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## REGENERATION OF PHOTOGRAPHIC FIXING BATHS

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15 Claims. (Cl. 23—87)

This invention relates to regeneration of photographic fixing baths; and it comprises a method of chemically treating fixing baths, which may have been de-silvered by known methods, to render them suitable for re-use; this method comprising adding to such a fixing bath a soluble thallos salt, such as thallos sulfate, and filtering off the thallos iodide and bromide thereby precipitated; all as more fully hereinafter set forth and as claimed.

The recovery of silver from photographic fixing baths is well known and is rather widely practiced. One of these methods consists in the addition of a reducing agent, such as an alkali metal sulfide, bisulfide or hydro-sulfite, to the bath, thereby reducing the silver to the metallic state. More recently electrolytic methods have been developed. Still another method which has been recommended is the addition of a powdered base metal such as zinc or iron to the bath. If it is attempted to re-use a fixing bath de-silvered in accordance with one of these methods, difficulties are encountered. It is found that the fixing action of the bath is greatly reduced in speed. This is true even though the strength of the fixing agent in the bath has been restored to its original value.

The cause for the reduced speed of the fixing action of a de-silvered fixing bath is the accumulation of iodides and bromides in the bath. Of these the iodides appear to be the most deleterious. In commercial practice a once-used 20 per cent sodium thiosulfate fixing bath which has been de-silvered rarely contains over 500 mg. of sodium or potassium iodide per liter. This amount, while small, appreciably decreases the speed of fixing and, if the bath is repeatedly de-silvered after use, the length of time required for the fixing operation soon becomes prohibitive. It is believed that the accumulated iodides and bromides produce this decreased speed of fixing by decreasing the solubility of the corresponding silver salts in the bath.

No methods have been suggested previously in the art for the removal of the iodides and bromides from used fixing baths. I have found that this may be readily accomplished by a simple precipitation procedure which consists in adding to the bath a soluble thallos salt followed by filtering off the precipitate. I have found that this precipitation will occur even in strong solutions of sodium thiosulfate and in the presence of neutral or acid sulfites, alum, or chrome alum, or of other common additions to fixing baths. The removal of the iodides and bromides is al-

most as complete as from pure aqueous solutions of the iodides and bromides. The bromides are not removed as completely as are the iodides but are less objectionable. The quantity of bromides remaining in a fixing bath after the addition of slightly more than the calculated quantity of a thallos salt appears to have no appreciable effect upon the speed of the fixing action. The iodides are removed almost quantitatively by the addition of a thallos salt in combining proportions. The yellow precipitate formed settles readily and can be easily filtered off. This addition may, of course, be made prior to the de-silvering of the fixing bath. Or the precipitation with a thallos salt can be accomplished simultaneously with the de-silvering of the bath. Advantageously, however, the thallos salt is added after the bath has been de-silvered; the procedure being essentially the same in each of the three cases. This permits the recovery of the thallium from the mixture of its iodide and bromide which is obtained as a precipitate. When the thallium is recovered in this manner my method can be operated very economically even at the present prices of thallium salts.

In a specific embodiment of the present invention I first de-silvered 100 liters of a once-used fixing bath by the addition of sodium sulfide and sodium hydrosulfite. The resulting precipitate was filtered off. The filtrate had a sodium iodide content of about 450 mg. per liter, as estimated from an analysis of its silver content made prior to de-silvering and from the known iodide content of the photographic emulsion. I added to this filtrate while stirring 100 grams of thallos sulfate dissolved in 2 liters of water. There was an instantaneous precipitation of a fine crystalline yellow sediment which settled quickly. This was removed by filtration. This precipitate was found to contain practically all of the iodides of the bath and a large proportion of the bromide content. The filtrate was reconstituted by the addition of sodium thiosulfate and its original content of sodium bisulfite was renewed by the addition of this material. The bath was then employed as a fixing bath and it was found that it was the full equivalent of a freshly prepared bath. The rate of its fixing action was fully restored. The thallium content was then recovered from the precipitate of iodides and bromides by gentle heating with a slight excess of concentrated sulfuric acid. In this operation the iodine and bromine evolved were recovered. The thallos sulfate recovered in this manner was employed in a repetition of the above process.

While I have described what I consider to be the best embodiment of my invention, various modifications can be made therein without departing from the spirit and scope of my invention.

5 My process can be conducted with the use of any of the soluble thallous salts which do not deleteriously affect the fixing bath. While I usually employ the sulfate; the carbonate, acetate and nitrate are also advantageous.

10 Even the thallous salts which are usually considered as being only slightly soluble, such as the sulfite, dithionate, thiosulfate and orthophosphate, can be used. Such salts are advantageously added in finely divided form and usually as

15 a magma or a fine aqueous suspension. When employed in this manner any thallous salt having a solubility somewhat greater than thallous bromide can be employed, such salts requiring only a short time to react with and to precipitate the

20 iodides and bromides. When thallous thiosulfate is employed in this manner, sodium thiosulfate is formed by metathesis and this partially reconstitutes the bath so far as this component is concerned. Other thiosulfate fixing baths can be

25 treated by my new process, the alkali metal and ammonium thiosulfate fixing baths being examples. The salts commonly added to such fixing baths do not interfere. Other modifications falling within the scope of the appended claims

30 will be evident to those skilled in the art.

What I claim is:

1. In the process of regenerating photographic fixing baths, the step which comprises adding to such a bath a soluble thallous salt.
- 35 2. In the regeneration of photographic fixing baths, the process which comprises adding to a used fixing bath a soluble thallous salt and filtering off the resulting precipitate.
- 40 3. The process of claim 2 wherein the thallous salt is added to the fixing bath prior to the de-silvering of the bath.
4. The process of claim 2 wherein the thallous salt is added to the fixing bath after the bath has been de-silvered.
- 45 5. The process of claim 2 wherein the thallous salt is added to the fixing bath while the bath is being de-silvered.
6. The process of claim 2 wherein the thallous salt is thallous sulfate.
7. In the regeneration of photographic fixing baths, the process which comprises adding to a used fixing bath a soluble thallous salt, filtering off the precipitate, recovering the thallium content of said precipitate as a thallous salt and adding the recovered thallous salt to a second used fixing bath.
8. The process of claim 7 wherein the thallous salt is thallous sulfate.
9. The process of claim 7 wherein iodine and bromine are also recovered from the said precipitate by heating with sulphuric acid.
10. In the process of regenerating used thiosulfate fixing baths, the process which comprises adding to such a bath a thallous salt having a solubility greater than that of thallous bromide and removing the resulting precipitate.
- 15 11. The process of claim 10 wherein the fixing bath contains a thiosulfate selected from a group consisting of the alkali metal and ammonium thiosulfates.
12. The process of claim 10 wherein the added thallous salt is selected from a group consisting of the sulfate, acetate, carbonate, nitrate, sulfite, dithionate, thiosulfate and phosphate.
- 25 13. In the process of regenerating used thiosulfate fixing baths, the process which comprises adding to such a bath a slightly soluble thallous salt in the form of an aqueous suspension and removing the resulting precipitate.
- 30 14. In the process of regenerating used thiosulfate fixing baths, the process which comprises adding to a used sodium thiosulfate fixing bath a quantity of thallous sulfate sufficient to precipitate the iodides and the bulk of the bromides,
- 35 filtering off the precipitate, treating the precipitate with sulfuric acid to obtain thallous sulfate and employing the so-recovered thallous sulfate in a repetition of the cycle.
- 40 15. In the process of regenerating used fixing baths, the steps which comprise precipitating substantially all the iodides and the bulk of the bromides from the bath by metathetical reaction with a thallous salt, and filtering off the precipitate.
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