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PHOTOGRAPHIC DEVELOPER

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The present invention relates to new and useful improvements in photographic developers.

Heretofore, photographic developers adapted to produce negative or prints having good detail and contrast have, as a rule, produced relatively large aggregates or clusters of silver particles commonly referred to as "grain." Such aggregates or clusters give a negative or print the undesirable appearance of graininess on enlargement. Prior developers producing relatively small aggregates or clusters of silver particles for the purpose of reducing the appearace of graininess require notoriously long development times. The use of such developers frequently results in the production of flat negative, that is, negative lacking contrast, and in many instances lacking good detail, especially shadow detail.

Consequently, no former developer has been wholly satisfactory, especially for use with small negatives, such for example as 35 millimeter negatives. Since enlargements are customarily made from these small negatives, they must possess good detail and be as free as possible from the appearance of graininess and must possess suitable, preferably long-scale, contrast and detail as all defects are accentuated in enlargements made therefrom.

Developers intended and adapted to produce images having the desired contrast and detail can do so only by producing images containing relatively large aggregates or clusters of silver particles and thus give the appearance of having a coarse, grainy structure. So-called "fine grain" or "ultra fine grain" developers heretofore used, while more or less effective in reducing the sizes of the clusters or agglomerates of the silver particles, are not wholly satisfactory for they produce negatives which usually are lacking in the desired detail and contrast, and they require an excessively long development time.

It is, therefore, one object of the present invention to provide a photographic developer adapted to produce a print or negative having little or no formation of clusters or agglomerates of the silver particles so that the photographic image developed therein is free from the appearance of coarseness or graininess, the present developer being also adapted to produce a photographic image possessing the desired properties of sharpness, contrast and detail, especially shadow detail.

It is another object of the invention to provide a photographic developer which is adapted to produce a clean print or negative free from any over-all deposit of silver or any other substance darkening its appearance and rendering its image indistinct or "muddy," as such prints and negatives are often termed. Accordingly, the present developer produces a negative or print not only free from the appearance of grain, but also possessing clear or "white" highlights, dark or black shadows, and distinctly differentiated intermediate gradations, which result in producing an image having good detail and contrast.

Another object of the invention is to provide a so-called "fine grain" photographic developer having a short development time, said developer being comparable in this respect to the faster acting of the present coarse grain developers, and having less than half the development time of conventional commercial so-called "fine grain" or "ultra fine grain" developers.

Still another object of the invention is to provide a photographic developer of the foregoing general character in which the ingredients may be predetermined or controlled to increase or decrease the development time, to increase or decrease the ability of the developer to produce contrasts in the negatives or prints, and to produce agglomerates or clusters of silver particles of a minimum size.

A further object of the invention is to provide a developer which may be used with panchromatic film or other film sensitive in the wave length span of light ordinarily employed in darkrooms, but which will permit inspection of said film in said light after a very short development interval, without fogging or other undesirable results.

Still a further object of the invention is to provide a photographic developer which is stable at room temperature ranges for a relatively long period of time even when exposed to the air, and which is adapted to be used satisfactorily over a wider temperature range than other known developers, the present developer being adapted to produce equally good results at all points within its temperature range, and if used repeatedly at or about any given point in said temperature range it will produce consistently duplicative results.

Other objects and advantages of the present invention will become apparent during the course of the following description and of the appended claims forming a part hereof.

Generally speaking, a photographic developer embodying the present invention is a chemical

compound or admixture of chemical compounds containing one or more of the following types of compounds or substances:

(1) A wetting agent adapted to cause adhesion or affinity between the aqueous solution of the present developer and the photographic emulsion to be developed. In particular, this wetting agent aids in causing the developer to permeate or penetrate the "pores" of the photographic emulsion and thus facilitates the reaction between the silver compound carried in the emulsion and the developing materials to be employed.

(2) A buffing agent adapted to maintain the solution as a substantially neutral solution.

(3) An anti-fogging agent adapted to prevent undesired precipitation of the silver or other image-forming compound uniformly over the emulsion. Such precipitation causes darkening of the image or may destroy it by what is known as "chemical fogging."

(4) A reducing agent adapted to reduce the light-struck or photo-sensitized silver compound to metallic silver, or to reduce the light-sensitive compound in the emulsion to the image-forming substance.

(5) A preservative which is also preferably a mild reducing agent, thereby aiding in the reducing action of the developer.

To the foregoing ingredients there may be added, if desired, an inhibitor for slowing down the developing time of the developer. This is recommended only if it is particularly desirable to secure an image having very small aggregates or clusters of silver particles which will result from a slower development.

It is to be understood, as hereinafter set forth, that the present developer does not necessarily contain an ingredient selected from each one of the aforesaid classes of compounds or substances.

The Wetting Agent

The wetting agent should be selected from the group of water-soluble or water-dispensable agents adapted to cut down the time required to bring the aqueous solution of the developer into reactive contact with the silver compound carried in the emulsion. Among such agents I have found that any one of the various dicarboxylic acids may be used satisfactorily. For example, the dicarboxylic acid sold under the trade name "Aerosol O. T." by the American Cyanamide Company, or a similar product sold under the trade name "Tergitol" by the Carbon and Carbide Chemical Company, may be employed with good results. However, it should be clearly understood that other wetting agents are also satisfactory. For example, the oleates, stearates or palmitates of triethanolamine also may be used, as may the polyhydric alcohols.

The amount of wetting agent employed will depend upon the particular agent selected. However, generally speaking, relatively small amounts of these wetting agents are all that is required. In general, the known proportions necessary for use in an aqueous solution may be used. For example, if the various dicarboxylic acids are employed, it has been found that a .12 to .2 percent solution produces good results, that is, 1.2 grams to 2 grams of the dicarboxylic acid per liter of the present solution comprises the preferred range of proportions. It will be understood, however, that this range is but a preferred range, and more or less of the wetting agent may be employed if particular results are desired, although the foregoing proportions have been found satisfactory for normal use.

While it is preferable to utilize a wetting agent, the present developer can be made up without any such agent. However, if it is made up the latter way, the development time is increased materially, but satisfactory photographic images can be produced under these circumstances.

The Buffering Agent

As the buffering agent, any suitable buffer may be employed which will maintain the solution approximately neutral or somewhat alkaline, that is, neither strongly alkaline nor strongly acidic. For this purpose it is recommended that dibasic sodium borate be employed. This compound has been found to be an admirable buffering agent, and is effective since a solution containing this salt possesses a very nearly constant pH of approximately 7.5.

It will be understood, however, that while dibasic sodium borate comprises a preferred buffering agent, other buffering agents may be used. For example, borax ($Na_2B_4O_7$) may be employed.

While the developer containing a buffering agent, as explained above, is distinctly preferable, a buffering agent may be dispensed with entirely. However, if the buffering agent is dispensed with, it is recommended that the concentration of sodium sulfite (another one of the ingredients of the present developer explained hereinafter) be kept at or near its maximum concentration. Also, if this buffer is not utilized, the wetting agent explained hereinbefore should be utilized. In other words, it is preferable that the developer contain both the wetting agent and the buffering agent. If either agent is omitted, it is desirable that the other agent be used.

The concentration of the buffering agent will, of course, depend to a large extent upon the particular compound selected. A skilled chemist can determine how much of the buffering agent is needed in a particular solution to maintain the solution at or near a pH of 7 to 7.5. If dibasic sodium borate is employed as the buffering agent, it is recommended that approximately 11 grams of this compound per liter of developer be employed. However, this concentration does not appear to be critical and may be reduced to approximately 4 grams per liter and may be increased to about 20 grams per liter. It is to be understood that this range of proportions is merely recommended in view of applicant's experience with the buffering agent, and it is contemplated that, for particular purposes, the concentration thereof may be further increased or decreased.

The Anti-Fogging Agent

Another of the ingredients utilized in the present developer is an anti-fogging agent. This agent may be any suitable compound effective to prevent an over-all precipitation of silver throughout the emulsion or the deposition of precipitated silver on the surface thereof. This precipitation, if carried to an extreme, may result in what is known as chemical fogging and ruin the negative or print. If such precipitation takes place but slightly, the print will be darkened somewhat and will suffer accordingly, especially through loss of detail and lack of contrast, although the image may be visible. Therefore, it is preferable to prevent any such precipitation.

However, if a very flat print (one not having much contrast and in which the detail is relatively unimportant) is desired, the present anti-fogging agent may be eliminated. However, as stated, for most purposes detail is desired, as is at least a certain amount of contrast; thus, the use of said agent is usually desirable.

I have found that any soluble bromide which will not react to form insoluble compounds may be utilized as an anti-fogging agent. In particular, ammonium bromide (NH_4Br) is recommended, although it tends to be acid in nature. If the aforementioned buffering agent is employed, the solution will retain its pH value despite this characteristic of the ammonium bromide. Also, sodium or potassium bromide (NaBr or KBr) may be utilized is desired.

I have found that approximately 1 gram per liter of ammonium bromide produces satisfactory results, although it appears that from ½ gram to as much as 25 grams may be employed if desired. However, the practical limits appear to be from ¼ gram, below which the compound appears to be used up, up to approximately 5 grams. If a concentration of over 5 grams per liter is employed, the developer tends to produce a very contrasty print or negative, that is, one having completely clear highlights and very dark backgrounds with very few gradations between the two. Where such contrast is sought, as in lantern slide development or half tone and line work, it may be desirable to use a relatively high concentration of the above-mentioned bromide. However, for normal development where such very high contrasts are not particularly desirable, the bromide concentration should not exceed approximately 5 grams per liter.

The Developing Agent

The present developing agent must, of course, contain a suitable reducing agent for reducing the light struck or photo-sensitized silver compound to metallic silver. However, it will be understood that the reducing agent may reduce any light-sensitive substance which the emulsion may contain, to the reduced substance which forms the photographed image. For present purposes, any of the well-known reducing agents utilized in photographic developers may be employed. For example, I have found that a mixture of hydroquinone and monomethyl para amino phenolsulfate produces satisfactory results. The latter compound is known commercially as "Elon" or "Metol" and is sold under such names by the Eastman Kodak Company. I have found that from ½ to 3 grams of "Elon" per liter of developer produces a satisfactory result when used with 1 to 12 grams of hydroquinone per liter. It is to be understood that any amount of either of these substances within the foregoing ranges, or any combination thereof, may be employed. Also, it is to be understood that one may be employed alone if desired. However, "Elon," if used alone, tends to produce a very soft or flat negative print having little detail of contrast, while hydroquinone, if used alone, tends to produce a very brilliant contrasty print. Thus, a mixture of the two appears to be more suitable and more desirable for most purposes, although "Elon" alone may be employed if a flat print is sought, and hydroquinone may be employed alone if a brilliant or contrasty print is sought.

As pointed out hereinbefore, certain of the other ingredients normally utilized in forming the present developer may be omitted, but it will be understood that the developer must contain a reducing agent.

The Preservative

Another one of the ingredients utilized in the present developer is a suitable preservative. Naturally this preservative is utilized chiefly to extend the life period of the developer after it has been made up, and it need not be added if the developer is to be used shortly after its preparation. Its use is recommended, however, since for some reason not now known to me, the use of the preservative appears to improve the results obtained from the use of the developer.

A suitable preservative is sodium sulfite, which is also a mild reducing agent and thereby appears to aid the hydroquinone and "Elon" in effecting the reduction of the light-struck or photo-sensitized compounds in the emulsion.

The amount of sodium sulfite employed may vary widely, although it is recommended that a relatively large amount be employed. I, therefore, recommend that approximately 90 grams per liter be used, inasmuch as this concentration appears to render the present developer particularly stable and does not appear to affect deleteriously the quality of the images. Sodium sulfite may be employed up to the saturation point of the solution, which is approximately 200 grams per liter. On the other hand, the concentration of this ingredient may be decreased considerably and may be as low as 20 grams per liter with effective results. As pointed out above, the principal purpose of the sodium sulfite is as a preservative and, therefore, still smaller amounts may be utilized or it may be dispensed with without materially affecting the characteristics of the present developer.

Substances for Producing an Especially Fine Grain

In addition to the foregoing ingredients, the present developer may include substances adapted to produce especially small silver particles or agglomerates thereby providing a print or negative which may be considerably enlarged without showing any "grain." Beta naphthol has been found satisfactory for this purpose although it considerably lengthens the development time. When but ½ gram of beta naphthol per liter is employed, it has been found to approximately double the development time. While normally this lengthening of the development time would not be desirable, it appears to be helpful in producing even the smaller aggregates or agglomerates of the silver particles. Therefore, I have found that the use of the presently disclosed additional substances does produce the finer aggregates or agglomerates, although a generally comparable result may be attained without its use. As explained above, I recommend that ½ gram per liter of beta naphthol be employed, although this amount may be increased to approximately 5 grams per liter.

Alpha naphthol, phenol, and naphthol sulfonic acids may be employed instead of beta naphthol if desired. Also, any suitable compound intended to slow down the reducing activity of the reducing agent may be employed provided that it does not have deleterious side reactions.

Inspection During Development

If desired, another ingredient which may be added to the present developer is an agent for making possible the inspection in light normally employed in the darkroom of a panchromatic

or similar film during development thereof. Normally films of this character would be sensitive to such light, and therefore could not be inspected during development if conventional developers were employed, for they would fog. The desirability of frequent visual inspection of such films during development is well known. For example, pinakryptol green may be added in amounts of approximately ½ gram per liter of developer, although this amount may be reduced or increased somewhat and may be used in quantities as low as .25 gram per liter. If this compound is added, a normal panchromatic film or the like may be inspected with a Wratton & Wainwright O. A. filter disposed over an ordinary lamp after approximately 1 minute of development. The light may be fairly bright; also a relatively bright green light may be employed.

Another ingredient suitable for this purpose is pinakryptol yellow which has the same general effect as pinakryptol green. Also, phenosafranine may be employed in amounts of approximately ½ gram per liter, and renders the aforesaid film suitable to be inspected with the usual dull green darkroom safe lights after approximately 1 minute of development.

Clearing the Print or Negative

If the present developer is employed for producing a print or negative, I have found that the time required for clearing the print or negative after development is greatly reduced. Apparently sufficient wetting agent is retained in the emulsion layer of the print or negative to accelerate the penetration of the clearing agent in the "pores" of the emulsion. This more rapid penetration enables said clearing agent to react with or dissolve the products in the emulsion other than the developed silver, thereby producing a cleared print. For instance, a solution of "hypo" (sodium thiosulfate or the like) may be employed as the clearing agent, and for the reasons set forth above, will clear the print more rapidly if the present developer is used.

Specific Developer

Although I have explained my invention in detail, the following general formula and specific example are given by way of further explanation and not of limitation:

General formula

Sodium sulfite	Approx. 20 gms. to saturation point
Monobasic sodium borate	Approx. 4 gms. to approx. 20 gms.
Potassium, sodium or ammonium bromide	Approx. ¼ gms. to approx. 25 gms.
A Dicarboxylic acid	Approx. 1.2 gms. to approx. 2 gms.
"Elon"	Approx. ½ gm. to approx. 3 gms.
Hydroquinone	Approx. 1 gm. to approx. 12 gms.
Water	To make one liter of solution

Specific example

		Gms.
"Elon"	Approx.	1.75
Sodium sulfite	Approx.	90
Dibasic sodium borate	Approx.	6.5
Potassium bromide	Approx.	.5
"Aerosal O. T."	Approx.	2.0
Hydroquinone	Approx.	2.0
Water	To make one liter of solution	

The foregoing example of the present developer was found to have a developing time of about 6 to 7 minutes at approximately 21° C. when used on "Agfa Finopan" film. This film was developed to approximately .8 gamma. Under like circumstances and conditions, the aforesaid developer was found to have a development time of from 6 to 7 minutes when used on "Agfa Supreme" film. The development time was approximately 6.5 minutes for Eastman "Panatomic" film; about 5 minutes for "duPont Superior" film; and about 75 seconds for "Eastman" positive film.

In order to develop these films to a comparable extent, that is, to approximately .8 gamma, the so-called "fine grain" or "ultra fine grain" developers now available on the market require from about 40 minutes to 60 minutes. Among such developers are Eastman DK—20, Champlin No. 15 and Edwal No. 12.

In addition to having much faster development time than the aforesaid presently available fine grain developers, the present developer was found to produce an image at least comparable in fineness if not superior thereto. In addition, the present developer produced negatives having much better detail than those produced by the aforesaid developers, especially shadow detail, and produced much sharper, clearer images.

Accordingly, the present developer appears to be an improvement over present developers since it not only produces more satisfactory results, but does so in a much quicker time and is therefore much more practical and convenient to use.

I claim:

1. A photographic developer containing a wetting agent, a buffer adapted to maintain the solution neither strongly acidic nor strongly alkaline, a water-soluble bromide, a developing agent, a preservative, and a naphthol sulfonic acid.

2. A photographic developer comprising an aqueous solution containing a dicarboxylic acid wetting agent, dibasic sodium borate, a developing agent, and beta naphthol.

3. A photographic developer comprising an aqueous solution containing a dicarboxylic acid wetting agent, dibasic sodium borate, a water-soluble bromide, hydroquinone, monomethyl para amino phenolsulfate and beta naphthol.

4. A photographic developer adapted to produce a rapid development of a photographic image with the production of very small agglomerates or aggregates of the light-struck photosensitive material, while preserving detail and a desired scale of contrast, said developer comprising an aqueous solution containing a wetting agent selected from the group consisting of dicarboxylic acid wetting agents and the oleates, stearates, and palmitates of triethanolamine, a buffering agent selected from the group consisting of dibasic sodium borate, borax, sodium carbonate and sodium bicarbonate, an anti-fogging agent selected from the group consisting of ammonium, sodium and potassium bromides, a developing agent comprising a mixture of hydroquinone and monomethyl para amino phenolsulfate, a preservative comprising sodium sulfite, an inhibitor selected from the group consisting of alpha and beta naphthol, phenol and naphthol sulfonic acids, and a dye selected from the group consisting of pinakryptol green, pinakryptol yellow and phenosafranine.

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