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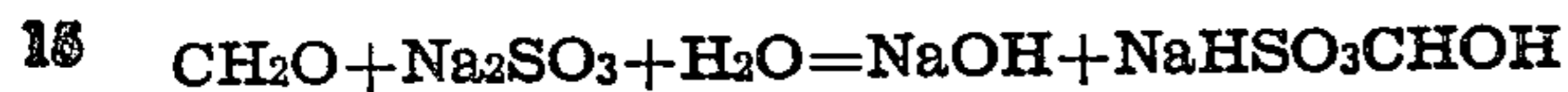
STABLE COMPOSITIONS USEFUL IN THE  
COMPOUNDING OF PHOTOGRAPHIC DE-  
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8 Claims. (Cl. 95—88)

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:



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 reaction 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 paraformaldehyde 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 to undergo a loss by formation of an insoluble polymer, such reactions taking place readily in the presence of alkali.

This invention has as an object to obviate the

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 employed 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 crystalline 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 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 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, 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 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 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 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

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 alkali 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 reaction or the solution may be buffered by means of di- or tri-basic acids or suitable buffering salts such as those indicated above. The solution then consists essentially of formaldehyde 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 desirable that the total concentration of alkali in the solution be as low as possible. While no definite low limit of pH of the solution can be set, this may be as low as two or three, the preferred range being from 3 to 11.

The following examples illustrate dry compositions suitable for the production of the formaldehyde stock solution and/or the developer per se. Inasmuch as these compositions are provided as one 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 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 composition being the source of the formaldehyde.

It will 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.

#### Example 1

B. Paraformaldehyde (trioxymethylene)			
	grams		30
Sodium sulfite (desiccated)	gram		1
Potassium metabisulfite (cryst.)			
	grams		10.5
Water (about 100° F.) to make	liter		1
A. Water (about 125° F.) (52° C.)	liters		2.0
Sodium sulfite, desiccated	grams		120.0
Boric acid	do		30.0
Hydroquinone	do		90.0
Potassium bromide	do		6.3
Cold water to make	liters		3.0

#### Example 2

B. Paraformaldehyde			
	grams		30
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. Paraformaldehyde			
	grams		30
Sodium carbonate (desiccated)	do		10
Sodium bicarbonate	do		40
Water (about 100° F.) to make	liter		1

A. Water (about 125° F.) (52° C.)			
	liters		2.0
Sodium sulfite, desiccated	grams		120.0
Hydroquinone	do		90.0
Potassium bromide	do		6.3
Cold water to make	liters		3.0

#### Example 4

B. Paraformaldehyde			
	grams		30
Sodium sulfite (desiccated)	do		20
Resorcinol	do		32
Water (about 100° F.) to make	liter		1

A. Sodium sulfite (desiccated)			
	grams		100
Hydroquinone	do		90
Potassium bromide	do		6.3
Water (about 125° F.) to make	liters		3

#### Example 5

B. Paraformaldehyde			
	grams		30
Sodium metaborate (Na <sub>2</sub> B <sub>2</sub> O <sub>4</sub> ·8H <sub>2</sub> O)			
	grams		15
Water (about 100° F.) to make	liter		1

A. Sodium sulfite (desiccated)			
	grams		120
Hydroquinone	do		90
Boric acid (crysts)	do		30
Potassium bromide	do		6.3
Water (about 125° F.) to make	liters		3

#### Example 6

B. Paraformaldehyde			
	grams		42
Sodium sulfite (desiccated)	do		52
Glycine (crystals) (aminoacetic acid)			
	grams		30
Water (about 100° F.) to make	liter		1

A. Sodium sulfite (desiccated)			
	grams		78
Hydroquinone	do		90
Potassium bromide	do		6.3
Water (about 125° F.) to make	liters		3

#### Example 7

B. Paraformaldehyde			
	grams		30
Sodium sulfite (desiccated)	do		20
Boric acid (crystals)	do		7.5
Water (about 100° F.) to make	liter		1

A. Water (about 125° F.) (52° C.)			
	liters		2.0
Sodium sulfite, desiccated	grams		120.0
Boric acid	do		22.5
Hydroquinone	do		90.0
Potassium bromide	do		6.3
Cold water to make	liters		3.0

#### Example 8

B. Paraformaldehyde			
	grams		30
Sodium sulfite (desc.)	do		24
Malic acid (crystals)	do		12.7
Water (about 100° F.) to make	liter		1

A. Water			
	liters		2.0
Sodium sulfite, desiccated	grams		120.0
Boric acid	do		30.0
Hydroquinone	do		90.0
Potassium bromide	do		6.3
Cold water to make	liters		3.0

#### Example 9

B. Paraformaldehyde			
	grams		30
Sodium sulfite (desc.)	do		11.9
Sodium hydrogenmalate (cryst.)	do		14.8
Water (about 100° F.) to make	liter		1

A. Water (about 125° F.) (52° C.)			
	liters		2.0
Sodium sulfite, desiccated	grams		120.0
Boric acid	do		30.0
Hydroquinone	do		90.0
Potassium bromide	do		6.3
Cold water to make	liters		3.0

## Example 10

5	B. Sodium sulfite	grams	11.9
	Paraformaldehyde	do	35
	Ammonium chloride cryst.	do	5
	Water to make	liter	1
10	A. Sodium sulfite	grams	120
	Hydroquinone	do	90
	Boric acid cryst.	do	30
	Potassium bromide	do	6.3
	Water to make	liters	3

## Example 11

15	B. Sodium sulfite	grams	11.9
	Paraformaldehyde	do	35.0
	Tartaric acid ( $\frac{1}{4}$ - $\frac{1}{2}$ " crystals)	do	7.9
	Water 100° F. to make	liter	1
20	A. Sodium sulfite	grams	140
	Hydroquinone	do	90
	Boric acid	do	30
	Potassium bromide	do	6.3
	Water to make	liters	3

## Example 12

25	B. Sodium sulfite	grams	3.5
	Paraformaldehyde	do	30.0
	Disodium hydrogen phosphate		
	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	do	20.0
	Water 100° F. to make	liter	1
30	A. Water (about 125° F.) (52° C.)	liters	2.0
	Sodium sulfite, desiccated	grams	120.0
	Boric acid	do	30.0
	Hydroquinone	do	90.0
	Potassium bromide	do	6.3
35	Cold water to make	liters	3.0

## Example 13

40	B. Sodium sulfite	grams	11.9
	Paraformaldehyde	do	30.0
	Sodium dihydrogen phosphate		
	(large crystal aggregates $\frac{1}{8}$ - $\frac{1}{4}$ " )		
	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	grams	13.0
	Water 100° F. to make	liter	1
45	A. Water (about 125° F.) (52° C.)	liters	2.0
	Sodium sulfite, desiccated	grams	120.0
	Boric acid	do	30.0
	Hydroquinone	do	90.0
	Potassium bromide	do	6.3
50	Cold water to make	liters	3.0

## Example 14

55	B. Sodium sulfite	grams	11.9
	Paraformaldehyde	do	30.0
	Phenyl acetic acid (large plate crystals)		
		grams	12.9
	Water 100° F. to make	liter	1
60	A. Water (about 125° F.) (52° C.)	liters	2.0
	Sodium sulfite, desiccated	grams	120.0
	Boric acid	do	30.0
	Hydroquinone	do	90.0
	Potassium bromide	do	6.3
	Cold water to make	liters	3.0

## Example 15

65	B. Sodium sulfite	grams	13.7
	Paraformaldehyde	do	30.0
	d-Glutamic acid ( $\frac{1}{8}$ - $\frac{1}{8}$ " cryst. aggregates)	grams	8.0
	Water 100° F. to make	liter	1
70	A. Water (about 125° F.) (52° C.)	liters	2.0
	Sodium sulfite, desiccated	grams	120.0
	Boric acid	do	25
	Hydroquinone	do	90.0
	Potassium bromide	do	6.3
75	Cold water to make	liters	3.0

## Example 16

B. Sodium sulfite	grams	10.0
Paraformaldehyde	do	30.0
Arsenic trioxide	do	9.3
Water 100° F. to make	liter	1
A. Water (about 125° F.) (52° C.)	liters	2.0
Sodium sulfite, desiccated	grams	120.0
Boric acid	do	30.0
Hydroquinone	do	90.0
Potassium bromide	do	6.3
Cold water to make	liters	3.0

In employing the above solutions, one part of solution B is added to three parts of solution A to make up the developing bath. 15

In general, a solid acid salt or acid having a relatively large particle size should be employed in compounding the dry composition in accordance with the present invention, since the rate of solution of the acid salt or acid should not be in excess of the rate of solution of the paraformaldehyde and sodium sulfite. If it is desired to use a solid acid in a relatively fine state of subdivision or small particle-size, agglomeration of the acid with suitable inert binder may be desirable in order to reduce its rate of solution below that of the paraformaldehyde. 20 25

As indicated above, the entire mixture of ingredients of the dry composition can be added to water and dissolved completely within a few minutes. Many variations of the formula are possible within the scope of my invention. For example, alkali bi-sulfites may be substituted by the alkali metabisulfite and other acid salts or acids may be substituted for the metabisulfite. The alkali sulfite may likewise be replaced with an alkali carbonate or other soluble alkaline salt if proper provision is made for neutralizing or decreasing the alkalinity of the solution by use of an acid or buffer salt as herein set forth. 30 35 40

Various fog-restraining or inhibiting substances may be added to either of the dry compositions, such as phenosafranine, Pinakryptol Green, arsenious oxide, or the alkali salts of arsenious acid such as sodium arsenite, potassium ferrocyanide or other alkali ferrocyanides and others. In the case of phenosafranine, varying amounts may be used, but a suitable restraining action is obtained when about one part in 150,000 parts of the mixed developer is used. When using arsenious oxide, sodium arsenite or similar compounds, two grams per liter give representative and satisfactory results. 45 50

The present invention has many advantages, the chief of which is the fact that it is possible to provide a two-package developer in dry form in which the package containing the source of formaldehyde is provided with a means of stabilizing the formaldehyde when dissolved to make up the B solution. By my invention one is thus enabled to purchase the dry material in a form in which it does not deteriorate, either in the package or in the stock solution when made up. 55 60

It is to be understood that the solid compositions of my invention constitute an entirely distinct and separate entity from the aqueous solutions resulting from dissolving these materials in water. In other words, whereas the dry mixture contains certain specific chemicals, many of these more or less completely lose their identity in solution. As is well known, photographic solutions are rather highly complex in their composition and the ingredients must be present in definite and exact proportions in order to obtain the desired result. 65 70 75

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

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 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 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 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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