United States Patent Office 2,816,026 Patented Dec. 10, 1957

2,816,026

STABILIZING AGENTS FOR SINGLE POWDER PHOTOGRAPHIC DEVELOPERS

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No Drawing. Application November 26, 1954, Serial No. 471,509

3 Claims. (Cl. 96—66)

This invention relates to photographic developer compositions, the components of which are mutually compatible and can, therefore, be packaged for merchandising as a mixture in a hermetically sealed package. Such photographic developer mixtures are commonly termed single powder photographic developers and the present invention relates to the use of a new type of stabilizing agent which will effectively prevent discoloration and deterioration of single powder photographic developer formulations.

Various compounds have been disclosed in the past that have been described as protectants for single-powder photographic developer formulations. These compounds, when added to the powders, act to prevent the interaction of the developing agent components with the alkali components of the powders, thus preventing discoloration and deterioration on storage. These compounds include boric anhydride, metaboric acid, and other hydrated forms of boric anhydride. Also included are organic anhydrides such as phthalic anhydride and maleic anhydride. Other compounds having an appreciable vapor pressure and which are essentially acidic in nature, such as phthalimide, have been employed as protectants.

In general, compounds used for the prevention of deterioration in single-powder photographic developer formulations must meet either or both of two requirements: (1) they should absorb water and thus eliminate the moisture in the powders that will otherwise promote discoloration and deterioration at the surface of the alkali components, and (2) they should have an appreciable volatility and be acidic in nature so that they can form essentially an acidic, non-reactive coating on the alkali. This non-reactive coating will prevent reaction between developing agents and alkali in single powder packages.

It is the object of this invention to provide a new type of compound which will effectively prevent discoloration and deterioration of single-powder photographic developer formulations. It is a further object of this invention to provide a type of protectant that combines both the dehydrating and coating mechanisms in preventing discoloration of alkalis in such developer powders. Another object is to provide stabilizing compounds that may be used for the protective coating of alkali hydroxides to facilitate their use in single-powder developers. Other objects will appear herein.

It appears in the single powder mixtures heretofore known that boric anhydride acts as a protectant through its dehydrating properties, while phthalic anhydride acts through its ability to sublime and to protectively coat the reactive alkalis of the single powder mixture. The presence of both protectants together in single powders has not shown any appreciable superadditivity in the extent of protection they will afford to photographic developer powders.

However, in accordance with our instant invention we have found that a reaction product of boric anhydride with another organic anhydride such as a compound selected from the group consisting of acetic anhydride,

benzoic anhydride, and phthalic anhydride has good protectant action in single powder developers. We have found that such compounds give more protection in single powder developers than a single mixture of boric anhydride with any of the other above named anhydrides in the equivalent amounts employed to form the new protectant.

The preferred protectant compounds are boro-acetic anhydride $(CH_3COO)_3B$, boro - benzoic anhydride $(C_6H_5COO)_3B$, and boro-phthalic anhydride

$$(C_6H_4(COO)_2)_3B_2$$

These compounds may be advantageously employed as protectants in single powder developers containing sodium borate, sodium metaborate, or sodium, potassium and lithium hydroxide as the alkali component. The sodium, potassium and lithium hydroxide should, however, have been treated by the method described and claimed in the copending application of Ralph W. Baxendale, Serial No. 471,510 filed of even date and entitled, "Alkali Hydroxides for Use in Single-Powder Photographic Developers." We have found that when one of the compounds: boro-acetic anhydride, boro-benzoic anhydride, and boro-phthalic anhydride has been intimately admixed with photographic developer powders containing one or more of the above-mentioned alkalis in a concentration of one-half percent, or more, discoloration and deterioration of the powders that would normally occur is prevented.

The present invention is further illustrated in the following examples:

Example 1

A commercial sample of boron acetate (boro-acetic anhydride) was used as a protectant in the following single-powder developer formula.

	Grams
Elon (mono methyl p-aminophenol sulfate)	5.0
Hydroquinone	10.0
Sodium sulfite	70.0
Sodium borate.$5H_2$	25.6
Ethyl benzoate treated sodium hydroxide	13.6
Boron acetate (boro-acetic anhydride)	1.3
Potassium bromide	5.0

The above single-powder mixture did not discolor or otherwise deteriorate when stored at 120° F. The example illustrates the effective use of this type of protectant in caustic-containing developer powders.

Example 2

The following single-powder developer mixture was prepared:

	Grams
Elon	2.5
Hydroquinone	5.0
Sodium sulfite	25.0
Sodium metaborate mono-hydrate (prepared by drying sodium meta-borate tetrahydrate crystal)	26.3
Potassium bromide	1.8
Boron acetate (boro-acetic anhydride)	0.8

The above powder did not discolor or otherwise deteriorate when stored at 120° F. This example illustrates the effectiveness of this type of compound in protecting a photographic single-powder that is ordinarily quite difficult to prevent from deteriorating. Adding boric anhydride and acetic anhydride separately to such a developer powder mixture caused severe deterioration.

Example 3

The use of borophthalic anhydride is illustrated by this example. Although this compound may be prepared in several ways, a product of good quality was

prepared by the following method: 2.0 grams of boron acetate (boro-acetic anhydride) and 2.6 grams of orthophthalic acid were mixed and heated at 110° C. for 2 hours. The acetic acid formed was taken off by evacuation and the resulting product dissolved and recrystallized from an equal volume mixture of benzene and acetone. The compound thus prepared was used as a protectant in the following single powder:

	Grams
Elon	2.5
Hydroquinone	5.0
Sodium sulfite	25.0
Sodium borate.$5H_2O$	25.6
Diethyl oxalate treated sodium hydroxide	7.1
Potassium bromide	1.8
Borophthalic anhydride	0.7

The above powder showed no objectionable discoloration or deterioration when stored at 120° F. However, a similar powder using as protectants the equivalent amounts of boric anhydride and phthalic anhydride necessary to prepare the same amount of borophthalic anhydride showed some deterioration when stored under the same conditions.

Example 4

Borobenzoic anhydride prepared by reacting boric anhydride and benzoic anhydride together was used to protect the following single-powder developer formula:

	Grams
Elon	2.5
Hydroquinone	5.0
Sodium sulfite	25.0
Sodium borate.$5H_2O$	25.6
Ethyl benzoate treated sodium hydroxide	7.1
Potassium bromide	1.8
Borobenzoic anhydride	0.7

The above powder, when stored at 120° F., showed no objectionable discoloration or deterioration.

Example 5

This example illustrates the use of this invention to improve the stability of sodium hydroxide specially treated for use in single-powder developer formulas.

Sodium hydroxide was treated with diethyl phthalate to make it possible to pack the alkali in single-powder developers. However, the treatment was not complete and did not fully stabilize the sodium hydroxide so that it would not cause deterioration. By thoroughly mixing boron acetate (boro-acetic anhydride) in a concentration of 1 percent by weight with the treated sodium hydroxide and allowing the mixture to stand for 24 hours at 120° F., it was possible to pack the product in the following single-powder developer.

	Grams
Elon	2.5
Hydroquinone	5.0
Sodium sulfite	25.0
Sodium borate.$5H_2O$	25.6
Diethyl phthalate treated sodium hydroxide post-treated with boron acetate (boro-acetic anhydride)	7.2
Potassium bromide	1.8
Boric anhydride	0.7

The above powder did not discolor or otherwise deteriorate when stored at 120° F.

The ingredients of a single powder developer composition in accordance with the present invention may consist of an organic developing agent such as monomethyl para-aminophenol sulfate (Elon or Metol), hydroquinone, p-aminophenol hydrochloride, p-aminophenol sulfate, pyrogallol, p-hydroxyphenol glycine, catechol, diaminophenol hydrochloride, and suitable mixtures thereof, sodium sulfite, and potassium bromide, the function of the alkali sulfite being that of preservative, lessening the oxidation in solution of the organic developing agent, while the known function of potassium bromide is that of a restrainer particularly inhibiting "fog" formation in the development of the silver image. Also sodium, potassium or lithium hydroxides may be present to regulate the pH of the developer solution.

In compounding the developer mixture one may proceed by first mixing the stabilizer and the basic or alkaline component, adding and mixing therewith the developing agent, which is followed by incorporating the other ingredients. However, one can mix all the ingredients together at the same time.

It is mentioned above that the stabilizing agents of the present invention may be advantageously employed with alkali hydroxides which have been coated with a protective coating in accordance with the copending application of Ralph W. Baxendale, Serial No. 471,510 filed November 26, 1954, and entitled, "Alkali Hydroxides for Use in Single-Powder Photographic Developers."

As described in that application the alkali hydroxides are treated in comminuted form with an ester of an organic acid or an ester of an inorganic acid. Alkaline hydrolysis occurs in which the alkali salt of the acid and an alcohol will be formed. The alcohol is expelled leaving the alkali hydroxide particles covered with an adherent alkali salt coating of the selected acid. The alkali salt coatings are substantially non-reactive in the presence of the ingredients of single powder developers.

We claim:

1. A stable single-powder photographic developer composition containing an organic silver halide developer, an alkali borate, an alkali sulfite, an alkali hydroxide, and a stabilizing agent selected from the group consisting of boro-acetic anhydride, boro-benzoic anhydride and borophthalic anhydride.

2. A stable single-powder photographic developer composition containing an organic silver halide developer, a sodium borate, sodium sulfite and sodium hydroxide, and a stabilizing agent selected from the group consisting of boro-acetic anhydride, boro-benzoic anhydride and boro-phthalic anhydride.

3. A stable single-powder photographic developer composition containing an organic silver halide developer, sodium metaborate monohydrate, sodium sulfite, potassium bromide, and a stabilizing agent selected from the group consisting of boro-acetic anhydride, boro-benzoic anhydride and boro-phthalic anhydride.

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