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STABILIZED CONCENTRATED PHOTOGRAPHIC DEVELOPING COMPOSITIONS

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This invention relates to photographic developing solutions and to their preparation. More particularly it relates to highly concentrated photographic developing solutions and to their preparation. Still more particularly it relates to concentrated developing solutions containing a high percentage of developing agent, alkali metal carbonate, and water-soluble sulfite, and at least 3 parts by weight of a crystallization inhibitor in each 100 parts by volume of solution. When the metric system of measurement is employed, a part by weight is then a gram and a part by volume is a milliliter. It also relates to the utilization of such photographic developers.

An object of this invention is to provide a satisfactory developer solution containing a high concentration of active ingredients. A further object is to provide such a solution which does not form crystals or precipitates on standing under ordinary storage conditions. A still further object is to provide a concentrated developer solution which is stable under abnormal temperature conditions and particularly at temperatures down to 32° F. Another object is to stabilize concentrated developing solutions in a practical manner with economical materials. Yet another object is to stabilize concentrated developing solutions which can be diluted with as much as 3 to 4 volumes of water and produce an energetic developer for radiographs. Still further objects will be apparent from the following description.

Concentrated photographic developing solutions capable of being diluted with 2 to 3 volumes of water for preparing the actual working developer solutions are known. Many commercial forms of such concentrated developers have appeared and, in general, they contain methanol as the crystallization inhibitor. This alcohol has a number of disadvantages in that it causes developer streaks, has an objectionable odor, causes hardening of gelatine and sometimes surface development.

The concentrated developers of the prior art in general contain, however, no more than approximately 350 grams per liter of solids. It is well known in photographic developer and development practices that developers for X-ray films require overall higher concentrations of active ingredients than those for the ordinary motion picture film. A primary reason for the requirement of higher concentrations of ingredients in X-ray developers is that there is a considerably greater amount of silver salts to be reduced in each of the two emulsion coatings on the ordinary X-ray film. Thus, the reducing solution is required to do a somewhat greater amount of chemical reduction in the case of X-ray film than with ordinary photographic emulsions. Inasmuch as developers for X-ray film must contain relatively higher concentrations of active ingredients, concentrated solutions of developers of such an order of concentration that they can be diluted with 3 to 4 volumes of water to produce the working solution, present the problem of finding some means of inhibiting crystallization of the developers as they cool from the hot solutions representing their state during preparation. An allied problem also is to prevent crystallization when a developer is chilled below normal temperatures while in storage, transit, etc.

An "ideal" developer would be one comprising active ingredients which are all liquids in the natural state, all miscible with each other and all soluble in water or in one of the other constituents. Such a developer would then be of maximum concentration and could be diluted with large volumes of water to prepare the working developer solution which is relatively dilute. Inasmuch as the majority of the usual essential constituents of developers are solids, the nearest approach to the ideal developer is one representing the highest concentration of active solids which will remain in a water-clear solution.

In order to show the order of concentration of constituents required in developers, the following table summarizes the average concentration ranges of the working solutions of three commonly used types of developers:

TABLE I

Concentration in grams per liter

	Positive (paper) developers	Negative developers	X-ray developers
Developing agents	1.8– 5.5	2.5– 6.5	9.5– 15
Accelerators	5.0–25.0	7.5–30.0	40 – 60
Preservatives	15.0–45.0	7.5–25.0	45 –105
Restrainers	0.5– 1.5	0.3– 1.5	4.0– 6.0
Total	22.3–77.0	17.8–63.0	98.5–186.0

If it is desired to prepare concentrated solutions of these average type of developers so that one volume of stock solution can be diluted with 3 volumes of water to make diluted, working solutions containing the concentrations set out in the above table, the following total concentration of active ingredients has been found necessary:

TABLE II

Concentration in grams per liter

	Negative developers	Positive (paper) developers	X-ray developers
Total	52 to 232	90 to 308	384 to 744

From this data it is seen that developers for X-

ray emulsions contain the highest concentration of active constituents and thus present the most difficult problem of preparing in concentrated form.

It has been found that the above objects may be accomplished and a satisfactory concentrated developer solution prepared containing at least 40% by weight of total solids by having present at least 15% of a water-soluble sulfite and at least 3% by weight of a crystallization inhibiting compound containing an ionizable hydroxyl group and being further characterized by the fact that a normal solution at 18° C. exhibits a degree of ionization of at least 60%. In the above and all following instances it is understood that the quantities expressed are parts by weight of solid per 100 parts by volume of solution.

The novel concentrated developer solutions of the invention contain a large amount of a developing agent, a large amount of preservative, and a large amount of accelerator in addition to various other ingredients such as restrainers, etc. and at least 3% of a crystallization inhibiting compound, preferably from 3% to 6% of an alkali metal hydroxide.

In a more limited aspect the concentrated aqueous developer solutions contain from 425 to 565 grams per liter of active ingredients in the amounts set forth in the following table:

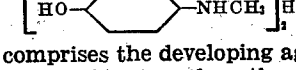
TABLE III

	Grams per liter
Reducers	40 to 60
Accelerators	160 to 195
Preservatives	170 to 200
Restrainers	25 to 50
Crys. inhibitors	30 to 60

The resulting solutions are stabilized against crystallization during storage or shipment over a wide range of temperature including temperatures slightly above freezing, e. g. 35° F.

While alkali metal hydroxides are preferred as crystallization inhibitors, other bases which have a high degree of ionization and provide hydroxyl ions in excess of those produced in the developing solution by hydrolysis or interaction of components can be used. Suitable additional inhibitors include hydrocarbon substituted-ammonium hydroxides and sulphonium hydroxides.

The novel concentrated photographic developer solutions hereof can be prepared by admixing the various components in any desired manner. It is generally preferable to first dissolve or disperse the metol having the formula:



when it comprises the developing agent in a moderate amount of water, then the sodium sulfite, then hydroquinone and then the remaining ingredients.

The invention will now be further illustrated, but is not intended to be limited by the following specific examples which describe various practical developer solutions.

EXAMPLE I

Monomethyl-p-aminophenol sulfate

	grams	20
Quinol 1,4-dihydroxy benzene	do	30
Potassium carbonate (86%)	do	110
Sodium sulfite (desiccated)	do	200
Potassium bromide	do	35
Potassium hydroxide	do	40
Water to make	liter	1

EXAMPLE II

p-Aminophenol hydrochloride	grams	30
Chlor-Quinol	do	15
Sodium carbonate ($Na_2CO_3 \cdot H_2O$)	do	130
Potassium sulfite	do	200
Sodium bromide	do	40
Potassium hydroxide	do	60
Water to make	liter	1

EXAMPLE III

Monoethyl-p-animonphenol sulfate

	grams	18
Quinol	do	25
Potassium carbonate (86%)	do	110
Sodium sulfite (desiccated)	do	200
Potassium bromide	do	37
Potassium hydroxide	do	35
Water to make	liter	1

EXAMPLE IV

Monomethyl-p-aminophenol sulfate

	grams	18
Quinol	do	29
Potassium carbonate (86%)	do	180
Sodium sulfite (desiccated)	do	190
Potassium bromide	do	32
Potassium hydroxide	do	38
Water to make	liter	1

EXAMPLE V

Monomethyl-p-aminophenol sulfate

	grams	18
Quinol	do	29
Potassium carbonate (86%)	do	170
Sodium sulfite (desiccated)	do	190
Potassium bromide	do	32
Sodium hydroxide	do	30
Water to make	liter	1

EXAMPLE VI

Pyrogallol	grams	60
Sodium carbonate ($Na_2CO_3 \cdot H_2O$)	do	195
Potassium sulfite	do	200
Potassium bromide	do	50
Sodium hydroxide	do	30
Water to make	liter	1

In place of one or both of the specific developing agents set forth in the above examples may be substituted one or more other developing agents in such an amount that the total is within the range of about 40 to about 65 grams per liter. The particular type of developing agent chosen depends somewhat on the result desired. Suitable other agents include the aminophenols, polyphenols, and arylene polyamines such as, for example, methyl-p-amino-phenol; 2-amino-5-hydroxy-toluene; methyl-o-aminophenol; 4-amino-carvacrol; p-hydroxy-phenylglycine; p-hydroxy-N-phenyl morpholine; p-amino-hydroxybenzyl alcohol; 2-methyl-4-hydroxy-phenol; 4-hydroxy-phenol; 2-chloro-4-hydroxy-phenol; 2-hydroxy-phenol; mono-tertiary-butyl-pyrogallol; 1:3-diamino-4:6-dihydroxy benzene; 4:4'-hydroxy-diphenylamine; 4-aminodimethylaniline; 1-amino-2-naphthol-6-sulfonic acid and 1-amino-2-3:6-disulfonic acid. Mixed developing agents such as the combination of 1 mol of 4-hydroxy-phenol and 2 mols of methyl-p-aminophenol or 2 mols of methyl-o-aminophenol may also be used. The aminophenols and arylene polyamines are used preferably in the form of their salts, such as the acid sulfates, hydrochlorides, oxalates and sulfonates. In addition the devel-

oping agents of each of the respective examples may be interchanged in any desired manner.

The specific crystallization inhibitors, that is, the hydroxides, described in the respective examples can be interchanged in any desired manner. Likewise, one or more alkali metal hydroxides may be used. As an additional suitable hydroxide mention is made of lithium hydroxide. Potassium and sodium hydroxide, however, are preferred as the alkali metal hydroxide in each of the compositions. Other suitable compounds which provide a suitable amount or supply of hydroxyl ions and can be substituted for all or a part of the specific hydroxides of the above examples include hydrocarbon substituted ammonium and sulfonium hydroxides, e. g. trimethylbenzylammonium hydroxide, tetramethyl ammonium hydroxide, tetraethylammonium hydroxide, trimethyl methylolammonium hydroxide, trimethyl brommethylammonium hydroxide, trimethylcyclohexylammonium hydroxide, dimethyl isobutylammonium hydroxide, triethyl - alpha - naphthylammonium hydroxide and N:N-diethyl piperidinium hydroxide, etc., trimethylsulphonium hydroxide, triethylsulfonium hydroxide, dimethylethylsulfonium hydroxide, benzyldimethylsulfonium hydroxide, propyldiethylsulfonium hydroxide and isobutyldimethylsulfonium hydroxide, etc. Of these, trimethylsulphonium hydroxide is preferred.

In place of all or a part of the specific preservatives set forth in the above examples which, of course, can be interchanged in any desired manner, can be substituted one or more other sulfites, bisulfites, etc. Suitable additional compounds of this type include lithium, potassium and pentavalent nitrogen salts of sulfurous acid, e. g. triethanolamine-, morpholine-, teramethylammonium, and trimethylbenzylamonnium - sulfites. A portion of the sulfites can be replaced by alkali metal bisulfites and meta bisulfites.

Various other accelerators can likewise be substituted for all or a portion of those listed in the specific examples. Thus, the particular alkali metal carbonates of the respective examples can be interchanged in any desired manner. Other alkaline carbonates which present a source of reserve alkali which will maintain the alkalinity balance of the solution include lithium carbonate. Potassium and sodium carbonates, however, are preferred.

Similarly, in place of the specific restrainers of the above examples which can be interchanged in any desired manner can be substituted one or more other compounds of this type. Suitable other compounds include sodium and lithium bromides and chlorides, potassium chloride, etc. However, potassium bromide is preferred.

The concentrated developer solutions hereof have considerable utility in the arts. They may be diluted with several volumes of water and used for developing various types of photographic, including radiographic films and plates. Upon dilution with 2 to 3 volumes of water, they are especially useful for the development of radiographic elements, e. g. films and plates. In fact, this use constitutes their most important and preferred commercial application.

This invention has a number of distinct advantages, the most important of which is that it permits the preparation of stabilized concentrated developing solutions containing in excess of 425 grams of active ingredients per liter of solution. A further advantage is that such solutions will remain clear and stable during storage and shipment and are unaffected by temperatures as low as 35° F. This immunity to precipitation makes it possible to use any part of such a solution by diluting it with 2 to 3 times its volume of water which would be impossible if even a small fraction of the dissolved materials were precipitated. A still further advantage is that the invention permits the use of concentrated solutions suitable for dilution with 2 or 3 times their volume of water to form developing baths for treatment of radiographic film. This is particularly notable in view of the high concentration of dissolved ingredients found in the working strength of baths for such processing.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited except as defined by the specific claims.

I claim:

1. A concentrated, aqueous, photographic developer containing from 425 to 565 grams of active ingredients comprising a developing agent, an alkali metal carbonate and a water-soluble sulfite in each liter of solution stabilized by the presence of from 30 to 60 grams of an alkali metal hydroxide in each liter of solution, wherein water is the only solvent.

2. A concentrated, aqueous, photographic developer containing from 425 to 565 grams of active ingredients comprising a developing agent, an alkali metal carbonate and a water-soluble sulfite in each liter of solution stabilized by the presence of from 30 to 60 grams of a hydroxide having a high dissociation constant, taken from the group consisting of hydrocarbon substituted sulfonium and ammonium hydroxides in each liter of solution, wherein water is the only solvent.

3. A concentrated aqueous photographic developer solution containing from 40 to 60 grams of a photographic developing agent, 160 to 195 grams of a water-soluble carbonate, from 170 to 200 grams of a water soluble sulfite, from 25 to 50 grams of a restrainer and from 30 to 60 grams of a crystallization inhibitor comprising a base yielding a large amount of hydroxyl ions in each liter of solution.

4. A concentrated aqueous photographic developer solution containing from 40 to 60 grams of a photographic developing agent, 160 to 195 grams of a water-soluble carbonate, from 170 to 200 grams of a water soluble sulfite, from 30 to 60 grams of an alkali metal hydroxide in each liter of solution.

5. A concentrated aqueous photographic developer solution containing from 40 to 60 grams of a photographic developing agent, 160 to 195 grams of an alkali metal carbonate, from 170 to 200 grams of an alkali metal sulfite, from 25 to 50 grams of an alkali metal bromide and from 30 to 60 grams of an alkali metal hydroxide in each liter of solution.

6. A concentrated, aqueous, photographic developer containing from 425 to 565 grams of active ingredients comprising a developing agent, an alkali metal carbonate and a water soluble sulfite stabilized by from 30 to 60 grams of an alkaline crystallization inhibiting base having a high degree of ionization and yielding a large amount of hydroxyl ions in aqueous solution, in each liter of solution wherein water is the only solvent.

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