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CONCENTRATED LIQUID COLOR DEVELOPERS CONTAINING BENZYL ALCOHOL

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ABSTRACT OF THE DISCLOSURE

Concentrated acidic solutions containing benzyl alcohol and water are prepared using simple liquid glycols, e.g., ethylene glycol. Such concentrates render feasible the packaging of photographic color developing agents together with benzyl alcohol in concentrated liquid color developer components.

This invention relates to compositions which contain benzyl alcohol and methods and materials for preparation of such compositions. In one aspect this invention relates to photographic processing compositions. In another aspect this invention relates to photographic developer components containing p-phenylenediamine silver halide developing agents as well as methods and materials for the preparation thereof. In still another aspect this invention relates to photographic color developer compositions wherein various components of the total developer are prepackaged in separate compartments in liquid form for ready mixing and use by the trade.

In the processing of photographic film and paper, wide varieties and large quantities of photographic processing solutions which contain benzyl alcohol, especially photographic developers, are utilized. To facilitate the preparation and use of these compositions, it has been found desirable to package the compositions in liquid form usually as concentrates. However, some of the individual components of these compositions, especially of color developers, react with one another and at the concentrations desired are not miscible or soluble. For these reasons the individual components have been conveniently packaged in separate compartments of a single package. In the separate compartments, the essential ingredients are desirably either liquid per se or in solution so that mixing the ingredients into a complete developer involves little time-consuming dissolution. The separate compartments have, for example, in color developers, respectively contained benzyl alcohol, base plus buffering ingredients, and an acidic solution of developing agent plus sulfite.

In these prepackaged photographic processing compositions, especially in the liquid concentrates having separate compartments for keeping various essential ingredients from interacting, it has been considered advisable to compartmentalize benzyl alcohol, which often is a desirable or necessary component of such compositions, separately. This requirement for separate packaging of the benzyl alcohol has been a significant cost factor in the packaging, shipping, and storage of color developers and has been found to be a limiting factor in general acceptance by the trade.

According to the present invention I have found compositions and methods which not only obviate the necessity of packaging benzyl alcohol separately from the other ingredients in liquid photographic processing concentrates, but also facilitate the dissolution of benzyl alcohol to form the ready-to-use processing solution, without detracting from the effectiveness of the overall processing characteristics of the solution. I have found that by combining simple liquid glycols in acidic solution with water and benzyl alcohol, clear, stable concentrated solutions

may be prepared. The benzyl alcohol may thus be incorporated into a compartment of the processing solution containing an aqueous solution of other processing, e.g., developer, components and can be packaged in plastic, e.g., polyethylene containers. The shipping, handling, and packaging costs for such processing compositions, therefore, can be substantially decreased. Such acidic compositions containing water, benzyl alcohol, and the indicated solvents can also effectively be diluted with more water and/or solutions containing other processing components with no appreciable "oiling out" of the benzyl alcohol and is frequently found to substantially diminish the mixing time normally involved in combining separated components of liquid processing concentrates, especially in forming color developers.

In accordance with the present invention it is possible to achieve an unexpectedly high ratio of benzyl alcohol to water in clear acidic solution. However, sufficient water should be present to afford incorporation of various salts and especially acid salts of p-phenylenediamine compounds in the concentrate. Water/benzyl alcohol weight ratios of about 1/6 to about 5/1 appear highly suitable for this purpose. The simple liquid glycols which are more advantageously utilized in the present invention are those diols having molecular weights varying between about 62 and about 150 and having carbon/oxygen weight ratios ranging from about 0.75/1 to about 1.5/1. Highly effective are the propanediols, especially propylene glycol, diethylene glycol, and triethylene glycol. Ethylene glycol appears extremely effective in maintaining clear concentrated solutions at relatively low ethylene glycol concentrations even at relatively high benzyl alcohol/water ratios. Ethylene glycol also exhibits little or no photographic activity at concentrations up to ten times the amount of ethylene glycol usually necessary to maintain clear solution.

In an extremely advantageous embodiment of my invention the packaging of color developing agents, i.e., p-phenylenediamine silver halide developing agents, in concentrated solution with benzyl alcohol is rendered feasible. Such a concentrate solution can decrease the number of necessary compartments, for example, from three in some standard formulas to two. This can amount to a savings of as much as one third in some of the packaging and shipping costs.

The silver halide developing agents especially useful in the unique developer compositions of the present invention are the p-phenylenediamine color developing agents well known in the art, especially those forming non-diffusing dyes with phenolic and active methylene couplers. These developing agents include p-phenylenediamine and N,N-dialkyl-p-phenylenediamines wherein the alkyl groups or the aromatic nucleus may be substituted, for example: N,N-diethyl - p - phenylenediamine monohydrochloride, 2 - amino - 5 - diethylaminotoluene monohydrochloride, 4-amino-N-ethyl - N - [β - methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate, 4-amino-3-methyl-N-ethyl-N-[β-hydroxyethyl]-aniline sulfate. 4-amino-3-(β-methylsulfonamidoethyl) - N,N - diethylaniline hydrochloride, 4-amino-N,N-diethyl - 3 - (N'-methyl-β-methylsulfonamido)-aniline hydrochloride and similar color developing agents disclosed in U.S. Pats. 2,552,241 and 2,566,271. Other useful p-phenylenediamine developing agents are disclosed in J.A.C.S. 73, 3100–3125 (1951). Especially effective p-phenylenediamines are those containing at least one alkylsulfonamidoalkyl substituent attached to the aromatic nucleus or to an amino nitrogen.

Other components can be prepackaged in the same solution with the benzyl alcohol and color developing agents such as antifoggants, e.g., benzotriazole, development restrainers, e.g., bromide, and auxiliary black and

white developing agents such as the 3-pyrazolidone silver halide developing agents, e.g., 4,4-dimethyl-1-phenyl-3-pyrazolidone. For optimum stability, however, two factors appear necessary.

First, it is important that the solution of water, benzyl alcohol, glycol, and p-phenylenediamine siliver halide developing agent be acidic to assist in the stabilization of the developing agent and also to keep the developing agent in solution. The pH is preferably less than about 4. However, the optimum pH will vary depending upon the particular developing agent in use, for example, when 4 - amino - N,N - diethyl-3-(N'-methyl-β-methylsulfonamidoethyl)-aniline hydrochloride is used, it is desirable that the solution have a pH less than 1 particularly to keep the developing agent in solution in a concentrate. The acid may be supplied in the form of the acid salt of the p-phenylenediamine compound or may be supplied as free acid.

Second, it is important that the sulfite/developing agent mole ratio be controlled in accordance with the disclosure of U.S. Ser. No. 676,623, filed Oct. 19, 1967, by Kanous and Bimmler, the subject matter of which is incorporated herein by reference. It is especially desirable to incorporate in the acidic solution that amount of sulfite which is necessary to inhibit aerial oxidation of the developing agent but not so much as to phomote a significant amount of developing agent degradation upon storage.

The minimum amount of sulfite useful in the acid solutions to retard aerial oxidation will vary somewhat depending inter alia upon the particular color developing agent in use since the p-phenylenediamines are oxidized at different rates, and upon the oxidizing agent such as air present in the solution. However, in the case of developing agent, 4 - amino - N - ethyl-N-[β-methanesulfonamidoethyl] - m - toluidine, especially useful results are obtained using more than about 0.08 mole of sulfite (e.g., about 10.1 g. sodium sulfite), i.e., the SO_2-containing moiety or moieties that are produced when various metallic (especially alkali metal) sulfites, bisulfites, sulfurous acid, etc. in combination or separately are added to water or water containing phenylenediamine developing agents and/or additional acid per mole of the developing agent (e.g., about 270 g. 4-amino-N-ethyl-N-[β - methane-sulfonamidoethyl]-m-toluidine). Similar molar proportions of the other p-phenylenediamine color developing agents may be used. The acid developer compositions containing insufficient sulfite are usually colored by the oxidation products of the developing agent and alkaline color developing solutions made therefrom tend to produce colored images of low density and contrast. The maximum amount of sulfite desirable will also depend in part upon the particular color developing agent in use since the various p-phenylenediamines can be expected to be degraded at different rates. However, in the case of 4-amino-N-ethyl-N[β-methanesulfonamidoethyl]-m-toluidine, less than about 1.50 moles of sulfite (e.g., about 189 g. sodium sulfite) per mole of developing agent (e.g., 270 g.) is advantageous.

Similar molar ratios of the other p-phenylenediamine color developing agents also give improved stability. Accordingly, in the acid solutions, from about 0.08 to 1.50 moles of sulfite per mole of p-phenylenediamine developing agent is useful to retard aerial oxidation and degradation of the color developing agent. For example, when sodium sulfite is used as the sulfite source and 4-amino-3 - methyl-N-ethyl-N-[β-hydroxyethyl]-aniline sulfate is used as the developing agent the weight ratio advantageously employed ranges from about .1–1.8 grams sodium sulfite:3 grams developing agent. The increase in stability is outstanding when the sulfite-developing agent mole ratio in acidic solution is about .08–1.0:1.0. The increase in stability is especially outstanding when the mole ratio is about .15–0.5:1.0. (Developing agent/sulfite mole ratios are calculated on the basis of the free base despite the fact that for practical reasons the free base is added in salt form and in some cases a "mole" of salt contains more than one "mole" of free base.)

The prepackaged developer solutions may be prepared by simply combining the various ingredients. However, to obtain maximum concentration and convenience while minimizing the necessity for rechecking the component quantity accuracy, it has been found necessary to combine the ingredients in a certain manner. An acidic aqueous solution is formed advantageously by first combining water with sulfite and then dissolving p-phenylenediamine developing agent (usually an acid salt) in the sulfite solution. Benzyl alcohol and simple liquid glycol are then combined with the acidic developing agent-sulfite solution most advantageously by first combining the benzyl alcohol with the solution to form a slurry and then adding at least sufficient simple liquid glycol to dissolve all the benzyl alcohol and thus form a clear solution, i.e., one that apparently has only one phase.

The developers are then prepared by combining the benzyl alcohol, etc. solutions and aqueous alkali with the amount of water necessary to complete the formulation. It is advantageous when operating from the prepackaged concentrate to first mix the benzyl alcohol-developing agent solution with the desired amount of water and subsequently to add the solution containing aqueous alkali.

The developer compositions when mixed and ready for use can and desirably do contain the usual amounts of developing agent, sulfite and alakali as disclosed generally in the Jelley et al. U.S. Pat. 2,322,027. According to this invention, packaged developer components advantageously are separated to the extent that in compartments containing the benzyl alcohol and developing agents, the sulfite concentration and the pH is controlled as indicated in U.S. Ser. No. 676,623, mentioned above. Other components which may form part of the mixed developer package, for example, additional sulfite, accelerators, complexing agents, e.g., polyphosphates, sodium hexameta phosphates, nitrilo acetic acid, methylamino diacetic acid, dimethylethylene diamino diacetic acid, ethylenediamine tetraacetic acid, diamino-propanol tetraacetic acid, buffers, e.g., citric acid-citrate, boric acid-borate, etc., are advantageously contained in the compartment containing the alkali, e.g., potassium hydroxide, although placing selected addenda in other or separate compartments may be desirable depending upon the particular ingredient chosen.

The packaged developer effectively may be a single package, for example, an outside container or cardboard box in which the developer components are compartmentalized. The compartments can be an integral part of the exterior packaging material but advantageously are, at least in part, merely bottles of, for example, glass and/or plastic enclosed in the outside container. The choice of sizes and shapes of the bottles which form the compartments can vary with the selected ingredients, concentrations desired, etc. Usually it is desirable to choose the bottle size, shape, etc. which will result in a total package of minimum size, and weight to minimize shipping and storage costs. As a result, it may in some instances be desirable to place a single component type in a plurality of compartments, e.g., to conserve space.

Packaging the benzyl alcohol in solutions containing water according to the present invention generally is advantageous in packaging any compositions which require or desirably contain benzyl alcohol ultimately dispersed or dissolved in aqueous solution. Such packaging is extremely significant in photographic silver halide developer packages especially those which are to be utilized with well-known color products, e.g., film products having differently sensitized silver halide emulsion layers containing non-diffusing coupler compounds, for example, those having superposed on a support, red, green, and blue sensitized emulsion layers containing cyan, magenta, and yellow dye forming couplers, respectively.

The advantages obtained according to the present invention will be appreciated in packaging developers for a wide variety of color photographic elements, i.e., multicolor systems containing superposed red, green, and blue light-sensitive silver halide emulsion layers containing a cyan-forming coupler (e.g., a phenolic compound), a magenta-forming coupler (e.g., a 5-pyrazolone compound), and a yellow-forming coupler (e.g., an open chain ketomethylene compound), respectively. Suitable non-diffusing couplers are disclosed in U.S. Pats. 2,956,876; 2,407,293; and 2,640,776.

The following examples illustrate my invention and/or advantages thereof:

EXAMPLE 1

A concentrated solution containing benzyl alcohol is prepared by adding with mixing 27.9 ml. benzyl alcohol to about 5.1 ml. water. To the resultant slurry is added about 8.6 ml. ethylene glycol. Upon brief stirring the mixture changes to a clear solution.

EXAMPLE 2

To about 5 gm. of demineralized water at about 110–120° F. is added about 0.15 gm. anhydrous sodium sulfite. To the resultant solution is added about 5 gm. developing agent (4-amino-N-ethyl-N[β-methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate). The mixture is stirred to assure complete dissolution. To the resultant acidic solution about 5.8 gm. benzyl alcohol is added with stirring. To the resultant cloudy slurry is added ethylene glycol. The mixture is a clear (single phase) solution when the quantity of ethylene glycol reaches about 6 gm. The solution is stable for periods in excess of 6 months at room temperature.

EXAMPLE 2A

The procedure according to Example 2 is followed except that about 7 gm. of ethylene glycol is utilized. Similar results are obtained except that the solution appears more stable at extremely cold temperatures.

EXAMPLE 3

The procedure according to Example 2 is followed except that 2-amino-5-diethylaminotoluene monohydrochloride is used as the developing agent. Similar results are obtained.

EXAMPLE 4

The procedure according to Example 2 is followed except that 4-amino-3-methyl-N-ethyl-N-[β-hydroxyethyl]-aniline sulfate is utilized as the developing agent. Similar results are obtained.

EXAMPLE 5

The procedure according to Example 2 is followed except that triethylene glycol is utilized in place of ethylene glycol. Similar results are obtained.

EXAMPLE 6

The procedure according to Example 2 is followed except that diethylene glycol is utilized in place of ethylene glycol. Similar results are obtained.

EXAMPLE 7

The procedure according to Example 2 is followed except that triethylene glycol is utilized in place of ethylene glycol. Similar results are obtained.

EXAMPLE 8

The procedure according to Example 2 is followed except that about .2 gm. sodium sulfite is utilized and about 17 gm. of benzyl alcohol is utilized. The slurry is transformed into clear solution by the addition of about 7 gm. of ethylene glycol.

EXAMPLE 9

The procedure according to Example 2 is followed except that about 26 gm. of water is utilized. The slurry is transformed into clear solution by the addition of about 18 gm. of ethylene glycol.

EXAMPLE 10

The procedure according to Example 2 is followed except that about 10 g. water is used. The slurry is transformed into a clear solution by the addition of about 8.3 gm. ethylene glycol.

EXAMPLE 11

A clear solution prepared according to Example 2 is added with stirring to about 900 ml. of demineralized water. To the resultant solution is added a solution containing the following: about 3.21 gm. sodium hydroxide, about 21 gm. potassium hydroxide, about 45 gm. water, about 1.8 gm. sodium sulfite, 1.2 gm. ethylene diamine tetraacetic acid, about 1.4 gm. sodium bromide, and about .4 mgm. iodide. The solution functioned effectively as a developer for color material having respectively superposed on a film support a red sensitive layer containing cyan dye-forming couplers, a green sensitive layer containing magneta dye-forming couplers, a yellow filter layer and a blue sensitive layer containing yellow dye-forming couplers, which has been exposed to a test pattern.

EXAMPLE 12

The procedure according to Example 11 is followed except that the solution according to Example 3 is utilized in place of that of Example 2. Similar results are obtained.

EXAMPLE 13

The procedure according to Example 11 is utilized except that the solution according to Example 4 is utilized in place of that of Example 2. Similar results are obtained.

EXAMPLE 14

The procedure according to Example 11 is utilized except that the solution according to Example 5 is utilized in place of that of Example 2. Similar results are obtained.

EXAMPLE 15

The procedure according to Example 11 is utilized except that the solution according to Example 7 is utilized in place of that of Example 2. Similar results are obtained.

EXAMPLE 16

The procedure according to Example 11 is utilized except that the solution according to Example 7 is utilized in place of that of Example 2. Similar results are obtained.

EXAMPLE 17

The procedure according to Example 11 is utilized except that the solution according to Example 9 is utilized in place of that of Example 2. Similar results are obtained.

The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. As a composition of matter an acidic solution comprising:

water,

benzyl alcohol,

a liquid glycol of carbon/oxygen ratio of from about .75 to about 1.5/1 and of molecular weight of from about 62 to about 150,

p-phenylenediamine silver halide developing agent, and a sulfite

wherein the developing agent/sulfite mole ratio is in the range of from about 1/0.08–1.5 the water/benzyl alcohol weight ratio being in the range of from about 1/6 to 5/1 and the amount of the glycol being at least sufficient to obtain a uniform dispersion.

2. As a composition of matter according to claim 1, an acidic solution containing ethylene glycol as the liquid glycol.

3. A concentrated solution of a color developer component according to claim 1 wherein the p-phenylenediamine silver halide developing agent is at least one member selected from the group consisting of N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, 4-amino-N-ethyl-N-[β-methanesulfonamidoethyl]-m - toluidine, 4-amino-3-methyl-N-ethyl-N-[β-hydroxyethyl] - aniline, 4-amino-3-(β-methylsulfonamidoethyl)-N,N - diethylaniline, 4-amino-N,N-diethyl-3-(N'-methyl-β - methylsulfonamidoethyl)-aniline, and salts thereof.

4. A packaged photographic color developer system in which at least some of the developer components are in separate compartments, said system comprising at least one compartment containing a solution according to claim 1.

5. A packaged photographic color developer system in which at least some of the developer components are in separate containers, said system comprising at least one compartment containing a solution according to claim 1 and at least another compartment containing aqueous alkali.

6. A method for the preparation of concentrated liquid photographic color developer components, said method comprising:

(a) forming an acidic aqueous solution containing p-phenylenediamine silver halide developing agent and a stabilizing amount of a sulfite; and

(b) combining with said solution benzyl alcohol and a liquid glycol of carbon/oxygen ratio of from about .75 to 1.5/1 and of molecular weight of from about 62 to 150, the water/benzyl alcohol weight ratio being from about 1/6 to 5/1.

7. A method as in claim 6 comprising:

(a) forming an acidic aqueous solution by steps comprising:

(a') combining water with a sulfite to form an aqueous sulfite solution and

(a'') dissolving p-phenylenediamine silver halide developing agent in the sulfite solution;

(b) combining benzyl alcohol and the liquid glycol with said acidic solution,

the weight ratio water/benzyl alcohol in the solution being from about 1/6 to 5/1 and the mole ratio of

sulfite developing agent being from about 1/0.08 to 1/1.5.

8. A method as in claim 6 comprising:

(a) forming the acidic aqueous solution by steps comprising:

(a') combining the water with a sufite to form an aqueous sulfite solution and

(a'') dissolving the p-phenylenediamine silver halide developing agent in the sulfite solution;

(b) combining the benzyl alcohol and the liquid glycol with said acidic solution by steps comprising:

(b') combining the product from (a'') with the benzyl alcohol with agitation to form a slurry and

(b'') combining the slurry with at least sufficient of said liquid glycol to form a clear solution.

9. A method as in claim 8 wherein the water/benzyl alcohol ratio is in the range from about 1/6 to about 5/1 and the simple liquid glycol is ethylene glycol.

10. A method for the formation of color developers as in claim 6 wherein the glycol is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, and the developing agent is selected from the group consisting of N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, 4-amino-N-amino-3-methyl-N-ethyl-N-[β-hydroxyethyl] - aniline, 4-amino-3-(β-methylsulfonamidoethyl) - N,N - diethylaniline, 4 - amino-N,N-diethyl-3-(N'-methyl-β-methylsulfonamidoethyl)-aniline and salts thereof.

11. A composition according to claim 1 wherein the glycol is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, and triethylene glycol.

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