

UNITED STATES PATENT OFFICE

2,649,376

SINGLE POWDER DEVELOPERS CONTAINING STABILIZED ALKALI HYDROXIDES

Arthur A. Rasch, Richard W. Henn, and John I. Crabtree, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application June 26, 1952,
Serial No. 295,805

6 Claims. (Cl. 95—88)

1

This invention relates to single-powder photographic developers which contain acidic stabilizing agents for preventing disadvantageous interaction between the organic developer component and the alkaline component of the single powder mixtures, and more particularly to such single-powder developers containing a specially treated alkali hydroxide to compensate for the loss of alkalinity due to the presence of the acidic stabilizing agents.

Single powder developer mixtures may contain an organic silver halide developer which may be a single developing agent or a mixture of such agents, including monomethylparaminophenol sulfate (Elon or Metol), hydroquinone, p-aminophenol hydrochloride, p-aminophenol sulfate, pyrogallol, p-hydroxyphenyl glycine, catechol, diaminophenol hydrochloride, and others, with an alkali component, a stabilizing component, an antioxidant, an anti-fogging component and a sequestering agent. A buffer component may also be included such as alkali salts of boric acid, carbonic acid and phosphoric acid. The alkali component may be the stable hydrate of an alkali carbonate, a desiccated alkali carbonate, an alkali metaborate, or an alkali sulfite. Generally the stable sodium carbonate monohydrate is preferred. The antioxidant may be an alkali sulfite, and the antifogging component may be potassium bromide or iodide, or an organic antifogant. Stabilizing components for such a single-powder developer are disclosed in Patent 2,384,592 of September 11, 1945, and include maleic anhydride, salicylic acid, alkali metabisulfite, benzoic anhydride, orthobenzoic sulfimide, phthalimide, and phthalic anhydride. In the copending application by William J. Rogers S. N. 210,284, filed February 9, 1951, now Patent No. 2,606,118, and entitled "Stabilizing Agent for Single Powder Photographic Developers," boric anhydride is disclosed and claimed as a protectant to prevent interaction between the alkali and acid components of the single-powder developers. Tetraboric acid and metaboric acid and partially hydrated forms of boric anhydride between boric anhydride and metaboric acid may also be employed as stabilizing agents.

In such methods the stabilization is generally obtained at the expense of a loss of alkalinity of the formula. In some special formulas the loss of alkalinity is great enough to affect disadvantageously the photographic properties of the developer.

An object of the present invention is, therefore, to provide a method whereby an alkali hydroxide

2

may be employed to compensate for loss of alkalinity due to protectant addends. It is a further object of the invention to provide a method of packing a single-powder developer in which the total alkalinity of the formula may be readily adjusted. Another object is to prepare and pack as single powders, formulas of types which cannot be so packed by other methods. This applies particularly to formulas containing borate alkalies. Still another object is to demonstrate a method requiring a minimum of handling and equipment for the preparation of single-powder formulas.

Other objects will appear hereinafter.

In accordance with the present invention we have found that single-powder developers can be prepared which are stabilized against reaction between the acidic and basic constituents of the single-powders without loss of alkalinity. This desirable relationship may be occasioned by employing boric anhydride as the stabilizing agent with specially treated sodium or potassium hydroxide as the compound to adjust the alkalinity of the single-powder mixture.

There are many instances when it is desirable to employ sodium or potassium hydroxide as a constituent of photographic developer powders but their use is limited by the extremely hygroscopic nature of these alkalis and their consequent propensity to cause caking and corrosion. In the copending application of one of the present joint inventors, Richard W. Henn, S. N. 295,803 filed of even date, entitled "Noncaking Sodium and Potassium Hydroxide For Photographic Developer Powders," sodium and potassium hydroxide, which have been treated to reduce their hygroscopic nature, are disclosed and claimed. It was found that when the surface of sodium or potassium hydroxide powders was coated with a thin coating of phthalic anhydride, the thin coating effectively prevents the alkali hydroxide from becoming damp enough to cause caking. The preferred method of coating the hydroxide is to add ground phthalic anhydride to finely divided sodium hydroxide in a concentration of at least 5%. The usefulness of this type of treated alkali may be extended to the field of single-powder photographic developers, where it is essential that the surfaces of the powders be in a dry state. In particular, the treated alkali may be advantageously combined with powders containing boric anhydride as a protectant to produce single powders of good stability. By varying the ratio of the boric anhydride to phthalic anhydride-sodium hydroxide mixture,

3

the alkalinity of a single-powder developer formula can be adjusted over a wide range. Metaboric acid, tetraboric acid and in some cases, sodium bisulfite or metabisulfite can be substituted for the boric anhydride, although stability in these cases may be somewhat less.

The ingredients of a preferred single-powder developer composition may, therefore, consist of an organic developing agent, such as monomethyl paraminophenol sulfate, hydroquinone, p-aminophenol hydrochloride, p-aminophenol sulfate, pyrogallol, p-hydroxyphenyl glycine, catechol, diaminophenol hydrochloride, and suitable mixtures thereof, sodium or potassium hydroxide which has been treated with phthalic anhydride to reduce its hygroscopic properties and boric anhydride, and may contain the other ingredients mentioned above normally present in a developer, such as sodium sulfite and potassium bromide, the normal and known 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.

In compounding the developer mixture, one may proceed by first mixing the treated alkali hydroxide with the salt components and boric anhydride of the formula and then in turn adding the developing agents.

The following examples will serve further to illustrate developer mixtures within the scope of the invention and will also indicate the proportionate quantities in which the respective components can be mixed together in a dry form to make up such single-powder photographic developer mixtures.

Example 1

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Sodium metaborate trihydrate containing 2% CO ₂	27.5
Potassium bromide	2.0
Sodium hydroxide containing 5% phthalic anhydride	2.3
Boric anhydride	1.9

The above formula did not discolor or otherwise deteriorate on incubation for two weeks at a temperature of 45° C. This formula illustrates the use of phthalic anhydride-sodium hydroxide mixtures to compensate for loss of alkalinity due to the addition of acid protectants.

Example 2

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Sodium tetraborate	14.7
Sodium hydroxide containing 20% phthalic anhydride	13.6
Potassium bromide	2.0
Sodium metabisulfite	2.2
Boric anhydride	2.2

The above single powder formula did not discolor or otherwise deteriorate on incubation for two weeks at 40° C. This example illustrates the use of phthalic anhydride-sodium hydroxide mixtures to both adjust the total alkalinity of the single-powder formulas and compensate for the acidic protectant addends.

4

Example 3

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Boric anhydride	12.3
Sodium hydroxide containing 5% phthalic anhydride	14.5
Potassium bromide	2.0

The above single powder formula did not discolor or otherwise deteriorate when stored four months at room temperature (75-85° F.).

Example 4

	Grams
Elon	2.2
Hydroquinone	8.8
Sodium sulfite	72.0
Boric anhydride	12.3
Sodium hydroxide containing 5% phthalic anhydride	18.3
Potassium bromide	2.0

The above single-powder formula did not discolor or otherwise deteriorate when stored for four months at room temperature (75-85° F.).

Example 5

	Grams
Elon	4.4
Hydroquinone	17.6
Sodium sulfite	72.0
Boric anhydride	12.3
Sodium hydroxide containing 5% phthalic anhydride	23.0

The above single-powder formula did not discolor or otherwise deteriorate when stored for four months at room temperature (75-85° F.). This example, along with Examples 3 and 4, illustrate the use of boric anhydride-phthalic anhydride-sodium hydroxide combinations to give stable single powder formulas of varying alkalinity.

Example 6

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Metaboric acid	17.0
Sodium hydroxide containing 5% phthalic anhydride	14.5
Potassium bromide	2.0

The above single-powder formula showed only slight discoloration when stored for two months at 45° C.

In all the above formulas, potassium hydroxide may be substituted for sodium hydroxide.

A pH of 9.3 to 10.1 corresponding to that obtained in Kodak developers is attained in the single-powder developers described in Examples 3, 4 and 5, supra.

Example 7

A high pH developer corresponding somewhat to the Kodak D-8 formula may be prepared from the following:

	Grams
Hydroquinone	45
Sodium sulfite desiccated	90
Sodium hydroxide containing 5% phthalic anhydride	40
Potassium bromide	30
Boric anhydride	5

The above single powder showed only slight discoloration when stored three days at 45° C.

5

In preparing a developer solution the composition of the above examples should be dissolved in water to make one liter of solution.

Samples of the mixtures as given in the examples have been found, even after the mixtures have been kept in hermetically sealed cans at raised temperatures for prolonged periods, to be unimpaired in developing properties and the powders were uncolored or only lightly tinted. However, when untreated sodium hydroxide was used in the above examples severe discoloration and deterioration of the powders took place almost immediately.

We claim:

1. A stable single powder photographic developer composition containing an organic silver halide developer, a stabilizing agent selected from the group consisting of boric anhydride, tetraboric acid, metaboric acid, partially hydrated forms of boric anhydride, intermediate between boric anhydride and metaboric acid, alkali bisulfite, and alkali metabisulfite, a preservative selected from the group consisting of alkali sulfite and alkali bisulfite, a buffer compound selected from the group consisting of the alkali salts of boric acid, carbonic acid, and phosphoric acid, and an alkali selected from the group consisting of sodium and potassium hydroxides, which have been coated with 2 to 20% by weight of phthalic anhydride.

2. A stable single-powder photographic developer composition containing an organic silver halide developer, a stabilizing agent comprising boric anhydride, an antifoggant, a soluble photographically compatible basic ingredient selected from the group consisting of alkali borates and sulfites, and an alkali compound selected from

6

the group consisting of sodium and potassium hydroxide which has been coated with from 5 to 20% by weight of phthalic anhydride.

3. A stable single-powder photographic developer containing an organic silver halide developer, an alkali sulfite, boric anhydride and an alkali compound selected from the group consisting of sodium and potassium hydroxide which has been coated with from 5 to 20% by weight of phthalic anhydride.

4. A stable single-powder photographic developer containing an organic silver halide developer, an alkali sulfite, boric anhydride, an antifoggant, and an alkali compound selected from the group consisting of sodium and potassium hydroxide which has been coated with from 5 to 20% by weight of phthalic anhydride.

5. A stable single-powder photographic developer containing an organic silver halide developer, an alkali sulfite, metaboric acid, an antifoggant, and an alkali compound selected from the group consisting of sodium and potassium hydroxide which has been coated with from 5 to 20% by weight of phthalic anhydride.

6. A stable single-powder photographic developer containing an organic silver halide developer, an alkali sulfite, an alkali borate, boric anhydride, and a buffer compound selected from the group consisting of sodium and potassium hydroxide which has been coated with from 5 to 20% by weight of phthalic anhydride.

ARTHUR A. RASCH.
RICHARD W. HENN.
JOHN I. CRABTREE.

No references cited.