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SINGLE-POWDER PHOTOGRAPHIC DEVELOPERS

Frederic R. Bean, Rochester, N. Y., assignor to
Eastman Kodak Company, Rochester, N. Y., a
corporation of New Jersey

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This invention relates to single-powder photographic developers wherein all ingredients of the developer are intimately mixed together in dry powder form.

Such mixtures are in themselves known. Their preparation has heretofore centered around stabilizing the organic developer either by coprecipitating it with stabilizers or by preparing stable derivatives of it, which then break down into their active components when put into solution. While these preparations proved moderately successful, it has until now nevertheless not been possible to prepare single-powder photographic developers containing in intimate admixture, in dry powder form, both an organic developer and an alkaline constituent, such as an alkali carbonate, as under these conditions they would undergo decomposition reactions resulting in the destruction of the activity of the developer. Thus it was not possible to prepare such mixtures for storage or packaging; for such purposes the alkali ingredient and the organic developer always had to be carefully kept separate in different compartments or containers.

It is therefore an object of this invention to overcome the aforesaid difficulties by preparing single-powder photographic developers which will keep and remain stable.

A further object of this invention is to prepare stable single-powder photographic developer mixtures containing an organic developing agent, whereby the term "developing agent" is to be understood as comprising either one or several separate organic developer compounds, such as shown by examples given herein below.

It is still a further object of this invention to prepare single-powder photographic developers containing both an organic developing agent and a preferred type of alkaline or basic compound in the presence of, and intimate admixture with, the other ingredients, notably, a stabilizing component, which latter is to be understood as comprising either one or several separate stabilizing substances, as illustrated in examples given hereinafter. Other objects will appear from the following description of the invention.

In accordance with my invention, these and other objects are accomplished by selecting an inorganic and/or organic compound from a group of acidic substances possessing stabilizing properties, such as described hereinafter, and incorporating the selected compound or compounds in the proposed single-powder photographic developer mixture together with the other ingredients, among these being the organic developing agent and an alkaline component, the characteristics of the latter being that it be stable in itself under ordinary conditions of temperature, pressure and atmospheric humidity, that it be soluble and photographically compatible in the re-

sultant aqueous developer solution. The alkalinity of the basic substances used is within the range of the alkali borates, carbonates, and phosphates, and stabilization of them may be achieved with one or more of these stabilizing agents. The degree of stability attained has been found to vary directly with the quantity and type of stabilizer or stabilizer admixture and the type of basic substance employed with a given concentration of developing agent in such single-powder developer mixture.

In the following examples I have given several of the preferred embodiments of my invention, but it is to be understood that they are set forth for the purpose of illustration only and not in limitation thereof.

The stabilizing substances forming the object of the invention comprise both organic and inorganic solid compounds which, in order to be suitable as stabilizers, should preferably be relatively colorless, odorless, and stable; they should have no deleterious action photographically; they should be of an acidic nature and should, in addition, be readily adsorbable on the surfaces of the ingredients of the single-powder developer, especially on the surfaces of the alkaline ingredients, thereby tending to exert an antidiscolorant action. One may thus expect that the degree to which the foregoing characteristics are found combined in one substance or in a combination of them, to that same extent will that substance or combination of substances present stabilizing properties. Examples of such substances are the alkali metabisulfites, phthalic anhydride, maleic anhydride, benzoic anhydride, salicylic acid, o-benzoic sulfimide, and phthalimide. The presence of alkali metabisulfites in developer compositions is not new, where they have been employed thus far as preservatives, i. e. to lessen the rate of oxidation of the organic developing agent present (in the developer solution). But according to the present invention, it has been found that the alkali metabisulfites, particularly the potassium metabisulfite, will also act as a stabilizer in the single-powder developer mixture, i. e. it will prevent or inhibit reaction between the alkali component and the organic developing agent jointly present in admixture in the dry, single-powder developer mixture, particularly if the alkali be a stable alkali carbonate monohydrate, such as according to this invention.

Thus, a preferred embodiment of the invention involves the use, in the said single-powder photographic developer mixture, of either the stable hydrate of an alkali carbonate or also a desiccated alkali carbonate. Generally, the stable alkali carbonate hydrate, particularly the alkali carbonate monohydrate, is to be preferred, as experiments have shown it to be much more

stable in the presence of an organic developing agent than a comparable quantity of the corresponding desiccated alkali carbonate. In most instances the sodium carbonate monohydrate single-powder developers are more easily and completely stabilized than those developer compositions containing an anhydrous alkali carbonate.

The invention is broadly applicable to stabilization with an acidic substance of an organic developing agent, such as elon, hydroquinone, para-phenylene diamine sulfate, paraminophenol sulfate, glycin, metol, and others, in the presence of a soluble and stable basic substance of medium-to-mild alkalinity and photographic compatibility. Thus, phthalic anhydride has outstanding stabilizing properties in the presence of either sodium carbonate monohydrate, desiccated sodium carbonate, or borax. Other substances, such as maleic anhydride and salicylic acid are only mildly effective with sodium carbonate monohydrate. Alkali metabisulfite, benzoic anhydride, orthobenzoic sulfimide, and phthalimide, either singly or in admixture, are particularly effective as stabilizers with alkali carbonate monohydrates.

Potassium metabisulfite in conjunction with one of the organic stabilizers, preferably phthalic anhydride, has proved to be a very good stabilizer admixture, especially in an alkali carbonate monohydrate or in a desiccated alkali carbonate developer mixture, when used in the requisite quantity.

The ingredients of a preferred composition of such a single-powder photographic developer mixture may therefore consist of an organic developing agent, such as elon and/or hydroquinone; a stable alkali carbonate, such as sodium monohydrate; and a stabilizer, such as an alkali metabisulfite, preferably the potassium metabisulfite and/or phthalic anhydride, and may contain the other 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. These known components and their known functions in a photographic developer are not to be considered as forming part of this invention, nor is their mention herein to be construed as delimiting thereto the scope of the proposed single-powder developer mixtures.

In compounding the developer mixture, one may proceed by first mixing the stabilizer and the basic component, adding and admixing thereupon the developing agent, which is followed by the other ingredients. However, if so preferred, all ingredients may also be mixed simultaneously. In another method of preparing the mixture, the stabilizer is vaporized and in the vapor state is diffused into the powdered alkali, such as, for example, by the sublimation of phthalic anhydride onto the powder.

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 admixed to form such single-powder photographic developer mixture.

Example 1

	Grams
Elon	0.62
Hydroquinone	2.40
Sodium carbonate monohydrate	21.60
Potassium metabisulfite	11.1
Potassium bromide	0.33
Sodium sulfite, anhydrous	9.0

The quantity of developer represented by the foregoing formula can be directly dissolved in water to make 400 c. c. of developer solution ready for immediate use; it also can be made up into a stock solution of 200 c. c., which on use is to be diluted 1:1. A very large quantity or proportion of potassium metabisulfite is used in this example. Single-powder developers made up according to this example remained unchanged (no discoloration) after storing for more than 18 months as a dry powder.

Example 2

	Grams
Elon	6.2
Hydroquinone	24
Sodium carbonate monohydrate	165
Potassium metabisulfite	1
Potassium bromide	3.8
Sodium sulfite, anhydrous	78

The quantity of developer given by Example 2 is sufficient to prepare a developer stock solution of 2 liters, or 4 liters ready for immediate use.

Example 3

	Grams
Elon	0.62
Hydroquinone	2.4
Sodium carbonate monohydrate	16.0
Phthalic anhydride	0.5
Potassium bromide	0.38
Sodium sulfite, anhydrous	9.0

Example 4

	Grams
Elon	0.62
Hydroquinone	2.4
Sodium carbonate, desiccated	13.5
Phthalic anhydride	0.5
Potassium bromide	0.38
Sodium sulfite, anhydrous	9.0

Samples were also made up as according to Examples 3 and 4, in which the respective quantities of phthalic anhydride were 0.2 gram and 0.1 gram.

Example 5

	Grams
Elon	49.6
Hydroquinone	19.2
Sodium carbonate monohydrate	1320.0
Potassium metabisulfite	88.0
Phthalic anhydride	40.0
Potassium bromide	30.4
Sodium sulfite, anhydrous	624.0

Example 6

	Grams
Elon	49.6
Hydroquinone	19.2
Sodium carbonate, desiccated	1160.0
Potassium metabisulfite	88.0
Phthalic anhydride	20.0
Potassium bromide	30.4
Sodium sulfite, anhydrous	624.0

Some of these single-powder mixtures containing small amounts of stabilizers remain colorless for 2 to 6 months—and with a very large quantity

of stabilizer (Example 1) they remain colorless more than 18 months.

Example 7

	Grams	
Hydroquinone	2.0	5
Sodium sulfite, anhydrous.....	75.0	
Sodium carbonate, desiccated.....	50.0	
Potassium bromide.....	3.0	
Potassium metabisulfite.....	11.0	
Phthalic anhydride.....	3.0	10

Example 8

	Grams	
Hydroquinone	2.0	
Sodium sulfite, anhydrous.....	75.0	15
Sodium carbonate monohydrate.....	58.5	
Potassium bromide.....	3.0	
Potassium metabisulfite.....	11.0	
Phthalic anhydride.....	3.0	20

Example 9

	Grams	
Elon	8.0	
Sodium sulfite, anhydrous.....	400.0	
Hydroquinone	20.0	
Borax	50.0	25
Phthalic anhydride.....	10.0	

Example 10

	Grams	
Elon	0.62	30
Hydroquinone	2.4	
Sodium sulfite, anhydrous.....	9.0	
Na ₃ PO ₄ · H ₂ O	12.0	
KBr	0.38	
Phthalic anhydride.....	0.5	35

The quantity per volume of developer solution that can be prepared by the formulas of the foregoing examples depends upon the concentration of the developing agent in the developer mixture and upon its concentration as desired in the developer solution and the purposes for which it is to be used. Known developer formulas may serve as a guide in this matter. It can, however, be said that 500 grams of such single-powder photographic developer mixture will be sufficient to prepare approximately 3.5 liters of developer solution used for general developing purposes.

Under some circumstances it may be advantageous to add a wetting agent to the single-powder developer, in order to increase the speed of solution in water.

But the invention is not to be limited to these examples, as numerous other mixtures and equivalents can be made up, varying both quantitatively and qualitatively, while still retaining the desirable characteristics of a single-powder developer mixture, such as hereinbefore described.

It was also found that the potassium form of the metabisulfite is superior to the sodium metabisulfite as a stabilizing agent.

In special cases it is also possible to use sodium sesquicarbonate dihydrate in place of sodium carbonate monohydrate as an alkali in single-powder developers.

The developer powder may also contain an aldehyde-bisulfite, such as sodium formaldehyde bisulfite.

Single-powder photographic developer mixtures of the type described, by reason of the invention obviate the necessity of separately packaging first the developer portion containing the organic

developing agent proper, and then the other portion containing the alkaline component; thus, this otherwise intricate packaging operation is much simplified, resulting in a considerable saving of time, labor, and packaging material. The packaging is expedited, and less costly containers can be used with this single-powder developer mixture. Furthermore, the developer mixture thus prepared and packaged will be ready for instant use, requiring merely solution in a proportionate quantity of water.

What I claim is:

1. A single-powder photographic developer composition, substantially as described, containing an organic developing agent; a soluble, stable and photographically compatible basic ingredient selected from the group consisting of alkali borates, carbonates, sesquicarbonates, and phosphates; and phthalic anhydride.

2. A single-powder photographic developer composition, substantially as described, containing an organic developing agent; a soluble, stable, and photographically compatible basic ingredient selected from the group consisting of alkali borates, carbonates, sesquicarbonates, and phosphates; and an alkali metabisulfite and phthalic anhydride.

3. A single-powder photographic developer composition, substantially as described, containing an organic developing agent; sodium carbonate monohydrate; potassium metabisulfite; and phthalic anhydride.

4. A single-powder photographic developer composition, substantially as described, prepared by admixing an organic developing agent; sodium carbonate monohydrate; and phthalic anhydride.

5. A single-powder photographic developer composition, substantially as described, containing in intimate admixture, in the dry state, an organic developing agent, phthalic anhydride and trisodium phosphate monohydrate.

6. A single-powder photographic developer composition, substantially as described, containing in intimate admixture, in the dry state, an organic developing agent, phthalic anhydride, and borax (sodium tetraborate).

7. A single-powder photographic developer composition, substantially as described, containing in intimate admixture, in the dry state, an organic developing agent, an acidic stabilizing component including phthalic anhydride, and borax (sodium tetraborate).

8. A single-powder photographic developer composition, substantially as described, containing in intimate admixture, in the dry state, an organic developing agent, phthalic anhydride and an alkali carbonate monohydrate.

9. A single-powder photographic developer composition, substantially as described, containing in intimate admixture, in the dry state, an organic developing agent, phthalic anhydride and an alkali metabisulfite and an anhydrous alkali carbonate.

10. A single-powder photographic developer composition, substantially as described, containing in intimate admixture, in the dry state, an organic developing agent, an alkali metabisulfite, phthalic anhydride, and a compatible basic ingredient selected from anhydrous and hydrated compounds.

FREDERIC R. BEAN.