Patented Sept. 11, 1934 1,973,466

UNITED STATES PATENT OFFICE

1,973,466

PHOTOGRAPHIC DEVELOPING SOLUTIONS

John I. Crabtree, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New York

No Drawing. Application August 7, 1931, Serial No. 555,859

4 Claims. (Cl. 95—88)

This invention relates to a photographic developer. The type of developer described is particularly suited to motion picture negative development and is especially useful for motion picture and sound record negatives which are to be printed on the same film. It is, however, applicable to development of photographic records of any type.

The idea of developing a photographic image by successive immersions in two separate baths is by no means new. A large number of workers have investigated the effect of starting development in a weak developer and then, according to the manner of appearance of the image, continuing the development in either a restrained, normal, or a very active developer. Other workers have claimed that in the case of an underexposed negative of a contrasty subject, if the negative is first immersed in a developing solution which does not contain alkali, and is then placed in a second solution containing only alkali and sulfite, the quantity of developer adsorbed by the film in the first solution is sufficient to insure adequate development of the shadows in the second solution; whereas, in the case of the high lights, the developing power of the developer is exhausted before full development is attained. In this way, it was claimed that good shadow detail was obtained while the high lights were not over developed.

My invention comprises a two-bath developer by means of which new results may be obtained. I use a first bath which contains the developing agent and a substance which I term an "inhibitor," which is more fully explained hereinafter. The film to be developed is immersed for a time in this solution and is then transferred to a second solution which contains alkali, as, for example, sodium carbonate. By adjusting the composition of these two baths it is possible by this two-bath method (i. e. by a first immersion in solution A followed by immersion in solution B) to develop a film to a predetermined degree of contrast which, over a reasonably wide range, is independent of the length of time of immersion in either solution. This two bath developer, therefore, allows accurate and controlled development to a predetermined degree irrespective of minor variations in time of development. This result is quite different from that attained with previously known developing solutions. To obtain a specified and accurately controlled degree of contrast or gamma usually requires accurate control of the developing times and of the temperature of the solutions. By my method reasonable variations both in times of development and in temperature are immaterial.

An important step in my invention is the inclusion in the first bath of what I have termed an "inhibitor". This substance is added to a solution containing a developing agent or agents with or without other ingredients and its function is to prevent or inhibit development during the given time in the first bath. The exact mode of its operation is obscure and it seems likely that the result may be brought about in any of several ways. The inhibitors which I have found particularly useful are sugar, glucose, glycerine, sodium sulfate, sodium bi-sulfite and free acids of a certain type. Of these, the action of the last two, that is, sodium bi-sulfite and free acid, is perhaps best understood. In the absence of a large amount of sodium sulfite, sodium bi-sulfite probably acts in the same way as a free acid. It is well known that the development process in the case of ordinary organic developing agents normally proceeds very slowly, if at all, in acid environment. Sodium bi-sulfite and weak acids such as citric acid, may, therefore, be used as inhibitors in the first solution of my two-solution developer. Only a small amount of acidity is required, however, and the pH of the solution is only slightly on the acid side. When a larger amount of sodium sulfite is used with bi-sulfite, the pH of the solution is likely to change over to the alkaline side.

While the mechanism of the action of such inhibitors as sugar, glucose and glycerine is presumably different from that of sodium sulfate, or of sodium bi-sulfite, all of the materials have in common the property that they inhibit the action of the developer and render possible the process and advantages herein described.

A practical method of carrying out the invention which is suitable for motion picture negative films generally is the following:

Two solutions are made up having the following composition:

Example I

A. Monomethyl p-amino phenol sulfate	5	grams
Hydroquinone	2	grams
Sodium sulfite	100	grams
Sugar	100	grams
Sodium bi-sulfite	5	grams
Water to	1	liter
B. Sodium carbonate	10	grams
Sodium sulfite	100	grams
Potassium bromide	1	gram
Potassium iodide	0.02	gram
Water to	1	liter

The film is immersed for from 3 to 5 minutes in Solution A and then is transferred directly to Solution B in which it remains from 4 to 8 minutes. With this treatment, depending on the character of the film used, a predetermined gamma of the order of 0.50 to 0.70 will be obtained at the normal temperature, 65° F. The

degree of contrast or gamma which can be obtained with the above times of development can be varied by changing the quantity of developing agents (mono methyl p-amino phenol sulfate and hydroquinone) in the first solution. The function of the sugar in Solution A, as has been explained, is to retard development and it may be replaced by one of the other inhibitors mentioned.

On immersion in Solution A very little, if any, visible development takes place. The gelatine emulsion layer absorbs a certain amount of Solution A and it appears that one of the chief functions of the inhibitor is to retard development by the absorbed solution. Since only a given quantity can be absorbed and this amount is taken up relatively quickly, the total amount absorbed will not be materially influenced by leaving the film in the solution a longer time. In this way the final result is, to a reasonable extent, independent of the time of immersion in Solution A.

When the film is now transferred to Solution B, it carries with it in the pores of the gelatine emulsion layer a fixed quantity of Solution A, which quantity, as stated, may possibly be variable according to the amount and kind of inhibitor used. In the alkaline environment of Solution B, visible development proceeds rapidly. The amount of this development, however, will be limited by the amount of developing agent available, that is, by the amount of Solution A which has been carried over. It will thus be seen that the degree of contrast finally developed can be regulated by certain factors which are easily susceptible to control. If the proportion of developing agents, the amount and character of the inhibitor and the alkalinity of the second bath are suitably chosen, the degree of contrast, which will be obtained by the method of treatment indicated, can, within reasonable limits, be made anything desired. At the same time this degree of contrast or gamma can be any predetermined value and, as shown, this result will be obtained irrespective of moderate variations in the time of treatment.

Another embodiment of the invention which is particularly useful for the development of sound record negatives on a positive type of film is the following:

Example II

A. Monomethyl p-amino phenol sulfate	7 grams
Sodium sulfite	10 grams
Sodium bi-sulfite	2 grams
Sugar	100 grams
Water to	1 liter
B. Sodium carbonate	10 grams
Sodium sulfite	25 grams
Water to	1 liter

The method of treatment with these solutions is the same as before. With a three minute immersion in Solution A practically complete development is reached in Solution B in about one minute, although the film may be left in Solution B for a considerably longer time without materially altering the result.

Example I given above is particularly adapted to the development of a picture record or negative, and Example II for a sound negative when recorded on the customary positive type of film.

Many advantages of the invention will be easily apparent. It is particularly true that with motion picture positives having a sound record thereon, a good deal of attention must be paid to the development of both the picture and sound negatives. The degree of contrast to which each is developed must be accurately controlled. Since this degree of contrast is influenced largely by the time of development and the temperature of the developing solutions, it is evident that for an accurately controlled contrast the time of development and the temperature must be also very accurately watched and controlled. My invention obviates the necessity for such careful supervision of the times of development. When a two-bath developer of the kind I have described is used as indicated, a constant result can be obtained in spite of considerable variations in time of development. The times of development may be varied over about the range stated, as, for example, 3 to 5 minutes in Solution A and 4 to 8 minutes in Solution B. The temperature, of course, must be kept within a moderate range as is customary. The method therefore possesses a simple and effective control of gamma or degree of contrast, as one of its chief advantages.

Another advantage of the two-bath type of developer described is the lack of graininess obtained. That is, while, of course, all alkaline developers produce graininess, to some degree, the type of developers I have described produce comparatively little and are as satisfactory in this respect as many formulæ which are especially designed to give fine grain.

Another principal advantage, which is of particular value in motion picture work, is the long life of the developing solutions. Since almost no development occurs in the first bath, it is exhausted only very slowly. The second bath accumulates sodium bromide and other restraining agents, but it also accumulates developing agents which are carried in by the film. The restraining agents slow down the development during the first part of the treatment in the second bath but the developing agents, on the other hand, increase the development during the latter part of the treatment. These two effects, therefore, serve to balance each other and keep the developer functioning in the expected manner over a long period of use. The result is that a larger amount of film may be developed per gallon of the combined baths than would be the case with a single solution developer.

It will be evident that Solution B will, with continued use, accumulate developing agent until it becomes itself a complete developer. As this point is approached, Solution B should be replaced, as it would no longer function to give a constant gamma, since development would proceed in it to an excessive degree. When this point is reached will depend on conditions such as the kind of film and the quantity of developer carried over, but it may be easily determined for any particular set of conditions by one skilled in the art.

The life of the second bath will be materially increased if the excess of Solution A adhering to the surfaces of the film is removed before the film passes into Solution B. This may be accomplished for example, by an air squeegee or by squeegeeing rolls.

It is, of course, understood that my invention is susceptible to numerous variations and modifications other than those specifically mentioned. The composition of either the first or second solutions may be varied in many ways without affecting the nature of the result obtained. Other steps may also be combined with those indicated.

For example, a desensitizing bath may be used before the film is immersed in the first solution so that a relatively bright light may be used during development to inspect the film during the development process. Thus I might use a bath of one to 50,000 Pinakryptol green in which to immerse the film before immersion in the first solution. Other desensitizing agents are also useful and they are all employed in a manner well known. With a suitable first bath, the desensitizer may be added directly to the first bath, if desired.

I contemplate as included in my invention the method of obtaining development of a photographic image to an automatically controlled degree of contrast by the use of a two-bath developer of the type described, and various modifications and equivalents useful to that end, as expressed in the appended claims.

What I claim is:

1. The method of developing an image in an exposed gelatino-silver-halide layer which comprises submitting the layer, after exposure, to a non-alkaline bath containing a developing agent and a material that inhibits the developing action of said agent, removing it from the bath and then submitting it while still wet to a separate bath containing alkali necessary for development and allowing the completion of development in the second bath.

2. The method of developing an image in an exposed gelatino-silver-halide layer which comprises submitting the layer, after exposure, to a non-alkaline bath containing a developing agent, a sulfite, and a bisulfite, removing it from the bath and then submitting it to a separate bath containing alkali necessary for development and allowing the completion of development in the second bath.

3. The method of developing an image in an exposed gelatino-silver-halide layer which comprises submitting the layer, after exposure, to a non-alkaline bath containing a developing agent, a sulfite, a bisulfite, and an additional material inhibiting the developing action of said agent, removing it from the bath and then submitting it to a separate bath containing alkali necessary for development and allowing the completion of development in the second bath.

4. The method of developing an image in an exposed gelatino-silver-halide layer which comprises submitting the layer, after exposure, to a non-alkaline bath containing a developing agent, a sulfite, a bisulfite, and sugar, removing it from the bath and then submitting it to a separate bath containing alkali necessary for development and allowing the completion of development in the second bath.

JOHN I. CRABTREE.