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SINGLE POWDER PHOTOGRAPHIC DEVELOPERS CONTAINING LITHIUM HYDROXIDE

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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 known as single-powder photographic developers, and the present invention more particularly relates to single powder developers containing lithium hydroxide monohydrate as an alkali component of the single powder developer.

For many years photographic developer powders have traditionally been packaged with the developing agents separated from the alkaline components to prevent interaction. More recently it has been disclosed that some developer mixtures may be protected by the addition of certain protectants so that the developing agents may be mixed directly with the other components of the developer and the resulting developer mixture can be packaged as a single powder developer.

Such single powder developers may contain, for example, an organic developing agent such as monomethyl p-aminophenol sulfate, hydroquinone, p-aminophenol hydrochloride, p-aminophenol sulfate, pyrogallol, p-hydroxyphenyl glycine, catechol, diaminophenol hydrochloride, and suitable mixtures thereof, stabie alkaline buffer salts such as sodium carbonate monohydrate, sodium metaborate tetrahydrate ($Na_2B_2O_4.4H_2O$) and sodium tetraborate pentahydrate ($Na_2B_4O_7.5H_2O$); and protectants such as boric anhydride, metaboric acid, phthalic anhydride and sodium or potassium bisulfites and metabisulfites and may also contain the other well known ingredients 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.

However, when employing sodium hydroxide in such protected single powder mixtures, the strongly hygroscopic nature of sodium hydroxide and the dampness of its surface has frequently been found to be the cause of discoloration even in the presence of the above named protectants. This is particularly serious since it is often desirable to add a strong alkali such as sodium hydroxide to a developer powder to give higher total alkalinity or to single powder mixtures to overcome the acidity introduced by the protectants.

It is, therefore, an object of this invention to provide single powder photographic mixtures containing a strong alkali which will not discolor the single powder.

Another object of this invention is to provide single powder developers containing lithium hydroxide from which developing solutions which are colorless, fully balanced and of a proper degree of activity can be prepared.

Another object of this invention is to provide a noncaking single powder developer containing lithium hydroxide monohydrate.

A further object of the invention is to provide a single powder photographic developer containing lithium hydroxide monohydrate and one or more protectant compounds to prevent interaction of the organic developing agents and the alkaline components and thereby prevent deterioration of the single powder developer.

Other objects will appear hereinafter.

In accordance with the present invention these and other objects are attained by preparing single powder developer compositions containing organic developer components, sulfite components and acidic protectant components with lithium hydroxide monohydrate having exactly 1 mole of water of crystallization. We have found that lithium hydroxide monohydrate is completely compatible with the other components usually employed in developers and although it is a strong alkali it is without harmful effect on developing properties.

Lithium hydroxide monohydrate is also compatible with alum hardening and fixing baths which may be used after development.

Furthermore while lithium hydroxide monohydrate is readily soluble in water yet it absorbs little moisture from the atmosphere. Since its surface is, therefore, relatively dry it is very suitable for admixture into single powder developers under normal conditions of temperature and humidity.

We have found that protectants which may be satisfactorily employed in single powder developers containing lithium hydroxide include boric anhydride, metaboric acid, phthalic anhydride, chlor phthalic anhydride, sodium and potassium bisulfites and metabisulfites. These protectants may be employed singularly and in various mixtures. Certain mixtures of the protectants have been found advantageous for use in single powder developers containing certain alkali components.

The following examples will serve further to illustrate single powder developer mixtures within the scope of the present 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 (N-monomethyl p-aminophenol sulfate)	2.2
Hydroquinone	8.8
Sodium sulfite	96.0
Sodium carbonate monohydrate	48.0
Potassium bromide	4.0
Lithium hydroxide monohydrate (57.1% lithium hydroxide, 42.9% water)	7.0
Boric anhydride	2.9

This example illustrates the uses of lithium hydroxide monohydrate in a single powder mixture as an addend to increase activity by increasing the alkalinity of the formula. This single powder mixture did not discolor or otherwise deteriorate when incubated at 120° F. for one week. However, powders containing lithium hydroxide monohydrate having slightly more than the theoretical amount of water of crystallization (56.2% lithium hydroxide, 43.8% water) or slightly less than the theoretical amount (58.0% lithium hydroxide, 42.0% water) did cause discoloration when stored under the same conditions. To insure maximum stability the lithium hydroxide having the optimum amount of water of crystallization was also employed in the following examples.

Example 2

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Sodium metaborate trihydrate, CO_2 treated	27.5
Potassium bromide	0.5
Lithium hydroxide monohydrate	3.0
Boric anhydride	1.9
Sodium metabisulfite	2.0

The use of lithium hydroxide in the formula did not affect the stability of the powders which remained free of discoloration on storage.

The sodium metaborate used in the above formula was prepared by drying the tetrahydrate form of the compound by heating it, after previously having treated it with carbon dioxide gas. This treatment increases the stability of the compound in that it inhibits the discoloration reaction that would normally occur if the tetrahydrate form were used.

Example 3

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Sodium metaborate tetrahydrate containing 10% boric anhydride	39.6
Potassium bromide	2.0
Lithium hydroxide monohydrate	6.0
Phthalic anhydride	2.0
Sodium metabisulfite	2.0

The use of lithium hydroxide in the formula did not affect the stability of the powders which remained free of discoloration on storage.

The sodium metaborate-boric anhydride blend was prepared by heating the mixture for 4 hours at 70° C. This treatment stabilizes the sodium metaborate in such a way as to make it suitable for use in single powder formulas.

Example 4

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Sodium metaborate tetrahydrate containing 10% metaboric acid	39.6
Potassium bromide	2.0
Lithium hydroxide monohydrate	5.5
Phthalic anhydride	2.0
Sodium metabisulfite	2.0

The sodium metaborate-metaboric acid blend was prepared by heating the mixture for 4 hours at 70° C. This treatment stabilizes the sodium metaborate in such a way as to make it suitable for use in single powder formulas.

This example and Examples 2 and 3 serve to illustrate the use of lithium hydroxide as an addend to single powder formulas to balance the acidic effect of the various combinations of compounds used to prevent discoloration and deterioration of the powders and thus to preserve the photographic properties of the formulas.

Example 5

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Anhydrous sodium tetraborate (finely ground)	14.7
Lithium hydroxide monohydrate	7.6
Potassium bromide	2.0
Boric anhydride	1.2

This example serves to illustrate the use of lithium hydroxide as an addend to a single powder formula to supplement the alkalinity of sodium tetraborate, without affecting the stability of the powders.

Example 6

	Grams
Hydroquinone	45.0
Sodium sulfite	90.0
Lithium hydroxide monohydrate	45.0
Potassium bromide	30.0
Boric anhydride	5.0

This example serves to illustrate the use of lithium hydroxide in substitution for sodium hydroxide in high energy formulas making it possible to pack the formula as a single powder.

Example 7

	Grams
Elon	2.0
Hydroquinone	4.0
Sodium sulfite	22.5
Sodium tetraborate pentahydrate	21.3
Lithium hydroxide monohydrate	7.9
Potassium bromide	2.0
Boric anhydride	1.2

This example serves to illustrate the use of lithium hydroxide as an addend to a single powder formula to supplement the alkalinity of sodium borate without affecting the stability of the powders. This formula also has the advantage of greater solubility over that given in Example 5 because of the greater ease of solution of the hydrated form of sodium borate as compared to the anhydrous form.

To make a developer solution, the compositions shown in the examples should be dissolved in water to make one liter of solution.

Samples of the mixtures as given in the foregoing examples have been found, even after the mixtures have been kept in tightly sealed bottles at 120° F. for prolonged periods to be unimpaired in developing properties, to be unchanged in color and to give a solution comparable in color to solutions prepared from such chemicals not previously mixed.

We have also found another, but more complicated, way to introduce sodium metaborate into single powder developer mixtures without the mixture decomposing. Sodium metaborate can be considered as the product of the reaction between sodium hydroxide and sodium tetraborate as follows:

$$2NaOH + Na_2B_4O_7 \rightarrow 2Na_2B_2O_4 + H_2O$$

By substituting LiOH for NaOH the resulting product is a mixture of sodium and lithium metaborate. Surprisingly enough, whereas mixtures of sodium borate and sodium hydroxide cause rapid deterioration if packed in single powder developer mixtures, the product of this lithium hydroxide-sodium borate reaction when added to a single powder developer causes no deterioration or discoloration of the developer.

The sodium-lithium metaborate can be prepared as follows: Lithium hydroxide was intimately mixed with sodium borate pentahydrate and with constant stirring, heated to about 100° C. After maintaining the temperature for a short time the resulting paste was cooled with constant stirring. The product formed was granular and free flowing. The ratio of lithium hydroxide to sodium borate pentahydrate can be varied from that of 2 moles to 1 mole. The resulting compounds will give a predetermined varying alkalinity. When these products are packed in single powder formulas containing protectant addends in a concentration of 1% no discoloration of the single powder developer occurs.

The following is an example of how to employ the sodium-lithium metaborate in single powder developers.

Example 8

58.2 grams (0.2 mole) of sodium borate pentahydrate was intimately mixed with 22.4 grams (0.53 mole) of lithium hydroxide monohydrate and the mixture heated,

with stirring, to 100° F. for 15 minutes. After cooling the resulting product was packed in the following single powder formula.

	Grams
Elon	2.5
Hydroquinone	2.5
Sodium sulfite	30.0
Prepared lithium-sodium-metaborate	6.9
Potassium bromide	0.5
Boric anhydride	0.4

No significant discoloration or deterioration of the powders occurred even after storage at 120° F. for 2 months.

Still another method of treating sodium metaborate so that it is compatible in single powder developer mixtures is to stabilize it by washing with a solution of an organic acid in an alcohol.

Sodium metaborate tetrahydrate can be suitably stabilized by washing in a 5% solution of citric acid in denatured ethyl alcohol so that it can be packed in a single powder developer containing a low concentration of boric anhydride as protectant. Without this treatment, protectant concentrations 5 to 10 times higher are necessary to obtain an equivalent protection against deterioration.

The preferred procedure of treatment requires that the sodium metaborate tetrahydrate be added to the acid-solvent solution in a ratio of 1000 grams of the metaborate compound to 1 liter of solution. The mixture is stirred thoroughly and the compound filtered off. The compound is then heated mildly to remove absorbed solvent. Best results are obtained when the solvent is anhydrous. It is necessary to remove nearly all of the absorbed solvent from the treated product to obtain maximum stability.

The choice of acid and solvent is not limited to any particular group. The basic requirements are that the acid be reasonably soluble in the solvent chosen and that the solvent does not excessively dissolve sodium metaborate tetrahydrate. There are, however, some combinations of acid and solvent that are much more effective than others.

Optimum results have been obtained with solutions of citric acid. Malic and tricarballylic acids have also given good results. Some degree of protective treatment has also been obtained using aconitic, glutaric, ortho-phthalic, and meso-tartaric acids. All of the above-mentioned acids were used in solutions of denatured ethyl alcohol. Excellent results were obtained using a solution of citric acid in anhydrous ethyl alcohol while solutions using methyl and isopropyl alcohols also gave good results.

The following example serves to illustrate this modification:

Example 9

Using sodium metaborate tetrahydrate treated with a solution of 5% citric, malic or tricarballylic acid in denatured ethyl alcohol the following single powder was prepared:

	Grams
Elon	2.5
Hydroquinone	2.5
Sodium sulfite	30.0
Acid-treated sodium metaborate tetrahydrate	7.4
Potassium bromide	0.5
Boric anhydride	0.4

The powder showed no objectionable discoloration after being stored for one week at 120° F.

The term developing agent in the claims is to be interpreted as comprising either one or several separate organic developer compounds.

We claim:

1. A stable single powder photographic developer composition containing a mixture of an organic silver halide developer, lithium hydroxide monohydrate and a stabilizing agent selected from the group consisting of boric anhydride, metaboric acid, phthalic anhydride, chlorphthalic anhydride, sodium bisulfite, potassium bisulfite, sodium metabisulfite and potassium metabisulfite.

2. A stable single powder photographic developer composition containing a mixture of an organic silver halide developer, sodium sulfite, sodium carbonate monohydrate, potassium bromide, boric anhydride and lithium hydroxide monohydrate.

3. A stable single powder photographic developer composition containing a mixture of an organic silver halide developer, sodium sulfite, sodium metaborate trihydrate, CO_2 treated, potassium bromide, boric anhydride, sodium metabisulfite and lithium hydroxide monohydrate.

4. A stable single powder photographic developer composition containing a mixture of an organic silver halide developer, sodium sulfite, sodium metaborate tetrahydrate containing 10% metaboric acid, potassium bromide, phthalic anhydride, sodium metabisulfite and lithium hydroxide monohydrate.

5. A stable single powder photographic developer composition containing a mixture of an organic silver halide developer, sodium sulfite, anhydrous sodium tetraborate, boric anhydride and lithium hydroxide monohydrate.

6. A stable single powder photographic developer composition containing a mixture of an organic silver halide developer, sodium sulfite, boric anhydride and lithium hydroxide monohydrate.

7. A stable single powder photographic developer composition containing a mixture of an organic silver halide developer, sodium sulfite, sodium borate pentahydrate, boric anhydride and lithium hydroxide monohydrate.

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