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STABLE COMPOSITIONS USEFUL IN THE COMPOUNDING OF PHOTOGRAPHIC DE-VELOPERS

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8 Claims. (Cl. 95—88)

This invention relates to photographic developers and more particularly to compositions in dry form which are adapted for addition to solutions of photographic developing agents to provide therein a suitable source of formaldehyde.

This application is in part a continuation of my co-pending application Serial No. 724,221,

filed May 5, 1934.

As is known, formaldehyde may be added to a developer with two objects in view: (a) To harden the gelatin, and (b) to generate alkali as a result of interaction with sodium sulfite according to the following equation:

CH2O+N82SO3+H2O=NaOH+NaHSO3CHOH

It is possible, therefore, to prepare package developers having a high degree of activity without the use of caustic soda.

Developing solutions containing formaldehyde and sodium sulfite possess the disadvantage that they are easily oxidized because some of the sulfite tends to form formaldehyde-bisulfite. Furthermore, such developers have the additional drawback that when they are allowed to stand in closed containers polymerization of the formaldehyde occurs and the polymer, either does not react at all with sodium sulfite, or it reacts so slowly that the normal course of the re-

action to produce alkali is not followed. In order to avoid the above reactions, namely, oxidation and polymerization, it has been proposed to separate the formaldehyde from the developing agent-sulfite solution by making up two separate solutions, one containing the formaldehyde and the other containing the developing agent per se, and the second solution added to the developer as desired. When a formalin solution, that is, a solution in which formaldehyde gas is dissolved in water, is employed, this is ordinarily sufficiently stable and no polymerization and no loss of formaldehyde due to polymerization occur. When, however, a solid polymer of formaldehyde such as paraformas aldehyde or trioxymethylene, as it is sometimes called, is employed in place of formalin, it is difficult to get the solid into solution. Consequently, it is necessary to add an alkali, for example, sodium sulfite, in order to cause the paraformaldehyde to go into solution. However, as indicated above, available formaldehyde tends

the presence of alkali.
This invention has as an object to obviate the

to undergo a loss by formation of an insoluble

polymer, such reactions taking place readily in

above-mentioned difficulties involved in the use of paraformaldehyde as a source of alkali in a developing bath. A further object is to provide a means whereby a solid polymer of formaldehyde, such as paraformaldehyde, may be em- a ployed in aqueous solution in connection with sodium sulfite without the resulting formaldehyde undergoing polymerization and thus decreasing the source of formaldehyde in the solution. Another and specific object is to provide in crystal- an line or powder form a composition which, when dissolved in water, will provide an appropriate source of formaldehyde for addition to a solution containing a photographic developing agent and sodium sulfite. A further specific object is 1% to provide a two-package photographic developer which may be sold in dry form and adapted for the making up of two stock solutions and the preparation of the developing bath itself. Other objects will appear hereinafter.

These objects are accomplished by the following invention, which, in its broader aspects, comprises the discovery that a composition in dry powder form possessing the ability to be dissolved in water to produce a stable formaldehyde stock 25 solution may be compounded by mixing in appropriate proportions paraformaldehyde sodium sulfite and a solid acid such as boric, glutamic, phenylacetic, citric, tartaric, malic acids or a buffering salt such as the alkali metabisulfites. An the alkali bisulfites, the alkali borates, metaborates, mono- and di-sodium phosphate, and the like. Ammonium salts such as ammonium chloride are also suitable neutralizing salts in the presence of the formaldehyde. I have found as that such dry powdered compositions are stable, readily handled, and when simply dissolved in water in appropriate proportions, provide a highly satisfactory and stable formaldehyde stock solution which is not subject to loss of formaldehyde an by polymerization.

Also included within the broad scope of my invention is the provision of a two-package developer in dry form, one package containing the ingredients essential for the provision of the above-mentioned stable formaldehyde stock solution and the other containing the ingredients necessary for the provision of the developer stock solution itself.

In the following examples and description I 50 have set forth several of the preferred embodiments of my invention, but it is to be understood that they are included merely for purposes of illustration and not as a limitation thereof.

As indicated above, the paraformaldehyde of

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alkali by a suitable acid or buffer salt after the paraformaldehyde has been placed in southout. From the solution by the straight neutralization reaction of the solution by a straight neutralization reaction of the solution by a straight neutralization reaction of the solution by a straight neutralization reaction of the bath. In general, I prefer that the plf is the definite pit depending upon the composition of the bath. In general, I prefer that you have the solution below 11 and this the plf is the desired value. It is also desirable that the total concentration of alkali in the solution be as low as possible. While no definite low the plf is the desired value. It is also desirable that the total concentration of alkali in the solution be as low as possible. While no definite low the parameters of the solution can be set, this may be easy for the solution can be set, this may be as of or the solution of the formal saltery of the preferred range being from 3 to 10 where, the preferred range of the solution and/or the developer put 20 st. Insagench as these compositions are provided composition which may be employed as the source of the developing agent. These two compositions being the source of the formal special parts of the production and the source of the developing agent. These two compositions being the solution solutions of the formal special parts of the solution and the solution an		5	commerce is insoluble in water, but readily soluble in solutions of alkalis and solutions of sodium sulfite. The main difficulty, however, has been that the excess alkali required to get the paraformaldehyde into solution results in the above-mentioned polymerization. The present invention is based upon the concept of neutralizing the		Nater (about 125° F.) (52° C.)liters_ Sodium sulfite, desiccatedgrams_ Hydroquinonedo Potassium bromidedo Cold water to makeliters_ Example 4	_ 120.0 _ 90.0 _ 6.3) }
asits such as those indicated above. The solution of the stock stock that the stock of the composition of the bath. In general, I prefer to keep the pit of the solution below It and this pure to keep the pit of the solution below It and this pure to the composition of the bath. In general, I prefer to keep the pit of the solution below It and this pure to the pit at the desired while the state and the pure that the total concentration of aliast in desirable that the total concentration of aliast in the production of the formal aliast the same of the developing parts. These two compositions are producted as one of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per se bands the source of the developing agent per		10	alkall by a suitable acid or buffer salt after the paraformaldehyde has been placed in solution. Thus, the excess alkali may be removed from the solution by a straight neutralization reac-	E	Paraformaldehydegrams_ Sodium sulfite (desiccated)dododododo	_ 20)
and water at a definite pH depending upon the composition of the bath. In general, I prefer to keep the pH of the solution below 11 and this may be accomplished by employing the acid or buffer salt in an amount sufficient to maintain the pH at the desired value. It is also dosirable that the total concentration of allral in the soft-distriction to the pH at the desired value. It is also dosirable that the total concentration of allral in the soft-distriction and the soft-distriction and the soft-distriction and the soft-distriction suitable for the production of the formal selection and/or the developer per sidence such as these compositions are provided as one of the components of a two-package combination for making up a developing path, the examples also include references to a typical composition as the composition and the accomposition which may be employed as the source of the developing agent. These two compositions are sufficiently only to indicate the appropriate of the developing agent. These two compositions are provided as composition as a temployed as the source of the developing agent. These two compositions are provided as composition as a temployed as the source of the developing agent. These two compositions are provided as composition as a temployed as the source of the developing agent. These two compositions are provided as a composition as a temployed as the source of the developing agent. These two compositions are provided as a composition and the source of the developing agent. These two compositions are provided as a composition and the source of the developing agent. There two compositions are provided as a composition and the source of the developing agent. There two compositions are formal to the source of the developing agent. There two compositions are formal to the source of the developing agent. There two compositions are formal to the source of the developing agent. There two compositions are formal to the source of the developing agent. There two compositions are formal to the		18	of di- or tri-basic acids or suitable buffering salts such as those indicated above. The solu-	44	. Sodium sulfite (desiccated)grams Hydroquinonedo	- 100 90	
Day be accomplished by employing the acid or 20 buffer sait in an amount sufficient to maintain the pf at the desired value. It is also desirable that the total concentration of alkelf in the solution be as low as possible. While no definite low 22 be as log of the solution can be set, this may 23 be as log of the conjung examples illustrated dry compatitions suitable for the production of the formal adversariation of the formal adversariation of the formal action of the formal action for making up a develocing bath, the composition which may be employed as the pour composition of the developing agent per se and the E composition, the A composition and the B composition, the A composition and the B composition of the developing agent per se and the E composition which may be employed as the pour composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing agent per se and the E composition of the developing		4,	and water at a definite pH depending upon the composition of the bath. In general, I prefer		Water (about 125° F.) to makeliters	- 0.5 - 3	
the pFi at the desired value. It is also desirable that the total concentration of alkel in the solution be as low as possible. While no definite low limit of pH of the colution can be set, this may be as low as two or three, the preferred range being from 3 to 15. The following examples illustrate dry compositions suitable for the production of the formal common the composition are provided as the composition which may be employed as a composition of the developing agent. These two summer of the developing agent per se and the B composition the A composition and per source of the developing agent per se and the B composition the A composition and per source of the developing agent per se and the B composition that the reference of the developing agent per se and the B composition that the reference of the developing agent per se and the B composition in the composition and per source of the developing agent per se and the B composition that the reference of the developing agent per se and the B composition in the composition and per source of the developing agent per se and the B composition in the composition and per source of the developing agent per se and the B composition in the composition and per source of the developing agent per se and the B composition and per source of the developing agent per se and the B composition and per source of the developing agent per se and the B composition and per source of the developing agent per se and the B composition and per source of the developing agent per se and the B composition and per source of		00	may be accomplished by employing the acid or		Paraformaldehydegrams_	. 30	
limit of ph of the solution can be set, this may be as low as two or three, the preferred renge being from 3 to 11. The following examples illustrate dry compositions suitable for the production of the formatidehyde stock solution and/or the developer per stock as the composition are provided as one of the components of a two-package combatation, for making up a developing bath, the composition that has composition as the source 35 of the developing search, These two compositions and the source of the developing search per provided as composition, the composition and the source of the developing search per send the 5 composition, the following compositions the formal dehyde. To will of course be understood that the reference to the advantage to the developing search per send the 5 composition being the source of the developing search per send the 5 composition the first the formal dehyde. To will of course be understood that the reference to the advantage to the following compositions the formal dehyde. To will of course be understood that the reference to the amounts of water (about 125° F) to make. liters. Defence to the amounts of water the solided to any of the following compositions the formal dehyde. To water (about 100° F) to make liters. Defence to the amounts of water the formal dehyde. To solid compositions and the f		20	the pri at the desired value. It is also desirable that the total concentration of alkali in the solu-		Water (about 100° F.) to makeliter	. 1	20
The following enamples illustrate dry compositions suitable for the production of the formal adehyde stock solution and/or the developer per 30 se. Insignate has these compositions are provided as one of the components of a two-peakage combination for making up a developing bath, the examples also include references to a typical composition which may be employed as the source of the developing agent. These two compositions may be referred to as the A composition heing the source of the developing agent. These two compositions may be referred to as the A composition being the source of the formal dehyde. The source of the developing agent ber se and the 3 composition being the source of the formal dehyde. The following compositions is included stamply in indicate the appropriate manner of making up the solutions desired in actual practice. The solid compositions comprising various B mixtures. Example 1 Example 1 Example 1 Example 1 Example 2 Example 2 Example 2 Example 2 Example 3 Example 5 Example 6 Example 1 Example 6 Example 1 Example 1 Example 1 Example 1 Example 2 Example 6 Example 6 Example 6 Example 6 Example 1 Example 3 Example 6 Example 6 Example 6 Example 1 Example 6 Example 1 Example 6 Example 6 Example 6 Example 1 Example 6 Example 1 Example 1 Example 1 Example 2 Example 6 Example 1 Example 1 Example 1 Example 3 Example 6 Example 7 Example 7 Example 7 Example 7 Example 8 Example 8 Example 8 Example 8 Example 8 Example 8 Example 9 Example 9 Example 9 Example 9 Example 9 Example 9 Example		25	tion be as low as possible. While no definite low limit of pH of the solution can be set this may	· Æ	Mydroquinonedo	- 90	
Social composition and/or the developer per section of the components of a two-package combination for making up a developing bath, the examples also include references to a typical composition which may be employed as the source of the developing agent. These two compositions are provided to make the composition which may be employed as the source of the developing agent per se and the B composition. The A composition being the source of the developing agent per se and the B composition being the source of the formaldehyde.			The following examples illustrate dry compo-	,	Potassium bromidedo	6.3	25
bination for making up a developing bath, the examples also include references to a typical composition which may be employed as the source of the developing agent. These two compositions may be referred to as the A composition and the B composition, the A composition being the source of the developing agent per and the B composition being the source of the developing agent per and the B composition being the source of the formaldehyde. It will of course be understood that the reference to the amounts of waker to be added to any of the following compositions is included simply to indicate the appropriate manner of making up the solutions desired in actual practice. The solid compositions comprising verious B mixtures. Example 1 Example 1 Example 1 Example 1 Example 2 B. Paraformaldehyde (trioxymethylene) Sodium sulfifte (desiccated) — grams 1 potassium bromide — do 6.3 Cold water to make — liters 2.0 Water (about 100° F.) to make — liters 2.0 Water (about 100° F.) to make — liters 2.0 Water (about 100° F.) to make — liters 2.0 Sodium sulfifte, desiccated — grams 30 Sodium sulfifte (desiccated — grams 30 Sodium sulfifte (desic		o.	aidenyde stock solution and/or the developer ner		·-		
Water (about 100° F.) to make. liter: 1 Sodium sulfite (desiccated) Grams 30 Sodium sulfite (desiccat	: .	3 ₩	as one of the components of a two-package combination for making up a developing bath the		Sodium sulfite (desiccated)do	42 52	
### Be referred to as the A composition and the B composition being the A composition the source of the developing agent per se and the B composition being the source of the formaldehyde. #### Twill of course be understood that the reference to the amounts of water to be added to any of the following compositions is included simply to indicate the appropriate manner of making up the solutions desired in actual practice. The present invention, however, relates only to the solid compositions comprising various B mixtures. ###################################		35	examples also include references to a typical composition which may be employed as the source		Water (about 100° F.) to makeliter	1	
Revert Columboshion being the source of the formaldehyde Reverted Rev		•	may be referred to as the A composition and the B composition, the A composition being the source of the developing agent per se and the B		Potassium bromidedodo	90 6.3	35
Solium sulfite (desiccated) Go. 20		40	It will of course be understood that the reference to the amounts of water to be added to any		Example 7		40
### Solid compositions comprising various B mixtures Example 1			of the following compositions is included simply to indicate the appropriate manner of making up the solutions desired in actual practice. The	;	Boric acid (crystals)do	20 7.5	
E. Paraformaldehyde (trioxymethylene) Sodium sulfite (desiccated) grams 30 Sodium sulfite (desiccated) grams 10.5 Sodium sulfite desiccated grams 10.5 Sodium sulfite desiccate		45	present invention, however, relates only to the solid compositions comprising various B mixtures.	440	Water (about 125° F.) (52° C.)liters Sodium sulfite, desiccatedgrams	2.0	45
Sodium sulfite (desiccated)					watering qo	0.0 n	
Water (about 100° F.) to make_liter 1		50	Sodium sulfite (desiccated)gram 1		Cold water to makeliters	_	50
Boric acid		55	Water (about 100° F.) to makeliter 1 A. Water (about 125° F.) (52° C.)liters 2 C		Paraformaldehydegrams Sodium sulfite (desc.)do Malic acid (crystals) do	24 12.7	R.E.
Potassium bromide			Boric aciddo30.0 Hydroquinonedogo o	A.	Water (about 100° F.) to makeliter Water	1 2 0	
B. Paraformaldehydegrams		60	Potassium bromidedo6.3 Cold water to makeliters 3.0		Hydroquinonedodo_	30.0	60
Sodium sulfite (disc.)gram 1 Sodium bisulfite (cryst.)grams_ 9.4 Water (about 100° F.) to make_liter_ 1 A. Same composition as A component of Example 1. Example 3 B. Paraformaldehydegrams_ 30 Sodium carbonate (desiccated)do 10 Sodium bicarbonatedo 40 Water (about 100° F.) to make_liter_ 1 Example 9 B. Paraformaldehydegrams_ 30 Sodium sulfite (desc.)do 11.9 Sodium sulfite (desc.)do 11.9 Sodium hydrogen malate (cryst.) _do 14.8 Water (about 100° F.) to make_liter_ 1 A. Water (about 125° F.) (52° C.) _liters_ 2.0 70 Sodium sulfite, desiccatedgrams_ 120.0 Boric acid do 30.0 Hydroquinonedo 30.0 Potassium bromidedo 6.3 Water (about 100° F.) to make_liter_ 1 Cold water to makedo 6.3			P Poroformoldoberdo	•			
A. Same composition as A component of Example 1.			Sodium sulfite (disc.)gram_1 Sodium bisulfite (cryst.)grams 9.4	B.	Paraformaldehydegrams	30	65
## The image is a second content of the image is a second content			A. Same composition as A component of Example		Sodium sulfite (desc.)doSodium hydrogen malate (cryst.)_do	11.9 14.8	
Sodium carbonate (desiccated)do 10 Hydroquinonedo 90.0 Sodium bicarbonatedo 40 Potassium bromidedo 6.3 Water (about 100° F.) to make_liter 1 Cold water to makedo 6.3			Example 3	A.	Water (about 125° F.) (52° C.) liters	20	70
Sodium blcarbonatedo40 Potassium bromidedo 6.3 Water (about 100° F.) to make_liter 1 Cold water to make_			B. Paraformaldehydegrams 30 Sodium carbonate (desiccated) do 10		Boric aciddo	30 O	•
Coiq water to makeliters 3.0 75		75	Sodium bicarbonatedododo		Potassium bromidedodo	63	
					Cold water to makeliters	3.0	75

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	,	Example 10		Example 16
\mathbf{B}	. ;	· ·	11.9	B. Sodium sulfitegrams 10.0
		Paraformaldehydedodo		Paraformaldehydedo30.0
5	•	Ammonium chloride crystdo Water to makeliter	อ 1	Arsenic trioxidedo9.3 g Water 100° F. to makeliter 1
				A. Water (about 125° F.) (52° C.)liters 2.0
A		Sodium sulfitegrams Hydroquinonedodo	120 90	Sodium sulfite, desiccatedgrams 120.0
		Boric acid crystdodo	_	Boric aciddodo 30.0
0	-,	Potassium bromidedodo	6.3	Hydroquinonedo 90.0 10
		Water to makeliters	3	Potassium bromidedo6.3 Cold water to makeliters 3.0
		Example 11		In employing the above solutions, one part of
B		Sodium sulfitegrams	11.9	solution B is added to three parts of solution A 15
5		Paraformaldehydedodo	35.0	to make up the developing bath.
		Tartaric acid $(\frac{1}{4}-\frac{1}{2})$ crysts)do Water 100° F. to makeliter	1.5	In general, a solid acid salt or acid having a
		Sodium sulfitegrams	140	relatively large particle size should be employed in compounding the dry composition in accord-
A		Hydroquinonedodo	90	ance with the present invention, since the rate of 20
0	-	Boric aciddodo	30	solution of the acid salt or acid should not be
		Potassium bromidedo	6.3	in excess of the rate of solution of the paraform-
		Water to makeliters	3	aldehyde and sodium sulfite. If it is desired to use a solid acid in a relatively fine state of sub-
		Example 12		division or small particle-size, agglomeration of 25
B E	3.	Sodium sulfitegrams	3.5	the acid with suitable inert binder may be desir-
		Paraformaldehydedodo Disodium hydrogen phosphate	อบ.บ	able in order to reduce its rate of solution below
		Na ₂ HPO ₄ .12H ₂ Ododo	20.0	that of the paraformaldehyde. As indicated above, the entire mixture of in-
· .		Water 100° F. to makeliter	1	gredients of the dry composition can be added to 30
AU A	١.	Water (about 125° F.) (52° C.)liters Sodium sulfite, desiccatedgrams	$2.0 \\ 120.0$	water and dissolved completely within a few
		Boric aciddosiccaseddo		minutes. Many variations of the formula are possible within the scope of my invention. For
		Hydroquinonedodo	90.0	example, alkali bi-sulfites may be substituted by
e de la composition della comp		Potassium bromidedodo	6.3 3.0	the alkali metabisulfite and other acid salts or 85
15		Cold water to makeliters	J.U	acids may be substituted for the metabisulfite. The alkali sulfite may likewise be replaced with
		Example 13	4 4 ^	an alkali carbonate or other soluble alkaline salt
I	3.	Sodium sulfitegrams	11.9 30.0	if proper provision is made for neutralizing or
		Paraformaldehydedodo Sodium dihydrogen phosphate	J.J.	decreasing the alkalinity of the solution by use of
10		(large crystal aggregates 1/8-1/4")		an acid or buffer salt as herein set forth. 40 Various fog-restraining or inhibiting sub-
		NaHaPO4.HaOgrams	13.0	stances may be added to either of the dry com-
		Water 100° F. to makeliter		positions, such as phenosafranine, Pinakryptol
1	A.	Water (about 125° F.) (52° C.)liters	2.0 120 0	Green, arsenious oxide, or the alkali salts of arsenious acid such as sodium arsenite, potassium 45
45		Soulim sumte, desicuateddodo	30.0	ferrocyanide or other alkali ferrocyanides and
		Hydroquinonedodo	90.0	others. In the case of phenosafranine, varying
		Potassium bromidedo		amounts may be used, but a suitable restraining
g., -		Cold water to makeliters	3.0	action is obtained when about one part in 150,000 parts of the mixed developer is used 50
5 0		Example 14	11.9	When using arsenious oxide, sodium arsenite or
•	Β.	Sodium sulfitegrams Paraformaldehydedodo		similar compounds, two grams per liter give rep-
		Phenyl acetic acid (large plate crystals)		resentative and satisfactory results. The present invention has many advantages,
Ei im		grams	12.9	the chief of which is the fact that it is possible 55
65		Water 100° F. to makeliter		to provide a two-package developer in dry form
	A	. Water (about 125° F.) (52° C.)liters	2.0 120.0	TAM IN TEROTE SHOO TO COMMENT OF COMENT OF COMMENT OF C
		Sodium sulfite, desiccatedgrams Boric aciddodo	30.0	formaldehyde is provided with a means of sta- bilizing the formaldehyde when dissolved to make
മര		Hydroquinonedodo		_
60		Potassium bromidedodo	6.3	enabled to purchase the dry material in a form
÷		Cold water to makeliters	3.0	in which it does not deteriorate, either in the package or in the stock solution when made up.
-		Example 15		It is to be understood that the solid composi-
65	B	. Sodium sulfitegrams	13.7	tions of my invention constitute an entirely dis- 65
ver		Paraformaldehydedbdb	. 30.0	
		d-Glutamic acid (18-1/8" cryst. aggregates)grams		tions resulting from dissolving these materials in water. In other words, whereas the dry mix-
		Water 100° F. to makeliter	_	ture contains certain specific chemicals, many of
70	A	. Water (about 125° F.) (52° C.)liters		these more or less completely lose their identity 70
, 0	43	Sodium sulfite, desiccatedgrams	. 120.0	in solution. As is well known, photographic solu-
		Boric aciddodo	~~ ^	
		Hydroquinonedododododo		
75		Cold water to makeliters_	_	
للم م			- 1	

Another distinguishing feature of the solid compositions herein described is that they constitute a specifically balanced mixture of ingredients which will go into solution in water in the proper order. In other words, in accordance with my invention, the solid acid or buffering salt must be of such nature and particle or crystal size that its rate of solution is less than the other constituents in order that the alkalinity of the solution be maintained at a sufficiently high value to dissolve the paraformaldehyde.

What I claim is:

1. A composition in solid form adapted to dissolve in water for the purpose of providing in solution a suitable source of formaldehyde for addition to a solution containing a developing agent and sodium sulfite to prepare a photographic developing bath, said composition comprising paraformaldehyde, an alkaline salt, and a solid agent adapted to act as a neutralizing or buffering agent.

2. A composition in solid form adapted to dissolve in water for the purpose of providing in solution a suitable source of formaldehyde for addition to a solution containing a developing agent and sodium sulfite to prepare a photographic developing bath, said composition comprising paraformaldehyde, sodium sulfite, and a solid agent adapted to act as a neutralizing or buffering agent.

3. A composition in solid form adapted to dissolve in water for the purpose of providing in solution a suitable source of formaldehyde for

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addition to a solution containing a developing agent and sodium sulfite to prepare a developing bath, said composition comprising paraformaldehyde, an alkaline salt, and a solid agent adapted to dissolve more slowly than the other 5 constituents and act as a neutralizing or buffering agent.

4. A composition in solid form adapted to dissolve in water for the purpose of providing in solution a suitable source of formaldehyde for 10 addition to a solution containing a developing agent and sodium sulfite to prepare a developing bath, said composition comprising paraformaldehyde, sodium sulfite, and a solid agent adapted to dissolve more slowly than the other constituents and act as a neutralizing or buffering agent.

5. The product of claim 1 in which the agent is a solid acid.

6. The product of claim 1 in which the solid 20 agent is selected from the group consisting of boric, glutamic, phenyl acetic, citric, tartaric, or malic acids.

7. The product of claim 1 in which the solid agent is a salt selected from the group consisting of the alkali metabisulfites, the alkali borates, alkali metaborates, and the mono- and di-sodium phosphates.

8. The product of claim 1 in which the solid agent is an ammonium salt which, in the presence of excess formaldehyde, gives rise to acid.

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