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PHOTOGRAPHIC DEVELOPER

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This invention relates to photographic developers for developing photographic film, print paper and other photosensitive surfaces having silver halide emulsions.

The object of the invention is to provide a rapid developer, i. e., one which will develop a silver halide-bearing coating in a length of time which is greatly reduced from that required in the use of conventional developers now available. For example, the invention provides for fully developing in five seconds a film emulsion now requiring from four minutes to twenty minutes for development, and a print paper emulsion now requiring from thirty seconds to two minutes for development.

A further object of the invention is to provide a developer having hypersensitizing qualities, i. e., the ability to increase the "speed" (sensitivity) of some emulsions up to ten times their normal speed.

Another object is to provide a developer having a wide temperature tolerance, i. e., which is capable of being used successfully in operating temperatures over a much wider range than that within which conventional developers are limited for successful operation. For example, whereas most conventional developers are used within a temperature range of from 68° to 75° for satisfactory results, the developer of my invention can be used through a range extending beyond both limits of said range of conventional developers, i. e., from 58° up to 85° F. and higher.

The invention deals with ingredients which are largely conventional, i. e. ingredients already in use in well known developers, but uses these ingredients in different proportions and utilizes a novel formulation in the assembling of the ingredients to produce the developer. The extra-ordinary results obtained by the invention are believed to be due to these departures in proportioning and formulation of materials.

The invention is particularly useful in connection with developing records which are produced in long rolls of exposed film or print paper such as oscillographic records (oscillograms), film exposed in military aerial photography, or other records which may call for development in as short a time as possible after exposure; or in other commercial developing operations; where, in order to reduce the cost of developing a high footage of film or print record, it may be highly desirable to attain development in a rapid passage of the sensitized strip through a developer.

Accordingly another object of the invention is to provide a developer paticularly suitable for such high volume military or commercial operations involving high footage of roll film or sensitized ribbon, for development.

Another object is to provide a developer which is capable of being used in developing a relatively large area of emulsion surface (as contrasted to the capacity of commercial developers now available) without a reduction in developer strength below a minimum requirement.

A further object is to provide a developer which may be kept for long periods of time in liquid form without having its strength or quality impaired.

Other objects of the invention will become apparent in the following detailed description of the invention.

The developer of my invention utilizes two aqueous solutions, which for convenience in referring to them will be designated "Solution A" and "Solution B" respectively. Solution A may be regarded as the basic developer solution and Solution B as an additive to be mixed with Solution A to formulate the complete developer solution, ready for use. Each of the solutions is preferably compounded in concentrated form i. e., as a concentrate embodying a minimum quantity of water to dissolve the other ingredients and each calling for dilution by additional water prior to use.

SOLUTION A

Solution A utilizes, in addition to water, simply the three ingredients, sodium sulphite, Na_2SO_3; Metol,

$$HOC_6H_4(NHCH_3).\tfrac{1}{2}H_2SO_4$$

also known by the name Elon and other names; and hydroquinone $C_6H_4(OH)_2$ or p-dihydroxybenzene. The function of these three ingredients, in general, is the same as in conventional developers utilizing them, i. e., the Metol and hydroquinone function as the active developing agents for reducing the activated silver halide grains, and the sodium sulphite functions as an agent to inhibit oxidation of the developing agents. However, the effective action of these ingredients is characterized by the greatly increased rapidity of developing action hereinbefore referred to, a result which is ascribed to the following facts:

(*a*) Additional ingredients used in other developers are omitted. For example, the Eastman high-contrast Kodak D–19 stock solution contains sodium carbonate and potassium bromide, which are not utilized in the developer of my invention, and the Eastman low-contrast (Kodak D–76) developer contains borax which is not utilized in my developer.

(*b*) The proportioning of ingredients is different from that in existing commercial developers utilizing the three ingredients mentioned above. For example, in the Kodak D–19 high contrast solution, the quantitatively predominant ingredient is sodium sulphite, and only relatively small proportions of hydroquinone and Metol are utilized, the total of the latter two ingredients being less than one eighth of the total of the three ingredients, whereas in my developer, the sodium sulphite is only a minor proportion of the total, being three percent or less.

(*c*) In the formulation of my developer, the ingredients are added to one another in the following order:

1. Water for dissolving
2. Sodium sulphite
3. Metol
4. Hydroquinone.

My invention is particularly characterized by a fairly narrow range of proportioning as between the Metol and hydroquinone ingredients. To illustrate by a unit portion containing between one half gram and one gram of sodium sulphite, the amount of Metol and hydroquinone which can be satisfactorily used to produce approximately the results stated above, fall within the fairly narrow ranges as follows:

Metol—11 grams plus or minus about 1.6 grams
Hydroquinone—22 grams plus or minus about 3.3 grams.

Stated differently, a solution containing between ½ and 1 gram of sodium sulphite may contain from about 9 to about 13 grams of Metol and from about 18 to about 25 grams of hydroquinone, the ratio of approximately 1:2 as between the Metol and hydroquinone, being observed.

In each of the instances mentioned above, the ingredients are added to an initial quantity of 400 grams

of water for solution, to produce a concentrated solution, and subsequently, an additional amount of water is added, sufficient to bring the total volume up to 500 cc.

The following specific examples are given to illustrate more fully the range of proportioning within which solution A of this invention may fall:

Example A–1.—Optimum

Water for solution	cc.	400
Sodium sulphite	grams	1
Metol	do	11
Hydroquinone	do	22
Water to make	cc.	500

Example A–2

Water for solution	cc.	400
Sodium sulphite	grams	1
Metol	do	9
Hydroquinone	do	18
Water to make	cc.	500

Example A–3

Water for solution	cc.	400
Sodium sulphite	grams	1
Metol	do	13
Hydroquinone	do	25
Water to make	cc.	500

Example A–4

Water for solution	cc.	400
Sodium sulphite	grams	½
Metol	do	11
Hydroquinone	do	22

In the examples given, where the proportions of Metol and hydroquinone vary 15% more or less than the respective quantities 11 grams and 22 grams, the values of one gram and one half gram given for the sodium sulphite are the respective upper and lower limits for that material. More specifically, the one gram and one-half gram values for sodium sulphite actually constitute the upper and lower limits of that material for the values of 11 grams and 22 grams of Metol and hydroquinone respectively.

In all examples given above, the quantity of 400 cc. of initial water for solution is the minimum for approximately saturation in the concentrated solution.

The following additional examples of proportioning which produce the characteristics of the invention, are given:

Example A–5

Water for solution	cc.	400
Sodium sulphite	grams	1
Metol	do	13
Hydroquinone	do	22
Water to make	cc.	500

Example A–6

Water for solution	cc.	400
Sodium sulphite	grams	1
Metol	do	10
Hydroquinone	do	20
Water to make	cc.	500

Example A–7

Water for solution	cc.	400
Sodium sulphite	grams	1
Metol	do	11
Hydroquinone	do	25
Water to make	cc.	500

Example A–8

Water for solution	cc.	400
Sodium sulphite	grams	½
Metol	do	9
Hydroquinone	do	17½

SOLUTION B

Solution B is added to Solution A immediately preceding the use of the developer solution. Solution B contains, in addition to water, the two active ingredients sodium sulphite and sodium hydroxide. As in the case of Solution A, the water includes an initial quantity of water for solution and a subsequent quantity of "water to make." For optimum developing speed (minimum time interval) equal parts of Solutions A and B are utilized. The water to make (1 part for Solution A and 1 part for Solution B) are added at this time, the two solutions having been preserved in the concentrate form up to the point of use.

As in Solution A, fairly narrow ranges of proportioning are observed; the range for sodium hydroxide being plus or minus 15% variation for a fixed amount of sodium sulphite and the range for sodium sulphite being somewhat greater, i. e. plus or minus 25% variation for a fixed amount of sodium hydroxide.

In the concentrate solution utilizing 400 cc. of water for solution, the amounts of the respective active ingredients are: sodium sulphite—70 grams plus or minus about 18 grams and sodium hydroxide 35 grams plus or minus about 5 grams; water to make 500 cc. is later added.

At this point, it may be noted that the unit quantity just given is the quantity that is mached to the unit quantity for solution A, which also contains 400 cc. of water for initial solution and water to make—500 cc. is later added. In the mixing of the two solutions for the complete developer, the two unit quantities as illustrated above will be mixed in the proportion of 1:1.

The following examples are given to illustrate the range of proportioning for Solution B which attains the characteristics of the invention:

Example B–1.—Optimum

Water for solutions	cc.	400
Sodium sulphite	grams	70
Sodium hydroxide	do	35
Water to make	cc.	500

For the optimum conditions, the ratio of sulphite to hydroxide is 2:1.

Example B–2

Water for solution	cc.	400
Sodium sulphite	grams	70
Sodium hydroxide	do	40
Water to make	cc.	500

Example B–3

Water for solution	cc.	400
Sodium sulphite	grams	70
Sodium hydroxide	do	30
Water to make	cc.	500

Example B–4

Water for solution	cc.	400
Sodium sulphite	grams	88
Sodium hydroxide	do	35
Water to make	cc.	500

Example B–5

Water for solution	cc.	400
Sodium sulphite	grams	52
Sodium hydroxide	do	35
Water to make	cc.	500

The quantities for sodium sulphite ingredient in each of the solutions A and B, are correct where the sodium sulphite is desiccated or completely anhydrous; i. e. for the quantities given, the invention contemplates the use of desiccated sodium sulphite.

For optimum results in developing film, the two solutions are mixed in 1:1 proportions of multiples of the unit quantities given in the examples above, with the "water to make" (2 parts, one part for each of the solutions)

being added just before use. This mixture, without additional water, is used for optimum results in the development of film. For the development of print paper, it is desirable to add a further quantity of the "water to make" to the extent of an additional 1000 cc. to the sum of 500 cc. plus 500 cc. for the two unit volumes of solutions, so that the total unit volume for the mixture would be 2000 cc.

SPECIAL FIXING SOLUTION

The invention contemplates the use of a particular hypo or fixing solution in connection with the fixing of photosensitive surfaces developed by the use of my improved developer. This fixing solution includes, for a unit volume proportioned to the unit volumes for the developer, as given above, a combination of the following ingredients:

Example I.—Optimum

Water for solution	cc.	400
Ammonium thiosulphate (active ingredient)	grams	700
Sodium sulphite	do	24
Glacial acetic acid	cc.	18
Boric acid	grams	10
Aluminum chloride	do	14
Water to make	cc.	500

As in the developer, the range for the respective ingredients is fairly narrow, extending above and below the respective quantities given above, as follows:

Ammonium thiosulphite	plus or minus 15% (105 grams).
Sodium sulphite	plus or minus 25% (6 grams).
Acetic acid	plus 5% minus 15% (.9 cc.–2.7 cc.).
Boric acid	plus 5% minus 15% (.5 gr.–1.5 gr.).
Aluminum chloride	plus or minus 15% (2.1 gr.).

The term "glacial acetic acid" is used to refer to an acetic acid from which water has been eliminated by freezing.

The water content in each case remains constant; i. e. the range of deviation given above is applicable to a fixed water content as given.

In the above formula, the ammonium thiosulphite is the active fixing ingredient. The sodium sulphite is also a preservative. The acetic acid is a neutralizer and buffer. The boric acid is likewise a buffer. The aluminum chloride is a hardening agent.

This fixing solution differs from conventional fixing solutions in utilizing aluminum chloride, which is not used in conventional hypos, and in utilizing ammonium thiosulphate instead of the sodium thiosulphate commonly used in hypos. My special fixing solution also differs from conventional hypos in having a different proportioning of ingredients. For example, a much higher percentage of ammonium thiosulphate is used in my hypos as do utilize this ingredient.

The following improved results are obtained by the use of this improved hypo:

1. It is much faster in fixing time, making it possible to reduce normal fixing time by at least 33⅓%.

2. It has a much longer life than conventional fixing solutions; i. e. it maintains its fixing strength through a much greater volume of use (much greater area of fixed photosensitive surface) than conventional hypos.

I claim:

1. In a developer for silver-halide-emulsion-bearing surfaces, the combination of the following ingredients in approximately the following optimum proportions for mixing with water to make a total volume of 1000 cc. of developer ready for use: water for solution—800 cc.; sodium sulphite—71 grams; sodium hydroxide—35 grams; Metol—11 grams; hydroquinone—22 grams.

2. In a developer for silver-halide-emulsion-bearing surfaces, the combination of the following ingredients in approximately the following optimum proportions for mixing with water to make a total volume of 1000 cc. of developer ready for use: water for solution—about 800 cc.; sodium sulphite—between 53 grams minimum and 89 grams maximum; sodium hydroxide—between 30 grams minimum and 40 grams maximum; hydroquinone—between 18.7 grams and 25.5 grams; Metol—between 9.4 grams minimum and 12.6 grams maximum, approximately a 1:2 ratio between the amounts of Metol and hydroquinone respectively, being maintained.

3. In a developer for silver-halide-emulsion-bearing surfaces, the combination of the following ingredients in approximately the following optimum range of proportions for mixing with water to make a total volume of 1000 cc. of developer ready for use: water for solution—about 800 cc.; sodium sulphite—between 52½ grams and 89 grams; sodium hydroxide—between 30 and 40 grams; Metol—between 9.4 grams and 12.6 grams; hydroquinone—between 18.7 grams and 25.5 grams.

4. In a developer for silver-halide-emulsion-bearing surfaces, the combination of the following ingredients in the following optimum range of proportions, for a volume of 1000 cc. of solution by the addition of water to make a developer ready or use: sodium sulphite—between 52½ and 89 grams; sodium hydroxide—between 30 and 40 grams; Metol—between 9.4 grams and 12.6 grams; hydroquinone—between 18.7 grams and 25.5 grams.

5. In a developer for silver-halide-emulsion-bearing surfaces, the combination of the following ingredients in the following optimum proportions, for a volume of 1000 cc. of solution by the addition of water to make a developer ready for use: sodium sulphite—71 grams; sodium hydroxide—40 grams; Metol—13 grams; hydroquinone—25 grams.

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