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REGENERATION OF PHOTOGRAPHIC DEVELOPERS

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This invention relates to the regeneration or re-conditioning of photographic developers, and to rendering them capable of further use after they have accumulated a considerable quantity of soluble bromides.

After the ordinary photographic developer is used it gradually accumulates larger and larger quantities of soluble bromides through the double decomposition and consequent reduction of silver bromide in the emulsion to metallic silver. As the quantity of bromide increases the developer becomes slower in its action until it becomes relatively useless. While this action is also accompanied by the gradual oxidation of the developer, under most normal conditions the accumulation of bromide will take place first and be the more important factor in the exhaustion of the developer.

It is apparent that if the accumulated bromides could be removed the developer could be restored or reconditioned so that it would again function in the manner similar to fresh developer of the same composition. On account of the very complex chemical nature of a photographic developer, however, it has not heretofore been possible to successfully accomplish the removal of the soluble bromides. If, for example, one adds to such a spent developer a solution of a silver salt the soluble bromides will be precipitated in the form of silver bromide but will very quickly be reduced to metallic silver by the action of the developer. In this process a large part of the bromides will again be released into the solution together with the other constituent of the silver salt added and the precipitate which can be recovered will represent only the silver of the added silver salt. To remove the silver bromide from the developer before most of it is reduced to silver is a difficult problem, involving the repeated centrifuging of the material within a few seconds after precipitation.

We have found a relatively simple and easy solution of this difficulty. We find that if we add to the solution of the soluble silver salt which is to be added to the developer a soluble compound of certain metals a precipitate is formed along with the silver bromide which has a protective action on the silver bromide formed and both precipitates settle simultaneously without any appreciable rapid reduction of silver bromide by the developer. Some of these precipitates which are formed by interaction with the metallic salt and a constituent of the developer have a colloidal form and it is possible that they act somewhat in the well known role of a pro-

fective colloid. Others of these precipitates are perhaps not accurately classifiable as colloidal but they appear at any rate to exert the same protective action and prevent the silver bromide from being developed rapidly enough to be harmful.

Our invention is carried out by adding to the spent developer to be reconditioned a solution of a soluble silver salt, as, for example silver nitrate, containing also one of the soluble salts of aluminum, chromium, cobalt, copper, nickel, bismuth, lead, barium, manganese, magnesium, and zinc. Under these conditions the silver salt forms silver bromide and the metal salt reacts with the developer in most cases to form corresponding hydroxides. The addition of a little gelatin solution to the silver salt and the metal salt is advantageous, particularly if the spent developer does not contain some gelatin which has been accumulated from the film developed. The resulting precipitates carry down also any gelatin or suspended matter which is still a further advantage in reconditioning the developer. After the precipitates have settled they may be filtered off or, if desired, they may be centrifuged without waiting for settling.

Of the salts mentioned we have found silver nitrate together with a soluble aluminum or chromium salt to be as satisfactory as any. A preferred formula contains silver nitrate and an alum and is given in the following formula:

Silver nitrate.....	2.5 cc. of 10% solution	
Potassium aluminum sulfate.....	7.5 cc. of 5% solution	90
Water to.....	100 cc.	

To this solution may be added 2 cc. of 1 percent gelatin solution. The amount of gelatin added may be varied.

The total amount of silver nitrate necessary should for large amounts of developer preferably be calculated. This is done by making a rough determination of the amount of soluble bromides present in the developer and then adding a little more than the amount theoretically required to convert the bromides to silver bromide.

It is also desirable while adding this solution to keep the temperature of the developer as low as possible. This is done for the purpose of slowing up the reduction of silver bromide by the developer and yields a consequent increase in the efficiency of the process. As is well known, developers have fairly high temperature coefficients and a moderate decrease in the tempera-

ture of the solution will considerably slow up their action.

Instead of the ordinary potassium alum used in the above formula we may, for example, use chrome alum or another soluble salt of aluminum or chromium such as aluminum sulfate, chromium chloride or chromium sulfate.

Our invention is particularly applicable to the reconditioning of large quantities of photographic developers as used in continuous machines in the motion picture industry, for example. In applying the invention to the problem special methods and apparatus will readily suggest themselves. In general it will be desirable to determine the footage of film which may be developed before reconditioning of the developer becomes necessary. This may be determined quite readily by chemical analysis after various lengths of film have been processed. The calculation of the amount of silver nitrate to be added is then a simple matter. The developer may be run off into a special treating tank and the solution may then be filtered or centrifuged. It will be evident to those skilled in the art that various procedures may be followed at this point. It will, for example, be possible to arrange suitable equipment so that the treating, filtering or centrifuging and returning of the reconditioned developer to the system would be a more or less continuous process.

It is also understood that a large number of variations and equivalents may be employed all of which we consider as included within our invention, as expressed by the appended claims.

What we claim is:

1. In the method of regenerating a used photographic developer and separating the soluble bromides therefrom, the step which includes adding to the developer a solution containing a soluble silver salt and a salt which forms an insoluble precipitate with components of the developer, said precipitate having the property of acting as a protective substance for the silver bromides formed.

2. In the method of regenerating a used photographic developer and separating the soluble bromides therefrom, the step which includes adding to the developer a solution containing silver nitrate and a metal salt which forms an insoluble precipitate with components of the developer, said precipitate carrying down with it the silver bromide formed and protecting the said bromide from the action of the developer.

3. The method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate and a water soluble aluminum salt, filtering off the resulting precipitate, and recovering the silver from said precipitate.

4. The method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate and potassium aluminum sulphate, filtering off the resulting precipitate, and recovering the silver from said precipitate.

5. The method of regenerating a used photo-

tographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate, gelatin and a water soluble aluminum salt, filtering off the resulting precipitate, and recovering the silver from said precipitate.

6. The method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate, gelatin, and potassium aluminum sulphate, filtering off the resulting precipitate, and recovering the silver from said precipitate.

7. The method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate and a water-soluble aluminum salt.

8. The method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate and potassium aluminum sulfate.

9. The method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate, gelatin and a water-soluble aluminum salt.

10. The method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate, gelatin, and potassium aluminum sulfate.

11. A method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a soluble silver salt and a metal salt selected from the group consisting of the water-soluble salts of aluminum, chromium, cobalt, copper, nickel, lead, barium, manganese, magnesium, and zinc.

12. A method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate and a metal salt selected from the group consisting of the water-soluble salts of aluminum, chromium, cobalt, copper, nickel, lead, barium, manganese, magnesium, and zinc.

13. A method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing a soluble silver salt, gelatin, and a metal salt selected from the group consisting of the water-soluble salts of aluminum, chromium, cobalt, copper, nickel, lead, barium, manganese, magnesium, and zinc.

14. A method of regenerating a used photographic developer and separating the soluble bromides therefrom, which comprises adding to the developer a solution containing silver nitrate, gelatin, and a metal salt selected from the group consisting of the water-soluble salts of aluminum, chromium, cobalt, copper, nickel, lead, barium, manganese, magnesium, and zinc.

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