsion layers. Other objects will become apparent from the following description and examples.

In accordance with this invention stabilized photographic developing solutions of the aforementioned type may be stabilized by the addition of diethylenetriamine pentaacetic acid, which has the structure:



in an amount from 0.10 gram per liter to 3.0 grams per liter. The color developer solutions in which this diethylenetriamine pentaacetic acid is effective contain alkali metal sulfite and hydroxylamine salt in addition to a suitable color developer and other desirable additives. The color developers are preferably of the phenylenediamine type which upon oxidation couple with the conventional coupling components employed in color photography. Such phenylenediamine developing agents include the hydrochloride or sulfate of N,N-diethyl-p-phenylenediamine, N-methyl-p-phenylenediamine, N,N-dimethyl - p - phenylenediamine, 2-amino-5-diethylaminotoluene, 4-amino-N-ethyl-N-(beta-methanesulfonamidoethyl)-m-toluidine, etc. In addition to its stabilizing effect, the diethylenetriamine pentaacetic acid has an unusually high sequestering power for calcium, iron and copper and prevents the formation of salt scums and sludges in the developer solution.

The following example will illustrate the manner of using and the effectiveness of the photographic developing solution of this invention.

Example

A color developer solution (Solution No. 1) was made having the following composition:

	G./l.
Color developer, CD–3 [1]	4.50
Sodium metaborate·4H_2O	36.00
Sodium sulfite	2.60
Hydroxylamine sulfate	3.60
Potassium bromide	0.30

[1] 4-amino - N - ethyl - N - (beta - methanesulfonamidoethyl) - m-toluidine sesquisulfate monohydrate.

Solution No. 2 was identical to Solution No. 1 except that it contained 0.8 gram per liter of diethylenetriamine pentaacetic acid (DTPA) in addition to the other ingredients.

Solution No. 3 was identical to Solution No. 1 except that it contained 0.8 gram per liter of ethylenediamine tetraacetic acid.

The three solutions were stored in both closed and open containers for 10 days at 75° F. The loss in concentration of the hydroxylamine sulfate, determined by chemical analysis after 10 days, is shown in Table I.

TABLE I.—LOSS IN CONCENTRATION OF HYDROXYLAMINE SULFATE, 10 DAYS AT 75° F.

	Closed container, Percent	Open container, Percent
Solution No. 1	41.4	54.2
Solution No. 2	2.8	3.5
Solution No. 3	76.1	95.1

Color photographic strips processed in Solution No. 2 after storage were quite comparable to the original strips processed in fresh solutions, while strips processed in Solution Nos. 1 and 3 after storage had an undesirable overall cyan color.

The above tabular results clearly show that the DTPA has a dramatic effect on the stability of the stored solutions.

The hydroxylamine sulfate concentration range was varied from 2 to 5 grams per liter, with the addition of DTPA varied from 0.10 to 3.0 grams per liter. In each case the addition of DTPA markedly stabilized the hydroxylamine sulfate.

A multilayer positive color photographic film was exposed and processed in Solution No. 2 for five minutes.

The developed film was then placed for two minutes in a stop-fix bath of the following composition.

	G./l.
Sodium thiosulfate (anhydrous)	200
Sodium sulfite (anhydrous)	15
Sodium bisulfite	22

The color film was then washed for five minutes and treated for four minutes in a bleach-fix bath of the following composition:

	G./l.
Sodium ferric ethylenediamine tetraacetate (12% iron expressed as metallic iron)	50
Sodium carbonate (monohydrate)	2.5
Sodium sulfite (anhydrous)	10.0
Sodium thiosulfate (anhydrous)	200.0

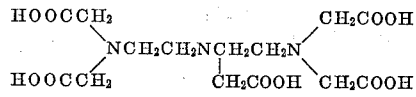
The film was then washed for five minutes, treated for two minutes in a hardener-stabilizer having the following composition:

Formalin	ml./l.	100
Tartaric acid	g./l.	20
Sodium acetate	g./l.	40

and dried to provide a good color print.

What is claimed is:

1. In a photographic developing composition comprising an alkaline solution of a phenylenediamine color developer, alkali metal sulfite and a hydroxylamine salt, the improvement which comprises from 0.1 to 3 grams per liter of diethylenetriamine pentaacetic acid having the formula



References Cited

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FOREIGN PATENTS

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—66.4

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

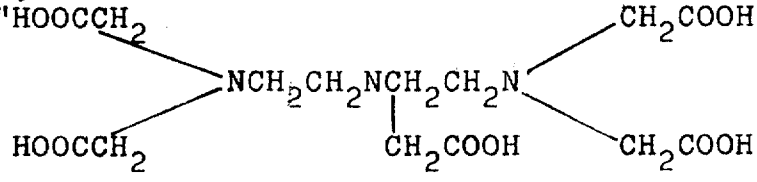
CERTIFICATE OF CORRECTION

Patent No. 3,462,269 Dated August 19, 1969

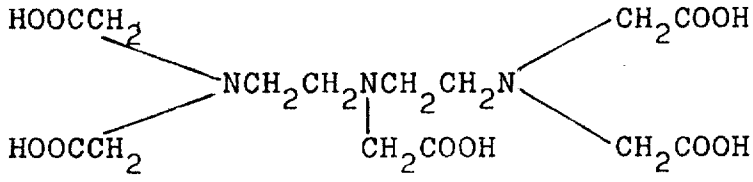
Inventor(s) Vincent A. Tassone

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, lines 20-23 and 68-71 and Column 4, lines 5-8 the formula "HOOCCH$_2$ CH_2COOH" should read



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(SEAL)
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