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PHOTOGRAPHIC FILM DEVELOPING COMPOSITION CONTAINING BETA,BETA'-DICHLOROETHYL ETHER

Leonard A. Robbins, Salt Lake City, Utah

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This invention relates to compositions of matter for use in the development of photographic films, and particularly to aqueous solutions for the purpose.

In the art of developing photographic film, it is highly desirable that there be rapidity of reaction between the developing solution and the exposed film, a maximum of shadow detail (sometimes refererd to as emulsion speed), good contrast, reasonably fine grain, and long useful life of the solution.

In the past it has been impossible to attain all of the above in a single developing composition. For example, prior art developing solutions that are rapid, impart coarse grain and chemical fog, accompanied by softening of the emulsion. Furthermore, such rapid-action solutions have an abnormally short active life. On the other hand, prior art developing solutions which impart fine grain, as well as protect the emulsion and inhibit chemical fog, are extremely slow in developing the film.

Thus, it has heretofore been necessary to sacrifice one or more of the specified desirable characteristics in order to attain the others. In other words a compromise, forfeiting one or more of such characteristics in order to achieve the others, has been necessary.

In photography as practiced under modern conditions, the attainment of maximum speed in developing negatives is not only desirable, but often imperative, as, for example, in the production of photographs for newspaper use, wherein time is short and deadlines are frequent. Furthermore, a composition having a long useful life is highly desirable in all instances, in order to eliminate the time and cost involved in frequent mixing of a fresh solution.

Among the principal objects of the invention, therefore, are:

To achieve maximum rapidity of processing in film development, while maintaining normal contrast and fine grain in the resulting negative;

To achieve maximum rapidity of processing while, at the same time, improving shadow detail;

To achieve maximum rapidity of processing, accompanied by long useful life of the developing composition;

To minimize possible damage to the emulsion surface during film development;

To condition the reaction between an inorganic alkaline agent and the film emulsion, thereby regulating the degree of softening of the emulsion.

It is well known that strong inorganic alkaline agents, such as the alkaline metal hydroxides

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and, to a lesser degree, the carbonates, speed the action of film developing solutions. They do this, however, at the sacrifice of contrast and clearness in the resulting negative, which suffers from chemical fogging due to softening of and harsh reaction on the film emulsion.

Some success in the use of such inorganic alkaline agents has been had in the past, especially in the case of the alkaline metal carbonates, phosphates, and metaborates, by the addition of an alkaline metal bromide to the solution. While this largely counteracts the harsh effects, the useful life of the solution is seriously shortened. Furthermore, grain structure is too coarse for best effect, and contrast is much greater than generally desirable.

In accordance with the present invention, I have found that the addition of a water soluble, aliphatic amine, especially and for example triethanolamine, to the developing solution, permits the use of such inorganic alkaline agents in the solution for the attainment of maximum developing speed, unaccompanied by the usual harsh reaction. To the contrary, the results achieved by this novel combination when employed in the preferred manner hereinafter set forth in detail, are often superior with respect to fine grain and contrast than are those produced by the use of conventional, slow-action developing compositions. Additionally, definite improvement in shadow detail is noticeable, and the developing solution has a long useful life.

I am aware of the fact that triethanolamine has been used heretofore in certain standard, slow-action developing solutions in place of alkalies normally used for the purpose of speeding development time. Nevertheless, this use of a water soluble, aliphatic amine, as a primary speed-imparting agent, differs essentially from its use pursuant to this invention, where it serves as a modifier for the primary speed-imparting agent, namely, an inorganic alkali.

Thus, a well known and widely used developing solution, producing fine grain but being slow in its developing action, is made up as follows:

	Grams
Monomethyl para aminophenol sulfate	8
Sodium sulfite	400
Hydroquinone	20
Sodium tetraborate (borax)	8

Water to make one gallon of solution.

The use of triethanolamine in place of sodium tetraborate (borax) in the above developing composition brings about a considerable reduction in processing time. Thirty (30) to sixty

(60) ccs. of triethanolamine per gallon results in cutting the processing time from approximately 16 minutes at 68° F. to approximately 6 minutes.

On the other hand, the addition of from thirty (30) to sixty (60) ccs. of triethanolamine to the following faster standard developing solution containing the inorganic alkali, sodium carbonate, cuts the film processing time down from approximately 6 minutes at 68° F. to approximately 3 minutes. Furthermore, the useful life of the solution is greatly extended, and somewhat greater shadow detail is attained with normal contrast.

	Grams
Monomethyl para aminophenol sulfate	6
Sodium sulfite	72
Hydroquinone	10
Sodium carbonate	72
Potassium bromide	4
Water to make one gallon of solution.	

While the above illustrates the invention in its application to standard developing solutions, I have gone further. For example, I have found that the highly desirable effects of the combined inorganic alkali and water soluble, aliphatic amine in the solution can be enhanced by careful control of the relative amounts of the other ingredients, as will appear hereinafter. In this way processing time can be cut to as low as sixty seconds and less at 68° F., without sacrificing quality.

In place of the sodium carbonate, other inorganic alkalies, such as the alkaline metal phosphates or metaborates, may be employed. The alkaline metal hydroxides, however, while operable, are not commercially desirable, due to their severe action and the relatively short life they impart to the developing solution.

Any of the organic developing agents commonly used in photography, such as amidol, pyrogallol, hydroquinone, chlorohydroquinone, toluhydroquinone, glycin, and catechol, may be employed in developing solutions conforming to this invention.

Relatively large amounts of sodium sulfite, as are customarily employed in fine grain developers, preserve the organic developing agents listed above and prevent undue softening of the film emulsion. However, as so used, sodium sulfite gradually oxidizes to sodium sulfate, which has no preservative action and actually slows down development by rendering the emulsion of the film less permeable to the action of the developing agents. Customary amounts of sodium sulfite as are currently used in fine grain developers, thus, lengthen developing time beyond the desired requirements of this invention. On the other hand, very small amounts do not properly preserve the organic developing agents from oxidation, nor prevent the emulsion of the film from becoming too soft.

An important aspect of the invention is the discovery that the addition to the solution of a water soluble, neutral, aliphatic, oxygenated, organic compound, for example an ether, alcohol, or ketone, and preferably a dichlorodiethyl ether compensates for a reduced amount of sodium sulfite, so far as protection of the film emulsion against softening is concerned. Accordingly, by reducing by approximately one-half the quantity of sodium sulfite customary in fine grain developers, and by adding a compensating quantity of the said organic compound, developing time is shortened and the film emulsion is protected.

This aspect of the invention is applicable to developing solutions generally, particularly the use of a dichloroethyl ether, but has its greatest importance in connection with the novel combination of an inorganic alkali and a water soluble, aliphatic amine herein disclosed. In this latter connection it should be noted that greater quantities of the inorganic alkali in the solution usually call for greater quantities of the oxygenated organic compound than would normally compensate for reduction of customary quantities of sodium sulfite.

The optimum range of sodium sulfite in developing solutions conforming to the invention is from 160 to 220 grams per gallon. However, more or less may be employed in particular instances.

While sodium sulfite is usually preferred, any of the alkali metal sulfites may be employed instead.

As stated hereinbefore, alkali metal bromides have in the past been used in developing solutions to modify the action of alkaline metal carbonates, phosphates, or metaborates, thereby greatly reducing the occurrence of chemical fog in the developed image. However, they also restrain development, especially in the weaker portions (shadow areas) of the negative, thus prolonging the time of development. Nevertheless, I have found that water soluble inorganic halides can be used to advantage in developing solutions of my invention, so long as care is exercised in the quantities employed.

Specific examples of water soluble inorganic halides found suitable are ammonium bromide, potassium bromide, sodium chloride, and potassium iodide. Because of superior results in practice, the bromides are preferred over the iodides and chlorides. Especially good quality negatives are obtained through use of compositions containing ammonium bromide.

I have found that, when an alkaline metal carbonate, phosphate, or metaborate, and a water soluble, aliphatic amine, such as triethanolamine, are used in combination with a water soluble, neutral, aliphatic, oxygenated organic compound, considerably less of the inorganic halide is required. In fact, the quantity is so small relatively speaking, that it is wise to strike a careful balance in the developing composition. Useful range of the bromide is from .25 to 10 grams, depending upon whether less or more of the oxygenated organic compound is utilized. A more preferred range is from 1 to 8 grams per gallon. A still more preferred range is from 1.25 to 6 grams per gallon. Optimum is from 1.5 to 3 grams per gallon.

In place of or in combination with the inorganic halide, benzotriazole can be used. If employed in place of an inorganic halide, it is added to the developing composition in the proportion of from approximately 1 to 3 grains per gallon of the solution.

Aliphatic amines particularly suitable for use in developing solutions of the invention include those which are soluble to at least 0.5% by weight in water. Oxygen-containing aliphatic amines form a preferred class, because of ease of handling and results obtained. Hydroxyalkylamines, particularly the beta hydroxyethylamines, form a still more preferred class, because of their low cost and effectiveness in low concentrations. Triethanolamine is particularly preferred, because of the outstanding results produced through

its use. Other specific amines suitable for use include monoethanolamine, diethanolamine, N,N-diethyl-N-beta-hydroxyethylamine, N-butyl-N,N-bis (beta-hydroxyethyl) amine and triethylamine. Mixtures of two or more amines can be used. For example, technical triethanolamine, which contains appreciable quantities of mono- and diethanolamines, gives excellent results.

The quantity of aliphatic amine required in any specific instance depends upon the amount of inorganic alkali used, and varies with the specific amine. The more alkali utilized, the less amine. In general, from 0.05% to 8% by weight, based on the particular composition of the developing solution, is useful. Little is gained through use of quantities above 4%, however. From 0.10% to 3% represents a preferred range, and the most satisfactory all around results are obtained in the range of 0.20% to 1.5%.

From 40 to 240 grams, or more, of sodium carbonate can be used in combination with substantially inversely proportional quantities of triethanolamine, within the range heretofore specified for the latter, to give a solution which will permit the development of well balanced negatives in from 180 to 60 seconds or less at 68° F. It is preferable, however, to use from 60 to 180 grams of sodium carbonate per gallon, since there is little advantage in using more, and amounts significantly less than 60 grams results in longer developing time.

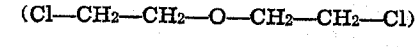
Better all around results are obtained with about 90 to 150 grams of sodium carbonate per gallon. Optimum results are realized however, when about 110 to 130 grams per gallon are used.

In place of sodium carbonate, there can be employed comparable quantities of other alkaline metal carbonates, such as potassium carbonate, or other inorganic agents of comparable alkalinity, such as the alkaline metal phosphates, and metaborates. Nevertheless, the inorganic alkaline carbonates are preferred for use in this developing composition, due to their availability and lower cost. Sodium carbonate is especially preferred.

The precise amount of any specific inorganic alkali for best results in any given developing composition, is easily determined by experiment. In general this will be from about 20 to 400 grams per gallon of the developing composition. In most cases the amount will vary from 50 to 200 grams per gallon.

For best all around results, it is essential to have what can be termed a balanced developing composition. For example, if a large amount of sodium carbonate, say 180 grams per gallon is employed, then it is desirable to use somewhat larger quantities of the water soluble, neutral, aliphatic oxygenated organic compound and inorganic bromide or the like than usual.

Halogen-containing anti-softening agents form a preferred class of the water soluble, neutral, aliphatic, oxygenated, organic compounds referred to hereinbefore, because of their effectiveness. Of these, because of low cost and availability, the chlorine compounds are preferred. Compounds containing a beta-chloroethyl group are preferred, because they are extremely effective in small quantities and give highly desirable results. Beta,beta'-dichloroethyl ether



is particularly preferred, because of its low cost, ready availability, and the outstanding results obtained through its use.

Propanol 2 gives excellent results, although larger amounts are required than certain of the chlorinated ethers to produce the desired effect.

In certain cases highly desirable results are obtained through a combination of anti-softening agents, as, for example, propanol-2 in combination with beta,beta'-dichloroethyl ether

Other preferred organic compounds of this group are acetone, ethylene chlorohydrin, 1,3-glycerol dichlorohydrin, tertiary butyl alcohol, cyclohexanol, alpha, beta-dichloroethyl ethyl ether, and beta,beta-dihydroxyether. Polyhalogenated ethers, alcohols and ketones can also be employed to advantage.

In the use of said water soluble, neutral, aliphatic, oxygenated, organic compounds, the range of 0.01% to 4% by weight of developing composition, depending upon whether more or less of the sulfite and less or more of the inorganic alkali are utilized, constitutes a useful range, while the range of 0.015% to 3% is preferred, and 0.02% to 2.5% constitutes an optimum range.

Sodium tetra phosphate is advantageously added to the water, before the addition of the other chemicals, as a water softening agent.

The following composition produces an ideal developing solution in accordance with the invention:

Example No. 1

Sodium tetra phosphate	grams	5
Monomethyl para aminophenol sulfate	grams	10
Sodium sulfite	do	180
Hydroquinone	do	20
Sodium carbonate	do	120
Ammonium bromide	do	2
Triethanolamine	cc	15
Beta,beta'-dichloroethyl ether	cc	1

Water to make one gallon of solution.

The triethanolamine and beta,beta'-dichlorodiethyl ether are advantageously dissolved in one another, and added to the aqueous solution of the other chemicals. The mixture is shaken, and is then ready for use.

The resulting developing solution represents a goal long sought in the photographic industry. It provides an average of 90 second processing at 68° F., fine grain, normal contrast, extremely good gradation, excellent shadow detail, long life solution, low cost, excellent protection for the emulsion surface, ready availability of the chemicals, and complete and easy control during process of development.

Other typical compositions in accordance with the invention, each affording approximately 90 second action at 68° F., follow:

Example No. 2

Sodium tetra phosphate	grams	5
Mono-methyl para aminophenol sulfate	grams	8
Sodium sulfite	do	200
Hydroquinone	do	20
Potassium carbonate	do	100
Monoethanolamine	cc	20
Potassium bromide	grams	1.8
Ethylene chlorohydrin	cc	5

Example No. 3

Sodium tetra phosphate	grams	4
Mono-methyl para aminophenol sulfate	grams	10
Sodium sulfite	do	180
Hydroquinone	do	20
Ammonium bromide	do	1
Sodium carbonate	do	140
Triethanolamine	cc	20
Beta-beta'-dichloroethyl ether	cc	1
Propanol-2	cc	20
Benzo-triazole	grain	*

Example No. 4

Sodium tetra phosphate	grams	5
Mono-methyl para aminophenol sulfate	grams	8
Sodium sulfite	do	200
Chlorohydroquinone	do	25
Potassium metaborate	do	160
Sodium bromide	do	2
Diethanolamine	cc	24
Acetone	cc	30

Example No. 5

Sodium tetra phosphate	grams	5
Mono-methyl para aminophenol sulfite	grams	10
Sodium sulfite	do	220
Toluhydroquinone	do	16
Potassium bromide	do	2.5
Morpholine	cc	10
Sodium carbonate	grams	120
Glycerol	cc	10
Beta-beta'-dihydroxyethyl ether	cc	10

Example No. 6

Sodium tetra phosphate	grams	4
Mono-methyl para aminophenol sulfate	grams	12
Hydroquinone	do	16
Sodium sulfite	do	140
Tri sodium phosphate	do	100
Potassium bromide	do	2
Triethanolamine	cc	20
Propanol-2	cc	10

Whereas this invention is here described in detail with respect to several specific embodiments thereof, it is to be understood that various changes may be made therein and that various other embodiments may be prepared on the basis of the teachings hereof, by those skilled in the art, without departing from the protective scope of the following claims.

I claim:

1. A photographic developing composition, containing an organic silver halide developer; sodium carbonate; triethanolamine; ammonium bromide; and beta-beta'-dichloroethyl ether.

2. A photographic developing composition, comprising sodium tetra phosphate, monomethyl para aminophenol sulfate, sodium sulfite, hydroquinone, sodium carbonate, ammonium bromide, triethanolamine, beta-beta'-dichloroethyl ether, and water.

3. A photographic developing composition constituted of the following ingredients in approximately the amounts indicated:

Sodium tetra phosphate	grams	5
Monomethyl para aminophenol sulfate	grams	10
Sodium sulfite	do	180
Hydroquinone	do	20
Sodium carbonate	do	120
Ammonium bromide	do	2
Triethanolamine	cc	15
Beta-beta'-dichloroethyl ether	cc	1

Water to make one gallon of solution.

LEONARD A. ROBBINS.

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