## UNITED STATES PATENT **OFFICE**

2,606,118

## STABILIZING AGENT FOR SINGLE POWDER PHOTOGRAPHIC DEVELOPERS

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No Drawing. Application February 9, 1951, Serial No. 210,284

11 Claims. (Cl. 95—88)

invention relates to single-powder photographic developers, and more particularly to a single-powder developer in which the ingredients of the developer are intimately mixed in the form of dry powder with powdered boric 5 anhydride, which contains free moisture not in excess of 15.0% by weight, as a stabilizing agent to prevent disadvantageous interaction between the organic developer component and the basic component of the single-powder mixture.

Single-powder developer mixtures may contain an organic developer component or mixtures of such components, including monomethylparaminophenol sulfate (elon or metol), hydroquinone, p-aminophenol hydrochloride, p-amino- 15 phenol sulfate, pyrogallol, parahydroxyphenyl glycine, catechol, diaminophenol hydrochloride, and others, with an alkali component, a stabilizing component, an oxidizing preventer and an may be the stable hydrate of an alkali carbonate, a desiccated alkali carbonate, an alkali metaborate, or an alkali sulfite. Generally the stable alkali carbonate monohydrate is preferred. The oxidation preventing component may be an 25 alkali sulfite, and the anti-fogging component may be potassium bromide or iodide. Stabilizing components for such a single-powder developer are disclosed in Patent 2,384,592 of September 11, 1945 and include maleic anhydride, salicylic 10 acid, alkali metabisulfite, benzoic anhydride, orthobenzoic sulfimide, phthalimide, and phthalic anhydride. The latter has outstanding stabilizing properties in the presence of either sodium carbonate or borax and has been employed con- 35 siderably more than the other stabilizers mentioned in the patent.

While the stabilizing effect of the phthalic anhydride is very good, it has been employed most successfully in developer compositions hav- 40 ing as the alkali component either sodium carbonate or sodium sulfite, or mixtures thereof. Less success has been attained in the case of the important class of developers containing sodium metaborate as the alkali ingredient. Also, the 45 presence of phthalic anhydride in the singlepowder developer involves other considerations which are not too desirable. In the first place, phthalic anhydride is slowly soluble in water. Furthermore, it is impossible to employ it in the 50 presence of benzotriazole, the latter being a desirable component of certain developer mixtures. But the greatest disadvantage of employing phthalic anhydride in single-powder developer mixtures, which contain alkali carbon- 55 hydrate appears to be more stable in the presence

ates and sulfite, is that phthalic anhydride may react due in part to temperature effects with these basic substances and form gas under sufficient pressure to distend the hermetically sealed can in which the developer powder is packaged, and often cause a portion of the powder to be ejected with some violence as the package is opened.

An object, therefore, of the present invention 10 is to provide an improved stabilizing agent for single-powder developers.

Another object of the invention is to provide an improved stabilizing agent for single-powder developers which does not possess the disadvantages caused by employing phthalic anhydride as the stabilizing agent.

A further object of the invention is to provide an improved stabilizing agent which makes possible the production of single-powder deanti-fogging component. The alkali component 20 velopers having improved stabilizing characteristics containing as the alkali ingredient, sodium metaborate.

In accordance with the invention these and other objects are attained by employing boric anhydride as the stabilizer instead of other previously known stabilizers in such single-powder developers which contain both organic developer components and basic components. The boric anhydride employed in accordance with my invention may contain free moisture up to 15.0% by weight and when the term boric anhydride is mentioned in this specification I mean boric anhydride with a moisture content within this

I have found that such boric anhydride eliminates the objectionable characteristics possessed by phthalic anhydride. It appears that boric anhydride being much less acid than phthalic anhydride does not react as easily or as violently as phthalic anhydride with alkali carbonates or alkali sulfites such as Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub>. In this respect it is noted that the pH of phthalic anhydride is about 2.4 while the pH of boric anhydride is about 5.4 at 3% concentrations. Boric anhydride is admirably suited as a stabilizer and has the characteristics required for a stabilizer. It is acidic, relatively colorless, odorless, and stable and has no deleterious action photographically.

A preferred embodiment of the present invention involves the use in the single-powder photographic developer mixture of either the stable hydrate of an alkali carbonate or also a desiccated alkali carbonate. The alkali carbonate

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of an organic developer than a comparable qu	uan	-	Example 5	
tity of the corresponding desiccated alkali bonate.	car	-		Gra
			Sodium sulfite	5
The ingredients of a preferred single-pow	vde	r	Soulum carbonate monohydroto	r
developer composition may therefore consis	t o	Í	5 Polassium bromide	
an organic developing agent, such as monome	thy	1	Boric annydride	
paraminophenol sulfate, hydroquinone, p-ami	mo.	-	Pyrogallol	
phenol hydrochloride, p-aminophenol sulf	.ate	,	Example 6	
pyrogallol, p-hydroxyphenyl glycine, cated	hoi			
diaminophenol hydrochloride, and suitable n	nix-	- 1	O Sodium sulfite	Gran
tures thereof, a stable alkali carbonate, such	j as	S	Sodium carbonate monohydrate	50
sodium carbonate monohydrate; and boric	an-	•	Potessium bromide	54
hydride, and may contain the other well kno	own	l	Potassium bromide	1
ingredients normally present in a developer, s	uch	ι	Boric anhydride	2
as sodium sulfite and potassium bromide,	the	; 1	Catechol	8
normal and known function of the alkali sul	lfite	•	Example 7	
being that of preservative, lessening the oxi	da-		The state of the s	Gran
tion in solution of the organic developing age	ent;		Sodium sulfite	E (
while the known function of notassium brom	ohir			OL
is that of a restrainer particularly inhibit	ing	٠.	Potassium bromide	29
log iormation in the development of the sil	lver	•	Boric anhydride	
image. These known components and th	ieir		p-Hydroxyphenyl glycine	2
known functions in a photographic developer	are		p 113 droxyphenyl glychie	8
not to be considered as forming part of this	in	•	Example 8	48.2.2.4
vention, nor is their mention herein to be co	111-			Gran
strued as limiting the scope of the propo	011-	2	Courain Buille	CITATI
single-powder developer mixtures.	sea		Douldin carbonate monohydrata	E 4
To compare diagrams.			Potassium promide	•
In compounding the developer mixture, of	one		Boric anhydride	l
may proceed by first mixing the stabilizer a	ınd		p-Aminophenol sulfate	
the basic component, adding and mixing the	re-	30	l control of the cont	· 7
with the developing agent, which is followed	bу		Example 9	
incorporating the other ingredients. Howev	er,			Gran
one can mix all the ingredients together at t	the		Sodium sulfite	50
same time.			Soulum carponate monohydroto	
The following examples will serve further	to	35	Polassium promide	
illustrate developer mixtures within the sco	pe	00	Doric amydride	0
of the invention and will also indicate the pr	ro-		p-Aminophenol hydrochloride	7
portionate quantities in which the respecti	ive			
components can be mixed together in a dry for	rm		Example 10	SING TAL
to make up such single-powder photograph	nic	40	Sodium sulfite	Gram
developer mixtures.		40	Sodium content	75
			Sodium carbonate monohydrate	30
Example 1			Potassium iodideBoric anhydride	0
Gran	ns		Boric anhydride Hydroguinone	2.2
Elon (monomethyl p-aminophenol sulfate)	3.1		Hydroquinone	9
Anhydrous sodium sulfite45	5.0	45	EIOU	1
lydroquinone12	2.0		Example 11	· · · · · · · · · · · · · · · · · · ·
Sodium carbonate monohydrate 81	1.3		· · · · · · · · · · · · · · · · · · ·	
otassium bromide	0.1		Elon	Gram
Boric anhydride4	1.2			
		50	Sodium metaborate	100.0
Example 2			Boric anhydride	20.0
Gran	ns			
ion1	. 5		Example 12	
unyarous sodium sulfite 22	.5		ElonSodium sulfite decisested	Grame
yaroquinone6	.3	55	EION	7
nhydrous sodium sulfite 22  (ydroquinone 6  odium carbonate, desiccated 15	.0 '			
otassium bromide 1 oric anhydride 1	.5		Boric anhydride	1 1
oric anhydride 1	.0		Transport of the	1.1
			Example 13	Tigyv sta
Example 3		20	Sodium sulfite	Grams
Gram	ıs (	30	Sodium carbonete	96
nhadaaa - di	.2		Sodium carbonate monohydrate	56
lon 2, nhydrous sodium suifite 96.	.0		Potassium bromide Boric anhydride Hydroquinone	5 ×
3 di oddinone	0		Hydroduinone	1.7
odium carbonate monohydrate 57	.5		HydroquinoneElon	8.8
otassium bromide	n 6	55	Elon	2.2
Orio onbridaido	4			_ <del></del> -
oric amyurue 3.			Example 14	er er er er er er er er kan bladen
			Diaminonhenol bergan	Grams
Example 4			Diaminophenol hydrochloride Sodium sulfite Potassium bromide	34.6
Example 4	S			
lon	5 7			
Example 4  don Gram 2. nhydrous sodium sulfite 200	5 7	0		
Example 4  don Gram  hlydrous sodium sulfite 30, ydroquinone	5 7 0	0		
Example 4  Ion Gram  Inhydrous sodium sulfite 30, ydroquinone 2, odium metaborate 10	5 7 0 5	0	Boric anhydride	3.2 2.9
Example 4 Gram ton	5 7 0 5	0		3.2 2.9

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Samples of the mixtures as given in the examples have been found, even after the mixtures have been kept in hermetically sealed cans at 120° F. for prolonged periods, to be unimpaired in developing properties and to give a solution comparable in color to solutions prepared from such chemicals not previously mixed. No expansion of the package in which the compositions were stored was noted as contrasted to the developers similar in composition except that phthalic anhydride replaces the boric anhydride of the present invention. The term developing agent in the claims is to be interpreted as comprising either one or several separate organic developer compounds.

What I claim and desire to secure by Letters

Patent of the United States is:

1. A stable single-powder photographic developer composition containing an organic silver halide developer, a stabilizing agent, comprising 20 boric anhydride having free moisture content not exceeding approximately 15.0% by weight and a soluble, stable, and photographically compatible basic ingredient selected from the group consisting of alkali borates, sulfites and carbonates.

2. A stable single-powder photographic developer composition containing an organic silver halide developer, sodium carbonate monohydrate, and boric anhydride containing less than 15.0%

free moisture.

3. A stable single-powder photographic developer containing an organic silver halide developer, alkali carbonate, an alkali sulfite and boric anhydride containing less than 15.0% by weight of free moisture.

4. A stable single-powder photographic developer containing an organic silver halide developer, an anhydrous alkali carbonate, an alkali sulfite and boric anhydride containing less than

15.0% by weight of free moisture.

5. A stable single-powder photographic developer composition, containing an organic silver halide developer, desiccated sodium sulfite and boric anhydride containing less than 15.0% by weight of free moisture.

6. A stable single-powder photographic developer composition containing an organic silver

halide developer, sodium sulfite, sodium metaborate, and boric anhydride containing less than 15.0% by weight of free moisture.

7. A stable single-powder photographic developer composition consisting of approximately 50 grams sodium sulfite, 54 grams sodium carbonate monohydrate, 1 gram potassium bromide, 1.1 grams boric anhydride containing less than 15.0% by weight of free moisture and 8.4 grams p-hydroxyphenyl glycine.

8. A stable single-powder photographic developer composition consisting of approximately 50 grams sodium sulfite, 54 grams sodium carbonate monohydrate, 1 gram potassium bromide, 1.1 grams boric anhydride containing less than 15.0% by weight of free moisture and 7.3 grams p-

aminophenol sulfate.

9. A stable single-powder photographic developer composition consisting of approximately 50 grams sodium sulfite, 54 grams sodium carbonate monohydrate, 1 gram potassium bromide, 1.1 grams boric anhydride containing less than 15.0% by weight of free moisture and 7.3 grams paminophenol hydrochloride.

10. A stable single-powder photographic developer composition consisting of approximately 3.1 grams monomethyl p-aminosulfate, 12 grams hydroquinone, 45 grams anhydrous sodium sulfite, 81 grams sodium carbonate monohydrate, 1.9 grams potassium bromide, and 4.2 grams boric anhydride containing less than 15.0% by weight of free moisture.

11. A stable single-powder photographic developer composition consisting of approximately
59 grams sodium sulfite, 3.2 grams potassium bromide, 34.6 grams diaminophenol hydrochloride and 2.9 grams boric anhydride containing less than 15.0% by weight of free moisture.

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## REFERENCES CITED

The following references are of record in the file of this patent:

## UNITED STATES PATENTS

Number	Name	Date
2,384,592	Bean	. Sept. 11, 1945